Life Cycle Assessment of Fuel Cell Vehicles – Dealing with Uncertainties

BY

JOSÉ FERNANDO CONTADINI
B.S. (Federal University of São Carlos – Brazil) 1987
M.S. (Federal University of Minas Gerais – Brazil) 1997

DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

ENVIRONMENTAL ENGINEERING

in the

OFFICE OF GRADUATE STUDIES

of the

UNIVERSITY OF CALIFORNIA

Davis

COMMITTEE IN CHARGE:

Prof. Daniel Sperling (Chair)
Prof. Patricia L. Mokhtarian
Dr. Robert M. Moore

May 2002

Life Cycle Assessment of Fuel Cell Vehicles – Dealing with Uncertainties

Abstract

Life cycle assessment (LCA), or “well to wheels” in transportation terms, involves some subjectivity and uncertainty, especially with new technologies and future scenarios. To analyze lifecycle impacts of future fuel cell vehicles and fuels, I developed the Fuel Upstream Energy and Emission Model (FUEEM). The FUEEM project pioneered two specific new ways to incorporate and propagate uncertainty within an LCA analysis. First, the model uses probabilistic curves generated by experts as inputs and then employs Monte Carlo simulation techniques to propagate these uncertainties throughout the full chain of fuel production and use. Second, the FUEEM process explicitly involves the interested parties in the entire analysis process, not only in the critical final review phase.

To demonstrate the FUEEM process, an analysis has been made for the use of three different fuel cell vehicle technologies (direct hydrogen, indirect methanol, and indirect hydrocarbon) in 2010 within the South Coast Air Basin (SCAB) of California (Los Angeles). The analysis covered topics such as the requirement of non-renewable energy sources, emissions of CO_2 and other greenhouse gases, and emissions of several criteria pollutants generated within SCAB and within other regions. The results obtained from this example show that the hydrogen option has the potential to have the most efficient energy life cycle for the SCAB, followed by the methanol and finally by the Fisher-Tropsch naphtha option. A similar pattern is observed for the greenhouse gas emissions. The results showing criteria pollutants emitted within SCAB highlight the importance of having a flexible model that is responsive to local considerations. This dissertation demonstrates that explicit recognition and quantitative analysis of the inherent uncertainty in the LCA process generates richer information, explains many of the discrepancies between results of previous studies, and enhances the robustness and credibility of LCA analyses.

Acknowledgments

Several professors and researchers from academia, government agencies, and laboratories helped me a lot on this journey. I want to thank all of them in the figure of Dr. Robert M. Moore, who was always willing to share his knowledge, experience, advice, and especially his friendship with me.

In the same way, dozens of experts and managers from different industries helped me, and trust me by answering my technical questions, providing me with data (sometimes confidential), and sharing with me their thoughts about the future. I would like to say thanks to all of them in the figures of three people who not only participated on our panel of international experts, but also made personal efforts to seek within their industries specific experts to cooperate with me in more detailed technological investigations. Thanks to Nitin M. Patel from Air Products and Chemical, Inc.; Mark Allard from Methanex Corporation, and J. Steve Welstand from former Chevron Products Company (now ChevronTexaco).

Finally, but not less important, thanks to Claudia V. Diniz and Yanê D. Contadini for their love, patience, and encouragement.

This study was funded by the CNPq (Brazilian Council of Science and Technology) and by the Fuel Cell Vehicle Modeling Program at the Institute of Transportation Studies at UCDavis.

Table of Contents

List of Tables

List of Figures

Abbreviations and Acronyms

atm	Atmosphere
bbl	Barrels
Btu	British thermal unit
CARB	California Air Resource Board
CEMS	Continuous Emission Monitoring System
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
DH	Direct hydrogen
DHFCV	Direct hydrogen fuel cell vehicle
EPA	US Environmental Protection Agency
FT	Fisher-Tropsch
FTN	Fisher-Tropsch Naphtha
FUEEM	Fuel Upstream Energy and Emission Model
gal	Gallon
GJ	Giga Joule
HHV	High heating value
IH	Indirect hydrocarbon
IHFCV	Indirect hydrocarbon fuel cell vehicle
IM	Indirect methanol
IMFCV	Indirect methanol fuel cell vehicle
km	Kilometer
L	Litter
lb	Pounds
LHV	Low heating value
MBtu	Mega or million Btu
MeOH	Methanol
MJ	Mega Joule
mg	milligram

MPa	Mega Pascal
MTPD	Metric tons per day
NG	Natural gas
NO_x	Nitrogen Oxides
N_2O	Nitrous Oxide
PM_{10}	Particulate matter smaller than 10 microns
PSA	Pressurized Swing Adsorption
psi	Pounds per square inch
SCAB	South California Air Basin (Los Angeles area)
scf	Standard Cubic Feet
SCR	Selective Catalytic Reduction unit
SMR	Steam methane reforming
SNCR	Selective Non-Catalytic Reduction unit
SO_x	Sulfur oxides

1 INTRODUCTION AND PROBLEM CONTEXT

1.1 Background and context definition

Transportation is an important contributor to world energy consumption (Greene, 1996). According to the US Department of Energy (TEDB, 2000), in 1997, the United States, the most automobilized country in the world, consumed 18.6 million barrels of oil per day, equivalent to 25.5 % of the world oil consumption. From that total, 67 % was used directly in transportation. In 1999, according to the same report, the transportation sector was 97.4 % dependent on petroleum energy. Similar values were presented in older studies. The USA was responsible for 30 % of the world energy use in the early 90's (Ackerson *et al.*, 1993). According to Gordon (1991), 41 % of that energy was spent directly or indirectly on transportation, and 97 % of the 22.66 quads directly used by the USA transportation sector were produced from petroleum.

Transportation-related air emissions can be also associated with greenhouse gas (carbon dioxide-CO_2, methane-CH_4, nitrous oxide-N_2O, carbon monoxide-CO, chlorofluorocarbons - CFCs, etc.). The concentration of these gases in the stratosphere may cause a global warming, and climatologists are expecting a global climate change to be associated with a lot of environmental impacts (Beckmann *et al.*, 1991; Walsh, 1993 and IPCC, 2000). CO_2 produced in the combustion of fossil fuels, such as petroleum, is the major contributor to the global warming. In 1998, the US emitted 6,514 million metric tons of $CO_{2\text{-equivalent}}$ per year and from that 32.6 % was attributed to transportation (DOE, 1999). In the early 90's the USA transportation sector was responsible for 30 % of the total 5.600 million tons of CO_2 emitted per year (EPA, 1992).

Transportation-related air emissions can be associated with urban air quality in terms of ozone formation, criteria pollutants (non-methane organic gases-NMOG, carbon monoxide-CO, nitrogen oxides-NO_x, sulfur oxides-SO_x and particulate matter-PM), and toxic pollutants (benzene, lead, etc.). Several health problems are associated with human exposure to these pollutants. In 1998, according to Davis (2000), 63.8 million tons of CO were emitted within the US by all transportation modes. From this total, 71.7 % is attributed to vehicles. A similar situation occurs with NO_x when, in 1998, the transportation sector emitted 11.8 millions tons of the pollutant with 59.5 % being accounted for by vehicles. For volatile organic compounds (VOC), 68.4 % of the total of 7.1 million tons emitted is attributed to vehicles. In the early 90's the transportation sector was responsible for 78 % of the USA's emissions of CO, 30 % of the NMOG, 5 % of the SO_x and 23 % of the PM_{10} (EPA, 1995).

These concerns are present in all developed countries but also in several developing ones. Within the same development and technologies pattern the situation tends to get worse especially with the increasing vehicle mileages traveled (VMT) in developed countries and with the rapid motorization occurring in developing countries (UNDP, 2000).

Solving these problems is the principal motivation for introducing new vehicle technologies and alternative fuels. However, since transportation is a very complex system, a change in practice to alleviate one problem could well exacerbate others. A comprehensive evaluation of the environmental aspects (air criteria pollutants, greenhouse gases emissions, non-renewable energy consumption, etc.) and the trade-off on the environmental impacts (human health, biodiversity, sustainability of the future generation, etc.) should include all life cycle activities from the vehicle operation to the feedstock (oil, natural gas, coal, etc.) extraction.

Urban air quality improvement, climate change concerns, and a reluctance to depend on non-renewable sources have been as well the main motivations for the development of fuel cell technologies and their applications in fuel cells vehicles (FCVs). Fuel cells are electrochemical devices that directly generate electricity using a fuel (hydrogen, in general) as required and an oxidant (oxygen) to complete the process. It emits only water vapor as a by-product and it is also more efficient than internal combustion engines (ICE) due to the possibility of controlling the electrochemical reaction.

The rapid development of these new vehicle technologies may also require the establishment of a new fuel infrastructure soon. Hydrogen can be used directly as the fuel cell fuel, as can other alternative fuels, such as methanol, or, alternatively, some special kinds of hydrocarbon fuels can be used indirectly as hydrogen carriers. Again, a technology change of this magnitude may require a good understanding of the major risks of environmental impacts in the entire cycle of activities. This understanding may be necessary in order to prevent “second order” problems and/or to help in the selection of the best social strategy to establish policy, allocate subsidies, and drive R&D programs.

The Life Cycle Assessment (LCA) methodology has the potential to be an important management tool in assisting decision-makers to achieve a holistic understanding of the entire system associated with a single product/service to be introduced. In spite of being a scientific management tool in development, LCA has been used more and more frequently, even presenting some necessity for improvements as discussed on the next sections. The amended ZEV rule (Zero Emission Vehicles), approved by the California Air Resource Board (CARB) in November 1998, highlighted the importance of vehicle life cycle analysis comparisons when it established partial credits for vehicles with low tailpipe emissions that use a cleaner fuel process than gasoline. Which alternative is more environmentally positive and by how much? This is the kind of question that LCA tries to answer.

1.2 Problem definition

Basically the methodology of Life Cycle Assessment has an inventory phase where the environmental aspects should be measured and a second phase where all the environmental impacts related with the aspects inventoried are assessed for a final comparison. As detailed section 2.1, the history of the methodology development has been marked by result manipulation attempts in order to push organization agendas or product benefits. Because of that, lack of credibility is a problem that LCA must reverse and the methodology improvements should prevent or minimize.

A critical element in the methodology is the subjectivity of the assessment phase in order to prioritize the importance of different environmental impacts. On the other hand, the inventory phase (sometimes called LCI – Life Cycle Inventory), that deals with the system input data compilations and also with the calculations of the system environmental aspects outputs, is in some sense considered a more mature methodology with more than 20 years of development. Apparently, it has all the ingredients to be an objective tool; however, analysis done over LCA result discrepancies have shown that the inventory phase is still presenting serious problems too and improvements should be interesting. The major problems for the inventory of the environmental aspects of an existing product are the lack of data, quality of existing data, lack of a single methodology to fill up the gaps, and also the decisions to deal with boundaries and co-products.

More complicated than that is a common characteristic in the fuel cell vehicle kind of situation where the “cleaner technology” will always occur in the future and, therefore, there will always be some subjectivity in the analysis, even in the inventory phase.

Transportation life cycle studies suffer from similar problems pointed out by studies done in other sectors according to my initial study done in 1998, when a comparison of the existing "cradle-to-grave" or "well-to-wheels" studies related to fuels for transportation and vehicle technologies was done. In general, these kinds of studies focus on the inventory of air emissions (grams) and energy requirements (Joules or BTUs) over the entire range of fuel upstream activities (life cycle) associated with the vehicle operation (per km or mile). Some of the studies also do an assessment analysis for the climate change effected by the greenhouse gas emissions by using global warming potential factors (GWP). As a general statement, it can be said that the existing studies do not agree in their results and, depending on the case, they disagree to the extent of several orders of magnitude. More details of this comparison are presented in section 2.5.

Basically, I identified three levels of disagreement:

Geographical differences (US national average, South Coast California Air Basin, Canada, UK, etc.). Geographical differences are related to the initial study objective and, in general, are clearly delineated in the reports. Problems arise only if attempts are made to generalize the result. Such an attempt is very common in conference presentations, study comparisons, and study press releases.

Technology scenario composition (for example, natural gas pipelines propelled by turbines, reciprocating engines or electric motors, pressure of the gas pipe, electricity production mix per region). Within the same area and under the same technology umbrella (for example, natural gas feedstock), the assumptions can be very different and generate different results. The use of a single situation to represent all the feasible and viable technologies possible in the real world is very common. There are few studies that perform sensitivity analysis at this level.

Technology data (efficiencies and emission factors of different equipment). A lack of data for some equipment, as well as the use of deterministic values to represent a complex system (the average of the USA methanol production plant efficiencies, for example), generate part of the disagreement in results. A robust study should be very clear about the technology considered and kind of data used. Several studies do only a kind of bookkeeping process, with generic assumptions about generic technologies and do not go to the level of calculation involving equipment design, level of equipment activity, and physical parameters. Even for the studies that do go to this level of detail in calculation, a lack of reported information about the details and assumptions used is unfortunately frequent.

1.3 Research approach and contributions

To deal with these uncertainties in the fuel cell vehicle life cycle assessment, I decided to develop a new model called FUEEM (Fuel Upstream Energy and Emissions

Model). The FUEEM operational unit is kilometer driven and the time frame is 2010, due to the development characteristics of the fuel cell vehicles and fuel development level. The boundaries are from the natural gas extraction to the vehicle operation, since the initial comparison is among three special fuels that use natural gas as feedstock (Hydrogen, Methanol and Fisher-Tropsch Naphtha). The model uses the global warming potential (GWP) and Economic Damage Index (EDI) to calculate greenhouse gas emissions (CO_2, CH_4 and N_2O) in terms of CO_2-equivalent and it also calculates the total energy required disaggregated in terms of petroleum and fossil fuel use. For five of the criteria pollutants (NO_x, CO, NMOG, PM_{10} and SO_x) which are considered in the study, the effort was to quantify how much is released in urban areas.

The model used two major approaches to explicitly recognize and quantitatively include the inherent uncertainties in LCAs:

1. For the technology data problems in the inventory, FUEEM works with specified equipment and system design performing a quantitative uncertainty analysis. This approach is suggested in the ISO 14041 (1998). To my knowledge, this project was the first to put it into practice. To use the approach, FUEEM establishes probabilistic curves as inputs and propagates the uncertainties over the calculation by using Latin-Hypercube sampling, Monte Carlo simulation, and rank order correlations. This approach is similar to performing thousands of sensitivity analyses at once, with the advantage of establishing the importance of each scenario (expressed in the occurrence probabilities) at the end. More details about it are presented in section 3.2.

2. The other uncertainties are related to subjective and necessary decisions, such as the future technology compositions (scenarios), the modeling approach that affects the results (allocation of co-product credits, for example), the filling process for missing data, etc. I made all these major decisions with the participation of the interested parties.[1] This participation occurred during the entire process and not only in the critical review process. This procedure takes item 7.3.3 of the international standard for Life Cycle Assessment (ISO 14040, 1997) a step further and is designed to enhance the credibility of the study results. This step is not a simple one since, in general, what differs among the parties are their different, and in most cases, conflicting interests. The methodology adopted in FUEEM to take maximum advantage of this participation and the explanation of the rationale behind the decisions made are presented in section 3.1.

Finally, since the inventory results are geographically specific it brings into question the advantage of having a flexible model to perform the analysis for different areas and situations. FUEEM performs most of it calculations at the level of detail where some physical parameters and scenarios (distances, temperatures, gas composition, level of control enforcement, etc.) can be manipulated to better represent the local situations. To demonstrate the FUEEM process, I conducted an analysis for three Fuel Cell Vehicle Technologies concepts hypothetically running in the South Coast Air Basin (SCAB) of California in 2010. The analyzed vehicle concepts were Direct Hydrogen Fuel Cell Vehicle, Indirect Methanol Fuel Cell Vehicle, and Indirect Hydrocarbon Fuel Cell

---

[1] The definition of interested parties according to the ISO 14.040 (1997), is an “individual or group concerned with or affected by the environmental performance of a product system, or by the results of the life cycle assessment”.

Vehicle. The analysis investigates the operational upstream activities of three zero-sulfur fuels (hydrogen, methanol and Fisher-Tropsch naphtha) produced from the natural gas. Several fuel pathways and scenarios were explored. The experts and I chose SCAB because of its well-known air quality problems and its high probability of leading fuel cell vehicle introduction. The details of the analysis and the results are presented in section 5.

2 LITERATURE REVIEW

2.1 Life Cycle Assessment (LCA) - General overview

Wouldn’t it be great if well-intentioned decision-makers had right in front of them a classification of the most environmentally friendly policy, process, product or technology? In fact, this is the dream of the scientific systemic management and the right way to go according to my view. But, how far are we from this dream?

The most important tool that has been developed for this purpose is called Life Cycle Assessment (LCA). Therefore, Life Cycle Assessment is an environmental management tool that generates information about the environmental consequences of the existence of a product or service through all of its life activities. It is in general called “from cradle to grave analysis” or in the transportation sector “from well to wheel analysis.” The definition of the international standard is: “Compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle” (ISO 14.040, 1997). The international standard also presents the general methodology to conduct a LCA, which and it can be found in several other studies as well (SETAC, 1993; Vigon *et al.*, 1993; Graedel, 1998).

Basically, the methodology has three phases with a general interpretation step for each phase: First the definition of the project goal, time frame considered, the functional unit, scope, and, most important, the activities boundaries, assumptions, allocations procedures, etc. The second phase is the life cycle inventory analysis where the data is collected and analyzed, and the calculations of the energy and material flows occur. The idea is to quantify all inputs and outputs of the product system focusing on the released waste for the environment (air, water and soil). Finally, the last phase is called life cycle impact assessment where, based on the inventory results, the significance of the potential environmental impact is evaluated. The evaluation may focus on resource depletion, on human health impacts, on ecological impacts such as biological diversity and habitat alteration, and on economic impacts such as damage to infrastructures, land requirements (food production), aesthetic values, etc. A graphical representation of these ideas is presented in Figure 2-1. Depending on the author, the improvement suggestion and analysis are separated from the impact assessment into a new phase called improvement assessment (Ayres, 1995).

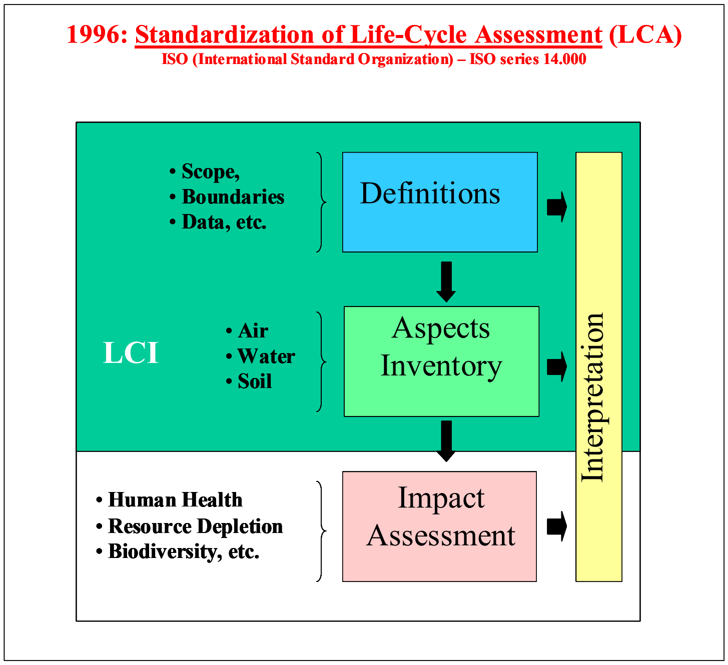


Figure 2-1: Graphical representation of LCA according to ISO 14.040 (1997)

Life Cycle Assessment (LCA) has been designed and used in different arenas. Companies have been using it internally for product development and improvement of the environmental characteristics of their system, and as a baseline for environmental audits. The European Commission has been motivating industries to perform internal

LCAs, and according to Ecobilan (1996) European car companies have conducted several studies in the last decade. Most of them focus on the material use. To some extent the companies have been using LCA for strategic planning and marketing to make comparisons with concurrent products (Lee *et al*., 1995). The idea of environmental labels for a product is based on this concept of product comparison. In the public policy making arena LCA could provide a framework for environmental taxes and incentives/subsidies for technological development (Lee *et al*., 1995). The amended ZEV rule (Zero Emission Vehicles), approved by the California Air Resource Board (CARB) in November 1998, highlighted the former idea when it established partial credits for vehicles with low tailpipe emissions that use a cleaner fuel process than gasoline. A life cycle study was used to support the amendment (Acurex, 1996).

The Life Cycle Analysis concept is attributed to Harry Teasley from the Coca-Cola Company who, in 1969, sponsored a comparison of different beverage containers. The analysis was conduced by MRI (Midwest Research Institute) and the concept became known as REPA (Resource and Environmental Profile Analysis). It was the basis of the Life Cycle Inventory methodology development within the existing LCA idea (Hunt *et al*., 1992). Several REPAs were conduced in the U.S.A. in the 70's and 80's initially focusing on the energy issue and later shifting to hazardous waste. A similar development pattern occurred in Europe inspired by the REPA studies. Christiansen (1993) comments on the 1984 Swiss model called BUS and the 1985 German qualitative model called PLA. Lee *et al*. (1995) complete the list with the Boustead model developed in the early 70's, and with the Sundström model in the mid 80's. Pedersen and Christiansen (1992) discovered that by that time 90 Life Cycle Assessments had been performed and published and that 50 % of them were done on packaging materials and 10 % on energy production and building materials. Derenne (1995) three years later reported 274 studies, with 36.9 % on packaging, 8.8 % on energy, and 4 % on transportation.

With more than 20 years of development the quantitative inventory phase (sometimes called Life Cycle Inventory - LCI) methodology is claimed by various authors (Hunt *et al*., 1992; Boustead, 1992 and implicitly the international standard ISO 14.040) to be well established. On the other hand, existing problems in this phase are always unanimously attributed to the lack of comprehensive data and data quality. This study does not share the vision of the previous authors. The hypothesis here is that uncertainties in the data will always occur and therefore the LCI methodology should incorporate them in the calculation and data treatment. This point is discussed later. If we move to the impact assessment phase, the LCA problems become much worse and we can say that a long time will be necessary to mature some acceptable methodology for the assessment final result – to provide an environmental ranking of the compared products, services or policies.

It is important to point out that there is no such thing as a single environmental problem. Several problems caused by several causes with strong interdependency among them are the common figure. A change in practices to alleviate one problem could well exacerbate others. If on one hand this is the situation that generates the necessity for the LCA development it also requires that the impact assessment compare the losses and gains in each area and prioritize them. Monetary valuation of the impacts using the contingency valuation approach (willingness to pay or willingness to accept payment surveys) appears to be one step ahead of other approaches such as single or multidimensional non-monetary measures (net-energy, material intensity per unit of service, etc.) or from other attempts using multi-objective decision-theoretic approaches (Ayres, 1995). Depending on the pollutant/impact in question, other complex calculations should be necessary such as external chemistry reactions, level of expositions, etc. These calculations are, in general, performed under the label environmental risk assessment. Each of these points is an entire study area and for logistic reasons the focus of this study covers none of them except the Life Cycle Inventory (LCI) phase and its previous and necessary definitions. Global warming impacts, for potential warming or economical damage, expressed in terms of $CO_{2\text{-equivalent}}$, are the only assessment performed in this study so far.

With all these uncertainties and potential economic interests on LCA results, it is easier to find comments in the literature about lack of credibility. Currently life cycle assessment (LCA) methodology involves many decisions, choices and exclusions that may intentionally or unintentionally influence the outcome of the study. A classical example is presented by Christiansen (1991; in UETP, 1996) where five studies comparing milk containers generate five different answers with the characteristic that the results always favor the product of the company sponsoring the study. The explanation for the differences is related to different qualities of data, different boundaries of the life cycle, different types of technologies and different priorities in the evaluation stage. Ekvall (1992) also presents a comparison of two LCAs of similar cardboard. In this case the two studies use the same data profile but the results differ 30 % in the thermal energy requirement, 60 % in the electrical energy requirement, 30 % to 100 % on air emissions and 80 % on solid waste. Several topics were pointed as the main differences, among them the content of the recycled fibers, share of waste going for incineration, energy recovered in the incineration process, mix of electricity generation, and the “avoided emission” approach assumed.

2.2 LCA in the fuel/transportation industry

A complete Life Cycle Assessment (LCA) in the fuel/transportation industry should be performed following these basic steps: For each stage in the life cycle (vehicle operation, fuel distribution, fuel production, feedstock transportation and storage, and feedstock extraction and processing) the idea is to quantify the water, soil and air emissions for different phases of the project. These phases are Pre-operations (R&D, Site Development and Construction), Operations and Post-operations (Recycling, Decommissioning and Dismantling). Figure 2-2 presents a graphical representation of these boundaries. The impact on the environment should be assessed and somehow compared after the inventory analysis. Photo-oxidant formation, acidification, eutrophication, global warming, stratospheric ozone depletion, ecotoxicological impacts, bio-diversity reduction, and habitat alterations are examples of environmental impacts.

For reliable results it is necessary to obtain data from different processes, which necessitates development of an ongoing data library and, as discussed before, the subjectivity involved in the evaluation phase of the LCA method is still critical. Christiansen (1993) reports the existence of several LCA done internally by the companies and never published but to the extent of my current knowledge only one “complete” LCA study has been published in the transportation sector so far. Spirinckx and Ceuterick (1996) include a comparative impact assessment of air, water, and soil emissions, and it is a comparative life-cycle assessment of fossil diesel and biodiesel. Unfortunately they did not publish their input assumptions for the inventory. For the evaluation, they used weighting factors from a Dutch report on eco-indicators (Goedkoop, 1995). Their conclusion is that the environmental index of biodiesel is a factor of 2 higher than the one for diesel with the following statement "However, weighting factors to a large extent have a subjective nature."

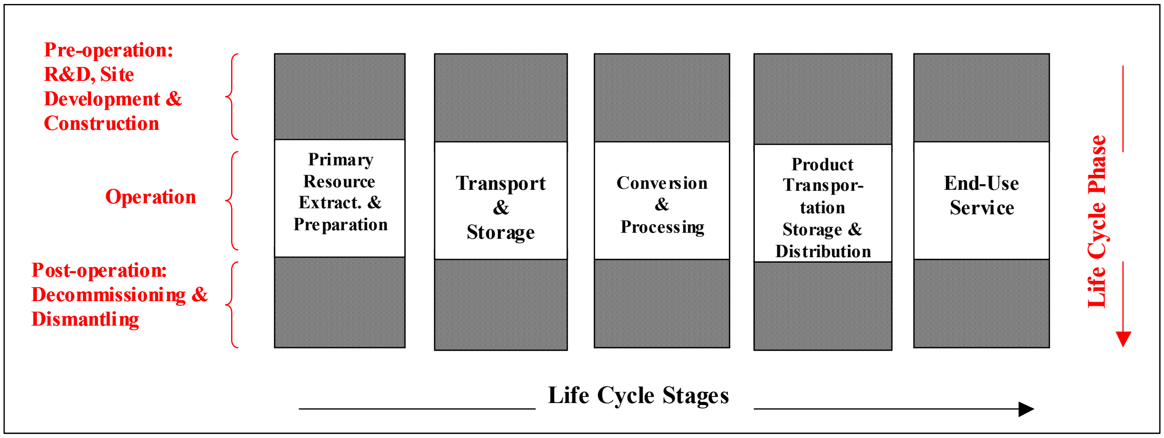


Figure 2-2: Boundaries concept for a life cycle inventory (source: Humphreys *et al.*, 1996)

All the other life-cycle studies in the fuel/transportation sector perform the inventory phase of the methodology only. Some of them perform an assessment of the global warming potential in terms of amount of $CO_{2\text{-equivalent}}$. A well-done life-cycle inventory (LCI) is already an important management tool providing interesting outcomes. The inventory results can be associated with costs to perform a cost effectiveness analysis, or, in a more simple way, by assuming that "less is better" for the energy requirement analysis and for the pollutant emissions analysis. More important, this kind of comparison for local situations can define where tradeoffs in the system may occur, providing information where attention should be concentrated. It is essential to point out that the LCA, and especially the LCI, was created as a technical tool and, in spite of the necessity to consider some economic and social factors to discuss the technology used in the calculation, it does not automatically take these factors into account (Derenne, 1995).

Examples of existing studies are: Unnash *et al*. (1996 and 2000), Delucchi (1991, 1993 and 1997), Greet (1998, 1999 and 2000), ETSU (1996, 1997 and 1998), GM (2001), MIT (2000), Pembina-Suzuki (2000), Methanex (2000), Adamson and Pearson (2000), Leveton (1999), Armstrong and Akhurst (1999), ANL (1998), Ogden *et al*. (1998 and 1995), DTI (1998), Ekdunge and Raberg (1998), Specht *et al*. (1998), ADL (1996), Berry (1996); Borroni-Bird (1996), Darrow (1994), Mark *et al*. (1994), Shelef and Kukkonen (1994), and Chang *et al*. (1991)

2.3 <u>Qualitative analysis of existing fuel/transportation LCIs.</u>

A qualitative analysis is performed here to highlight some of the difficulties in conducting a quantitative comparison among the results of selected existing studies. Andress (1998) did a qualitative comparison between Greet and Delucchi’s Model for the ethanol fuel cycle, in which some general similarities and differences are addressed. No quantitative comparison was done in Andress’ study and the results can be summarized in terms of how they calculate greenhouse gas emissions and make parametric assumptions (determined inside or outside of the models). A quantitative analysis however is possible at a more detailed level, some of which are discussed later.

2.3.1 Scope

Based on what was presented above, the principal motivation to evaluate the existing fuel use and eventual new alternative fuel use is to assess the potential to consume less petroleum and non-renewable fuels, so as to reduce air pollution and greenhouse gas emissions. According to Kordesch *et al*. (1995) spills, leaks, strip mining and other environmental aspects are also important points to consider; however, most of the existing LCI in the transportation sector focus on the energy requirement and air emissions (criteria pollutants and greenhouse gases) only. This simplification was adopted as a strategy to reduce the cost and necessary effort in the projects as well.

An exception to that can be attributed to the NREL studies (NREL 1991 and 1992) on bioethanol and reformulated gasoline, Mann and Spath (1997) on biomass gasification plants, and also to a similar study done by Spath and Mann (2000) on a hydrogen steam methane reforming plant. They included in their analyses the solid waste generation and the water emissions. The total amount of water pollutant was found to be small compared to other emissions (0.2 g / kg of H_2 produced) and the waste generated is reported in an aggregated form (205.6 g / kg of H_2 produced) attributed mainly to electricity consumption grid with coal generation. A similar conclusion was reached by the previous studies. The studies assess the criteria pollutants (NO_2, NMOG, SO_2, CO and PM_{10}), the toxic pollutant benzene (C_6H_6), and the greenhouse gases (CO_2, N_2O, CH_4 and $CO_{2\text{-equiv.}}$). All the emissions are calculated with a U.S.A. global perspective, i.e., without separating them into urban area emissions. The energy requirement is presented in terms of the total and feedstock content.

Other examples of the scope of some of the most robust and updated studies:

1. Delucchi (1991, 1993 and 1997): Calculated in a spreadsheet (Lotus123), this study focuses on standard greenhouse gas emissions ($CO_{2\text{-equiv.}}$, CO_2, CH_4, and N_2O) and also includes some criteria pollutants (CO, NO_2, and NMOG). The criteria pollutants, including SO_x and PM_{10}, are calculated with a global perspective. The total energy is presented as well as at the activities' phases (feedstock recovery, feedstock production, fuel production and fuel distribution). The model includes the following U.S.A. pathways: reformulated gasoline, standard gasoline, and diesel from crude oil; LPG from crude oil and natural gas (NG); compressed NG and Liquefied NG; methanol from NG, coal, and wood; ethanol from wood and corn; hydrogen from solar, hydrogen from nuclear, and several electricity generation technologies.
2. Greet (1998, 1999, 2000 and 2001): Calculated in a spreadsheet (Microsoft Excel), this model independently focuses on standard greenhouse gas ($CO_{2\text{-equiv.}}$, CO_2, CH_4, N2O) and criteria pollutant emissions (NMOG, CO, NO_x, PM_{10} and SO_x). It creates a "virtual" urban area for roughly local criteria pollutant analysis. The energy is presented in terms of petroleum consumption, fossil fuel consumption, and total. It has 26 fuel USA pathway calculations and 49 vehicle technologies. The result is a comparison of 77 fuel/vehicle combinations.
3. Unnash *et al*. (1996 and 2000): Done in a relational data base environment (Microsoft Access), this model focuses on the photochemical reactivity of NMOG for California's South Coast Air Basin but also assesses other emissions such as NO_x, CO, CO_2, and CH_4 and their regional occurrence (California, USA, and rest of the world). The initial study investigated the following fuels: gasoline and

reformulated gasoline, diesel, LPG from crude oil, methanol from NG and biomass, ethanol from corn, compressed and liquefied NG, hydrogen and electricity (aggregated mix). The latest report evaluates diesel, reformulated diesel, and LPG from crude oil; synthetic diesel, methanol, and LPG from NG; methanol from landfill gas and biomass, and electricity from crude oil, NG, coal, biomass and hydroelectric.

4. ETSU (1996, 1997 and 1998): Calculated in a spreadsheet, the model focuses on the criteria pollutants (NO_x, NMOG, CO, SO_x, and PM_{10}) and on CO_2 and CH_4. All the pollutants are calculated in a global perspective for the UK cases. The initial study is done for the following fuels: gasoline, diesel, and LPG from crude oil; compressed NG, electricity, biomethanol, bioethanol, and biodiesel, and includes the generic passenger car, light-duty and heavy-duty vehicles, and buses. The following studies incorporate in the calculations some new and more detailed vehicle technologies: gasoline vehicle, diesel passenger car, methanol fuel cell vehicle, and NG fuel cell vehicle.

The other studies referenced before have a much more limited scope, or different goals than the ones selected here, for example, a cost analysis goal. Some of them used the data generated in one of the above selected robust studies; others were out-of-date. Whenever possible these studies were used for a more detail analysis or in data acquisition.

2.3.2 Boundaries

According to the definition of the international standard (ISO 10.040, 1997) the system boundary is "the interface between a product system and the environment or other product system." Complex systems like industrial and fuel production systems have practically no final limit. One can trace back materials and energy indefinitely depending on the level of detail used. Therefore, every assessment must limit its analysis at some point. Different studies having different system boundaries may have different results and this detail must be taken into account when comparing them. In fact, several LCA result manipulations used this flexibility in the past. Lee *et al*. (1995) present the example of washing machine studies including or not the services (heating, lighting, compressed air, etc.) of the manufacturing plant and having different conclusions. Ayres (1995) comments on the classical McDonalds's study comparing groundwood (papier-mache) and polystyrene hamburger shells.

The main sequence of operations in the product production and consumption is usually the easiest to identify. In the fuel/transportation case, for example, the sequence should be the feedstock recovery (crude oil, coal, NG, etc.), feedstock processing, feedstock transportation and storage, fuel production (gasoline, methanol, etc.), fuel transportation and storage, fuel distribution, and vehicle operation. The idea is that the boundaries include all important activities that may change the final results. However, this definition is not so direct and in most cases a previous study must have been completed to make sure it was accurate (ISO 14041, 1998). The solution presented by the ISO 14040 (1997) is that the system boundaries shall be identified and justified, but only these do not prevent situations found in Blinge and Lumsden (1995) where several subjective justifications were presented not to include the raw material in the energy balance involving ethanol analysis. In general, when the activities get far from the main operational sequence, the probability of their significantly changing the final results decrease and, therefore, the importance of including them in the calculation also decreases. However, several studies (Delucchi, 1993 and 1997; Greet, 1996 and 1999; ETSU, 1996 and NREL 1992 and 1997) investigating fuels from biomass showed the importance of including the fertilizers and other materials used in the agricultural activities. Similar problem can be found in Unnash *et al*. (1996 and 2000) that include the fuel consumption of the farm equipment but do not include the material to farm (fertilizers, herbicides, etc.).

The objective of the study defines on the first hand the minimum necessary boundaries. Some studies, in spite of the name life cycle, truncate the analysis at some point because the study is only a piece of a bigger puzzle to be assembled over time. This is the case of Spath and Mann (2000) and most of the NREL studies where the objective is to analyze the hydrogen production only. The Unnash *et al*. (1996 and 2000) studies present the results in terms of pounds of pollutants per mile but they do not include the vehicle operation in the analysis. Vehicle fuel efficiencies are used to bring all the fuel results to the same operational unit but the studies are a fuel upstream analysis only and do not include the emissions of the vehicle operations, for example.

All the other analyzed fuel/transportation studies (Delucchi, Greet and ETSU) consider at least the energy requirement of the main operational activities "from the well to wheels." The energy requirement calculation includes all the primary energy consumption (input in the main operational activities) and also the secondary energy consumption (input in the production activities of the fuels required in the primary activities). This secondary energy calculation is not performed in Unnash *et al*. (1996 and 2000). From the existing studies it is not possible to analyze the importance of Unnasch's decision since the results are calculated in an aggregated form; however, from the pathways analyzed in this dissertation, it can be said that they are not significant. See section 5.4.1.3 for more details.

The emissions and energy requirement involved in the construction material of the plants (concrete, steel, etc.) are calculated in the Delucchi and NREL studies. Therefore, the final (or total) result incorporates these boundary differences and it must be considered for purpose of comparison. Greet's model includes the emission associated with the vehicle material but not with the plant construction. According to Delucchi (1997), for light duty vehicles the energy requirement and CO_2 emissions increase about 2.7 to 3.6 % when the plant and retailers location are considered and also they increase 9 to 12 % when the vehicle material is considered. For the special case of solar-hydrogen vehicles (with Internal Combustion Engines) where the operational emissions are lower the increment is 19 and 72 % respectively.

2.3.3 Time frame

The time frame considered in the analysis is very important because it defines the technology to be considered in the study. It becomes more critical for the impact assessment phase, especially when the boundaries involve disposal, recycling, and decommissioning of plants. Material decomposition time, atmosphere reaction time, system regeneration time, and the life of the product/components may play an important role (for example, consider the replacement of batteries for electric vehicles within the time frame of 5 years and 10 years).

Unnash *et al* (1996) calculate their scenario 1 based on the year 1990 and other three scenarios (2, 3 and 4) for the year 2010. Unnash *et al*. (2000) present the evaluation for one scenario in the year 1996 and two scenarios for the year 2010. Greet (1998, 1999 and 2000) is a model that has two levels of combustion technology: one called "current" that was done in the early 90's before the 1990 Clean Air Act Amendment took effect, and one called "future" that does not specify any precise time. Theoretically, changing the percentage of current and future combustion technology for different calendar years can be analyzed. However, the model default for near-term vehicle technology analysis is 20 % for current and 80 % for future combustion technologies set for the year 2006 according to Greet (1999). ETSU (1996, 1997 and 1998) reports do not state the time frame of their analysis but at the same time they use the UK power generation mix composition of the year 1996 and analyze future vehicle technologies (i.e., fuel cell vehicles) that will not be on the market in the short term. NREL (1997 and 2000) studies give no specific time of consideration. NREL (1997) is done for a hypothetical plant that could be placed at any time and it considers that the life of the plant has been 30 years; however, for the material analysis it uses the TEAM – Tools for Environmental Analysis and Management data that is a software developed by Ecobalance, Inc. containing data for current processes. Finally, Delucchi (1991 and 1993) has the base case for the year 2000. On the other hand, according to Delucchi (1997) the model user can specify any year between 1995 and 2015 so that the model applies factors to scale up and down to the base year. Unfortunately, his model was not available, and in the report, results are presented for the year 2000 and 2015, but somehow all the tables, and results are equal.

2.3.4 Data

According to the ISO 14041 (1998), Life Cycle Inventory is “a collection and analysis of input/output data” and the data treatment is the most important phase of the entire assessment that will be done based on the LCI results. On the other hand, the majority of the authors investigating the LCA methodology agree that there is a lack of comprehensive data available for these studies and also that the quality of the existing data is in most of the cases questionable (Hendrickson *et al.*, 1997; UETP, 1996; Ayres, 1995; Lee *et al.*, 1995; Boustead, 1994; Denison, 1993; Franklin and Hoffsommer, 1992 and Hunt *et al.*, 1992). Data collection and data analysis have been pointed out as important sources of LCI results discrepancies.

The common advice provided by the studies presented before is that a company that can work with their suppliers’ information should prefer primary data (collected by the study). However, the cost of doing this is always a problem, for a very extended analysis it may not be possible, and finally, proprietary information cannot be checked or published. In addition, if the analysis involves a more generic product such as fuel, a single company’s data may not be sufficient to represent the possible mix of technology. According to the authors (referenced above) secondary data (from literature) can be out-of-date, especially for advanced technologies, to represent a large range of technology and in most of the cases gaps must be filled in. The solution suggested so far is that the steps used to fill the gaps must be identified in the report.

As a basic principle of any scientific study the data should be available for all researchers who want to reproduce the results. Today it is more and more common in LCI publications for only the results to appear and very few comments are made about generic assumptions in the model. Those studies are in most cases useless because they generate the situation of “believe me or not.” The selection of the so-called “most comprehensive” existing studies analyzed here was based mostly on the concern of the authors to publish their assumptions. Even with these selection criteria, one trying to reproduce the studies' results may have no success due to the lack of necessary information. All the assumptions used in Greet (1999 and 2000) can be checked since the model is publicly available; however, several inputs are the author's subjective assumptions with no explanation of the rationale for the decision. Some reports, like Unnash *et al*. (1996) and ETSU (1997), publish the spreadsheet table which helps somewhat more than the ones that do not publish them (e.g., Delucchi's report). When a subjective assumption is not the case, a common practice is the use of a single source of reference as input; could be cleaver sometimes it is not the case of a lack of other sources. A critical example is Unnash *et al.* (1996) using data from the early 70's for hydrogen plants. Similarly, ETSU (1996) uses U.S. EPA emission factors from 1985.

The data problem in the LCI methodology is so critical that Derenne (1995) suggests that all studies should establish an independent authority charged with supervising data collection and processing. Also, Ayres (1995) suggests that when more than three firms use the same process at the national level the data about that process should be available. The international standards (ISO 14040, 1997 and ISO 14041, 1998) suggest several levels of critical review: from an internal expert, from an external expert, or from a panel of experts representing the interested parties. Denilson (1993) goes further and suggests that the peer review should not be only a post-study activity but should also be integrated into the study design and execution phases.

According to Denison (1993) aggregation of data has been used to mask proprietary information. It is also used to preserve a standard routine in the model when external calculations are performed to generate a standard input format (like the plant energy efficiency). An important difference pointed out by Andress (1998) in his qualitative comparison between Delucchi and Greet models for ethanol fuel is the higher amount of external calculation performed by the Greet model. The problem with this external calculation approach is that, in general, the input and methodology of the external calculation is not published and the situation "believe me or not" appears again.

Denison (1993) comments about the difficulties of comparing different studies and figuring out the importance of some decision when the results are generated and/or presented in an aggregated form in the fuel/transportation studies. For example, Greet (1998, 1999 and 2000) include in all calculations the secondary emissions and energy requirement in such a way that one cannot check the importance of the secondary pathway in the calculus or compare the result with another study that does not include the secondary calculation in it. A similar problem occurs with Delucchi (1991 and 1997) in reference to the material for plant construction.

Finally, another common reporting problem in these analyzed studies is related to the technologies that they are considering. In general, they report well the combustion engine assumed (turbines, reciprocating 2 strokes, etc.); however, for air emission controls a certain kind of control is assumed without specifying it. It is useful to point out that the EPA/AP-42 (1995) reports several emission factors for equipment like boilers, reciprocating engines, etc. and that all of them are for uncontrolled situations. For some control technologies a factor is provided to reduce the uncontrolled emission factor, but not for all. The transparency in the assumed air control technology is also important to understand the potential for improvements in the future.

2.4 Methodology of calculus of existing fuel/transportation LCIs

What the previous Life Cycle Inventories (LCI) studies did well was to establish the calculus methodology to inventory the air emissions and energy requirement in the fuel/transportation sector. Basically, for each fuel that is analyzed one can define two different aggregations: the fuel pathway, defining the process involved in specific upstream-connected activities (or stages), and the system definition. For example, in the first aggregation, one pathway example is hydrogen fuel delivered as compressed gas at the fuel station, distributed by pipelines from bulk storage and produced from natural gas (NG) in a centralized steam reformation plant inside the analyzed area. A similar specific pathway is extended for the NG (feedstock) back to the extraction process.

The second aggregation is related to the system definition. For example, considering only the hydrogen pipeline pressure, some systems may assume the pressure of 200 psi (Greet, 1998) and others 1000 psi (ADL, 1996). Each new alternative considered should define a new pathway in a tree configuration; however, in practice, a single pathway may contain more than one system definition. The Figure 2-3 presents this idea. It is essential to point out that a single change in the system aggregation or in the pathway aggregation will change the final result.

The calculus is performed initially at the stage (or activity) level, and later a composition of the various stages defines the pathway result. This sequence idea is presented next.

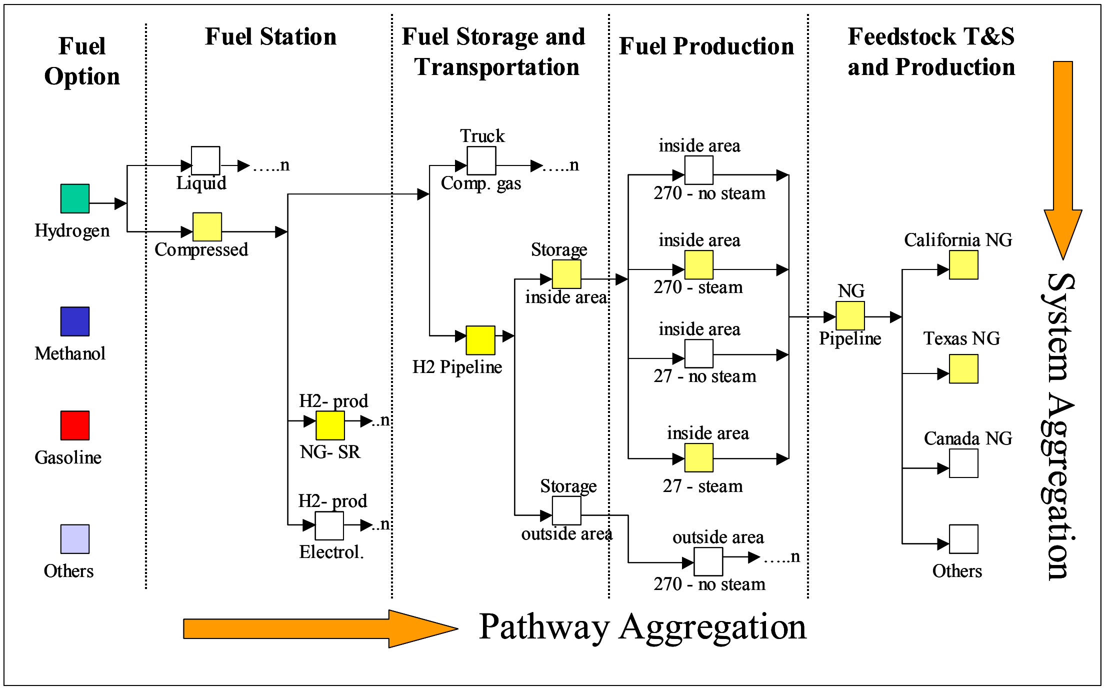


Figure 2-3: General idea of the fuel upstream calculation

2.4.1 Calculus for the stage (activity) level

The existing emission factors are, in general, established at the equipment level and they are associated with the equipment load or activity level. For example, grams of pollutant emitted per fuel consumed by a boiler, or pounds of pollutant emitted per work produced by an engine. These factors should be the representative average value of a long-term process activity and, in general, they are reported by organizations such as EPA and CARB. The EPA/AP-42 (1995) is the typical example of an emission factors publication. One interesting point here is that the AP-42 presents the emission factors for uncontrolled equipment only, and for certain equipment it presents a factor to adjust the uncontrolled value to an air control device assumed. The percentage of uncontrolled equipment versus controlled ones, as well as the percentage per type of air control technology assumed for a region is, most of the time, a subjective assumption due to lack of specific data, especially for a broad national analysis like the ones performed by Delucchi (1997), Greet (2000) and ETSU (1996). What is more common in the existing studies is the assumption of an aggregated emission factor, theoretically a weight average of all technologies assumed, without too much explanation or the rationale behind the assumption. Environmental policies and policies enforcement level may help make the decision of the assumption. In complement of that, the police analysis can be easier for a more restricted area, like in SCAB performed by Unnash *et al*. (1996) where it does not present the state's diversity of laws, enforcement strategies and success in their execution.

On the other hand, equipment of different sizes may also have different emission factors; therefore, by assuming one specific emission factor a scenario composition is created (explicitly or not). For this dissertation, the explained system aggregation is called the technological scenario composition. All these necessary assumptions in the technological scenario composition lead to discrepancies among the existing studies and also to the discrepancies in their final results.

Other information commonly available is the thermal efficiency of fuel production plants, or other activities, used, in general, in cost analysis. The thermal efficiency is defined as the total usable energy output from the system divided by the total energy input into the system. As presented in Figure 2-4, the thermal efficiency is the energy content in the products divided by the energy content in the fuels and feedstocks. When the thermal efficiency value is available, a required connection with the energy consumed at the equipment level is necessary. This connection is achieved by understanding the plant design and translating it into the energy share and equipment share. The energy share (E_{share}) is defined as

$$(E_{share})_n = F_n / \sum_{1}^{n} F_n \ , \qquad \text{Equation 2-1}$$

where F is the energy consumed from each different source (natural gas, oil, electricity, etc.) and n is the number of energy sources used by the stage. Similarly, the equipment share (Eq_{share}) is defined as

$$(Eq_{share})_m = Q_m / \sum_{1}^{m} Q_m \ , \qquad \text{Equation 2-2}$$

where Q is the energy consumed by each different equipment type (boilers, engines, etc.) and m is the number of equipment type used by the stage. Figure 2-5 shows the details of this idea where the “fuel-1” is the feedstock for the products production process. Eventually, depending on the available data, another pre-calculation is done to achieve the equipment load or the equipment energy requirement. These pre-calculations specify the detail level of the model. According to Andress (1998) a major difference between the Delucchi (1997) and Greet (1998) models for the ethanol calculation was that the detail level was much higher in Delucchi’s case. The majority of the existing studies use this efficiency approach presented that, in fact, is a complex "bookkeeping process." In other words, until this level of calculation (well represented by Greet models up to the version 1.5a), the analysis assumes the character of "if-then." For example, if the efficiency of the process "X" is "w," then the result "Y" is equal to "z." This situation reinforces the necessity for well-discussed input assumptions, in order to avoid a "garbage in – garbage out" situation.

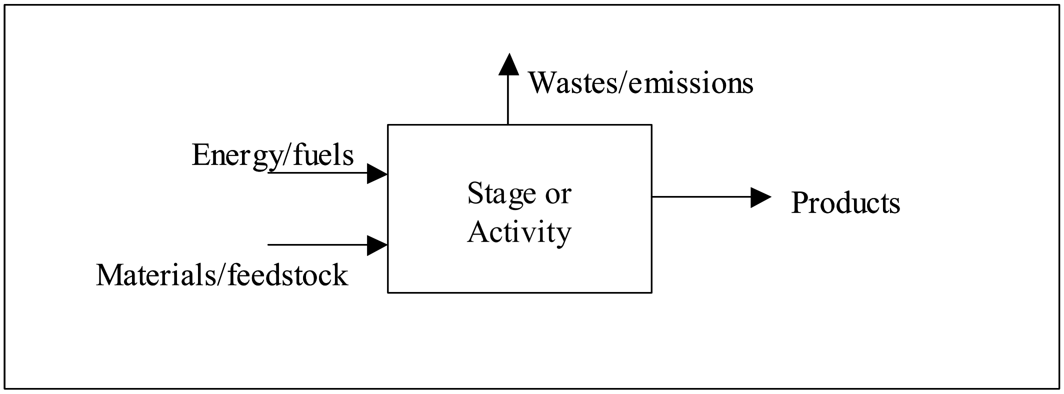


Figure 2-4: Input/Output idea at the stage level

For certain activities Unnash *et al*. (1996) uses physical parameters like work, volume, etc., to calculate the activity level of the system analyzed. This "component-model" brings the analysis to the level where a worker-expert from a plant (or system) similar to the one analyzed can provide accurate information and even some new data. Of course, because the ultimate target is the energy (fuel, materials, electricity) consumed, it is necessary that a unit conversion involving some kind of efficiency concept (vehicle fuel efficiency, compressor efficiency, etc.) be made.

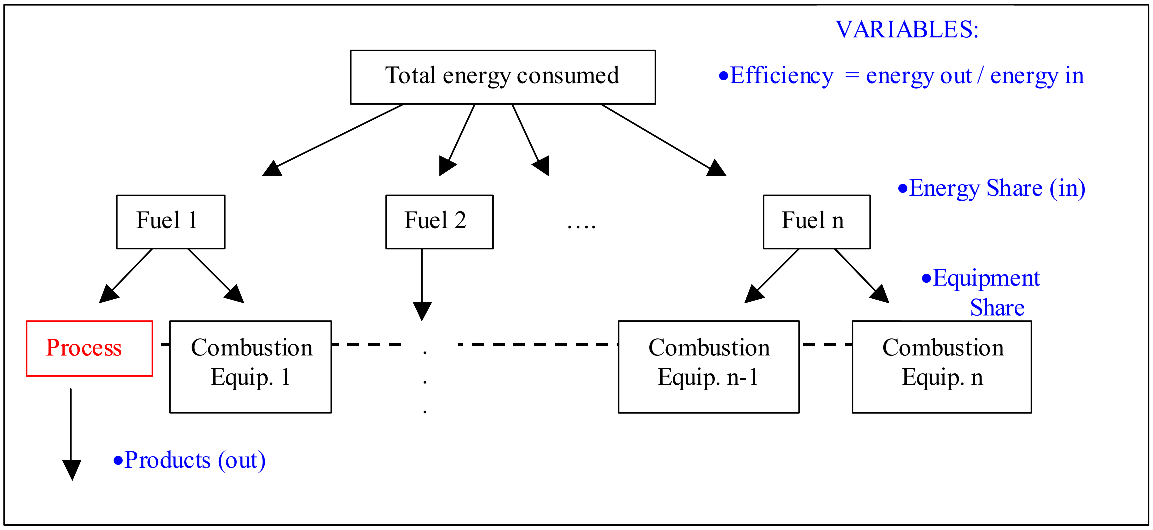


Figure 2-5: Establishment of the equipment activity or load process

A small difference should be considered for transportation stages where the final efficiency is associated with the distance transported. The lack of this distance association in the calculation was one of the main constraints for this project to use the available Greet (2000) model at that time for local analysis (the other one was that all the equipment assumptions are supposed to reflect the U.S. national average data only). He and Wang (2001) solved the distance dependence problem in the Greet version 1.6.

Having established the equipment loads, the final result is the sum of the multiplication of every equipment load per its associated emission factors. In this dissertation, these emissions are called process emissions and, in most cases, they are associated with combustion activities and with the designed air control equipment. Another kind of emission is the fugitive emissions associated with maintenance, malfunctioning, spills, leaks and losses in junctions, purges, etc. For certain kinds of equipment or activities (e.g., natural gas extraction or fuel storage tanks) there are similar emission factors, as explained before, and the way to calculate the emissions is the same.

However, in most cases no emission factors are available and a percentage of the fuel consumed by the equipment or activity is assumed to be lost. The amount of pollutants presented in the composition of the fuel lost is then calculated and added to the process emissions to give the total emission of the activity. Figure 2-6 shows a graphical representation of this idea. By looking into the literature, one can note that the assumption of the average process design, translated into energy share and equipment share, as well as the amount of fuel lost, is not well documented. To some degree the input assumption becomes a subjective matter and a source of uncertainties and disagreement about the final results of existing studies.

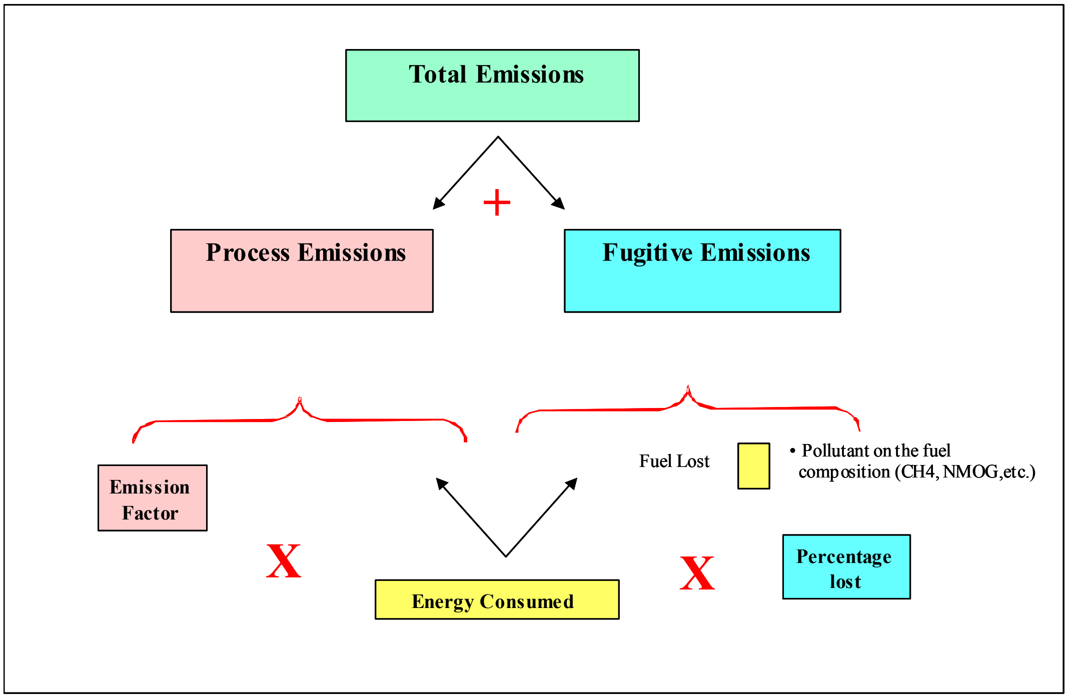


Figure 2-6: Graphical representation of the emission calculation at the stage level

The emissions calculated are attributed to the geographical region where the activity is considered. For the life cycle approach it is also necessary to consider the emissions associated with the production and distribution of the fuels consumed. The life cycle of these fuels, called here secondary emissions, may occur in different regions and should be kept separate if geographical occurrences are considered. None of the models but Unnash *et al* (1996) considers the geographical occurrences, and what they do is to sum, in most cases, the secondary emissions into the primary emissions calculation. These aggregated results also make comparative analysis difficult to understand whether the eventual differences are related with the secondary emissions, and to understand the importance of these emissions.

2.4.2 Co-products allocation

Since a single process can generate more than one product (with market value) the energy requirement and the emissions generated by the process should be allocated among all these co-products. Some authors like Weidema (1993) call main-product the co-product which is used in the next step of the investigation, and by-products the co-products that are outside of the investigation's scope. For simplification and following Vigon *et al*. (1993) denomination, only the term co-product will be used and it will be applied every time the activity generates a product different from the main product investigated.

Different approaches can be used to allocate the co-products credits (or debits) of the environmental aspects calculated and, in most cases, the final result is very sensitive to the allocation procedure assumed. Currently, there is a search for an acceptable single allocation criterion to become standard to eliminate this source of disagreement and eventual manipulation. So far, all the proposed criteria suffer from several limitations, and according to EETP-EEE (1996) none of the allocation criteria is universally applicable. Therefore the choice must depend on the type of product.

Allocation connected with physical properties such as weight, energy content, or chemical equivalents has been used and sometimes suggested as a general procedure (Hunt *et al*., 1974; Consoli *et al*., 1993 and Vigon *et al*., 1993). According to Boustead (1992) the benefit of using physical properties is to keep the allocation stable under a given technology. However, one should not use weight allocation, which works well for metals, for energy services or use chemical equivalent for agricultural crop products and so on.

The economic or market value of the co-products has the obvious advantage of being universally applicable. According to Weidema (1993) Basler and Hofman had first used this approach in 1974, and Heijungs *et al*. (1991) suggested it as a general methodology. According to EETP-EEE (1996), the transient nature of economic values is the main problem adopting in this approach. Even when an averaged price over long periods of time is used, fluctuations are unavoidable and emissions will vary without any change in the technology itself.

The market displacement approach works with the rationale that most of the co-products can replace or substitute for other products, eliminating the environmental aspects associated with the ones replaced. In other words, the accumulated environmental aspect of the process minus the accumulated environmental aspects of all co-products will be the associated environmental aspect of the analyzed product. Vigon *et al*. (1993) used this approach to analyze waste incineration and Heintz and Baisnee (1991) suggested it as a general method. This approach involves the addition of a new life cycle "branch" to the process tree for every co-product, and it may be too complicated if several co-products are involved. Also, the decision of the replaced product can be subjective and it also may change over time (Weidema, 1993).

The international standard ISO 14041 (1998) suggested three ranked steps for the allocation procedure: first, wherever possible avoid the allocation necessity by splitting the unit process or by expanding the product system. Second, where allocation can not be avoided, use some kind of physical relationship between the products, and, finally, where physical relationship is not possible, another kind of relationship like economic value shall be applied as last choice. Weidema (1993) presents an interesting comment that allocation by physical properties can be seen as a special case of the allocation by economic value. In the fuel analysis, for example, the market value of the fuel has a strong correlation with the energy content in the fuel and therefore the fuel energy content should be chosen as the allocation method. However, this idea does not apply for fuel productions that involve other kinds of co-product, like food in the corn ethanol case.

For fuel co-products, like natural gas liquids, Greet (1998, 1999 and 2000) and Delucchi (1991 and 1997) use the energy approach. For the ethanol production from corn, the Delucchi study uses the co-product displacement approach and Greet gives the option to alternate between the displacement approach and a mix of market value and energy content. Wang *et al* (1997) did a sensitivity analysis to test the importance of using this approach for ethanol calculation. According to his analysis the most significant factor in the study was the co-product credit allocation. Using different approaches the authors got results with differences up to 40 %.

It is not clear in the report how ETSU (1996) handle the allocation process. The only statement about the issue is this one: "by-products are excluded from the analysis in the case of well-established processing operations. However, for new biofuels where by-products markets are weak and under-development, potential energy credits for by-products have been included in the range of possible outcomes."

2.4.3 "Average emissions" versus "marginal emissions" calculation

Unnasch *et al*. (1996 and 2000) have been pushing the idea of using the life cycle approach to calculate the "marginal emission" as opposed to the "average emission" performed by all the other studies. Unnasch *et al* (1996) take no internal co-product credits into account and use the "average emissions" in their study, but they introduced the idea of "marginal emissions" for the electric generation inside South Coast Air Basin (SCAB). The "marginal emission" idea was inspired by the fact that SCAB has a law called RECLAIM that caps the amount of NO_x emitted inside the basin, based on a fixed amount of emission credits that the companies must have to emit NO_x. The companies claim that it does not matter which technology is used because the final emission must comply with the law and therefore the "marginal emission" in this case will be always zero.

Unnasch *et al*. (2000) uses only the "marginal emissions" approach to come up with their results. In order to do that, it was necessary to use the co-product replacement method, which presents the problems discussed by Weidema (1993). The life cycle "branches" of the co-products are not included in the Unnasch *et al*. (2000) analysis introducing much more uncertainty.

It is also my personal opinion that the “marginal emissions” idea goes against the general idea of life cycle analysis which has been developed to compare the environmental aspects of two different products or services. Some of the outcomes are interesting to analyze if the “marginal emission” approach is considered in a study. For example, if a methanol car replaces a gasoline car, no upstream benefit is found since the oil refineries inside the area are going to produce gasoline for exportation. In fact, the methanol ship tankers, fuel terminals, etc., can introduce more upstream emissions. In a landfill gas case example, if one tries to analyze what the best way (in terms of NOx emission) to use the gas would be, the answer will be “it doesn’t matter” - the marginal emission will be zero whether producing electricity or methanol. However, in reality, methanol production may emit less and other mechanisms (e.g., RECLAIM) will allow the pollutants to be generated later somewhere else.

It is important to point out that various important aspects of the “marginal emissions” approach have been previously incorporated in the “average emissions” approach calculation when the technologies designs are selected; i.e., to choose the technologies design it is necessary to analyze the local emission control enforcement, cost, existing fuel production capacity, etc. In fact, the “average emissions” approach is an average calculation of the “marginal technology” selected.

In summary, the decision about which is the best methodology for the calculation is based on what fundamental question the study wants to answer. If the question is “Which fuel technology has the highest potential to emit less air pollutants?” or “How much emissions will be released by a specific technology over its life cycle activities?”, then the best methodology, in my opinion, is to use the “average emission” approach.

On the other hand if the goal-question is “ What amount of pollutants will the population breathe?” then I am afraid a very complex model will be necessary, accounting for the location of the emission sources, atmospheric conditions (wind directions, temperature, etc.), population densities, and so on. What the “marginal emission” approach tries to do is to figure out the “net” emissions considering all the sources in an area. In some sense this approach is one step towards the solution for the proposed second goal-question, but, unfortunately, it is moving towards greater complexity and therefore a more complex model is needed. My suspicion is that making huge assumptions without modeling them, as it is the case in Unnasch (2000), only increases the uncertainties of the study without knowledge of these uncertainties. Specifically, I am talking about the assumptions for displacement of fuels (without any economic or demand modeling being performed) and the emission credits based on the displaced technology (without a complete life cycle analysis of that technology within the study).

2.4.4 Pathway level calculation

At the pathway level, the calculation is basically the total of the emissions and energy requirement calculated for every stage of the pathway – this is what I called, above, a “bookkeeping calculation.” However, some other sections are important to point out here. The first one is the downstream own-use factor that takes care of the consumption of the analyzed fuel in the downstream activities. In other words, if part of the input fuel in a stage has been consumed there, for example, transporting diesel in a diesel truck or losing fuel in fugitive emissions, the previous stage must supply more fuel to account for the delivered and consumed fuel in each stage. In general, an own-use factor is generated in each stage (similar to efficiency) and a multiplication of them gives the downstream own-use factor. In spite of considering minor mistakes, some pathways of some studies present problems in this calculation when they try to aggregate activities in one single block, like considering storage and transportation together.

At this level may also occur the mixing of more than one pathway to generate different combined scenarios for analysis. To do that, generally a weight average of the pathways results is used. Also, if the study accounts for areas of the emission occurrence, as in Unnasch *et al*. (1996 and 2000), the separation of the areas occurs at this level too, allocating each stage's results into different cells and totaling them later.

A second important point is the consistency in the values of energy content used to add up the results of each stage. Theoretically, for some stages where the fuel combustion water remains as a gas; if the sensible heat and latent heat of a water vaporization is not used by the process, then net calorific value or low heat value (LHV) can be used in the stage calculation. Examples of these stages are truck transportation and pipelines. On the other hand if the stage utilizes the heat of the water condensation, like refineries and power plants, the use of the gross calorific values or high heat value (HHV) is recommended. The most important point is to care about the use of both heat assumptions to add the stages' results and get the final pathway results. This inconsistency was not found in any study, but all the studies do choose one single heating system to perform all the calculations and, therefore, to compare their results one should account for these possible differences. Delucchi (1991 and 1997), Unnash *et al*. (1996 and 2000) and ETSU (1996, 1997 and 1998) use HHV. Greet (1998, 1999 and 2000) use

LHV. Boustead *et al*. (1992) suggest the use of HHV for fuel calculation and so do I. Since the sensible and latent heat of water vaporization is there, in the process, and can even be measured, it is only a technological strategy to use them or not. Low heating values are only a subterfuge to show better efficiency in a process.

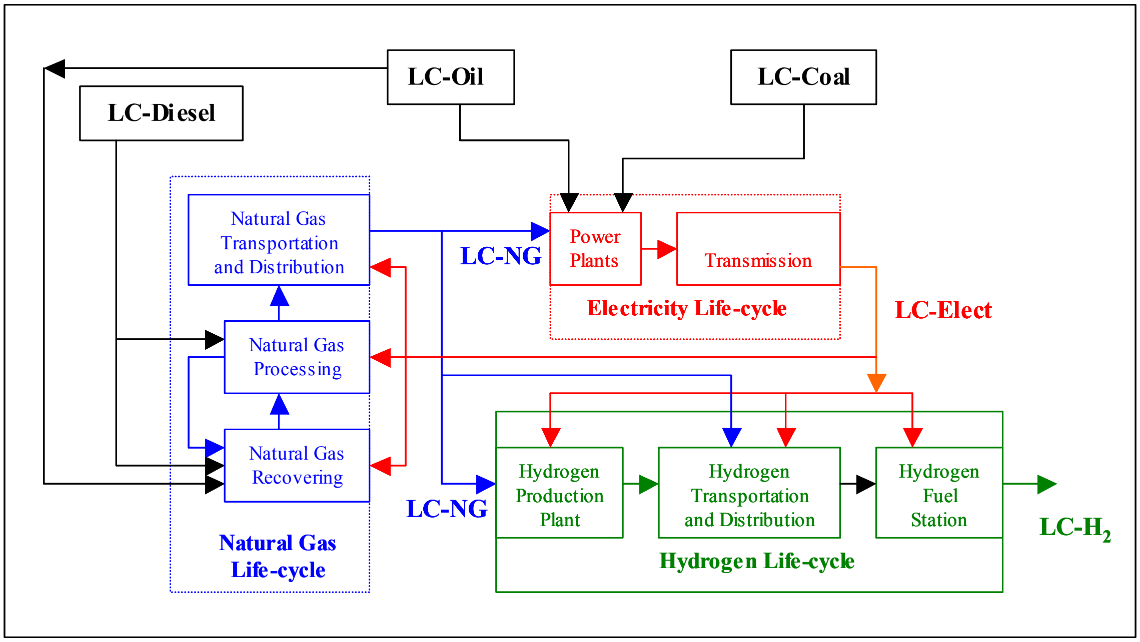


Figure 2-7: Complexity of the life cycle calculation showing the interdependence among fuels (LC = life cycle results).

The third section is the interdependence among fuel production processes. The Boustead model was the first study to solve the problem of interdependence of energies by performing simultaneous interactions in the model where the first results are used as inputs for the second interaction and so on, until some convergence is achieved (Boustead, 1992). It accounts, for example, for the convergence of the energy consumption of electricity and natural gas use in Figure 2-7. Since electricity can be used in the natural gas process that later can generate electricity, the circular calculation is necessary. The importance of it will depend on the initial inputs assumed, and simplification of the system into linear sequences to avoid the problem may give rise to significant errors according to Boustead (1992). Delucchi (1991 and 1997) and Greet (1998, 1999 and 2000) use this approach. Unnasch *et al.* (1996 and 2000) and ETSU (1996, 1997 and 1998) do not.

A possible problem occurring in the existing studies that do use the circular calculation approach is that it should be done geographically, and there is no evidence that it was done. For example, the electricity produced in the US is not used to process natural gas (NG) in Canada, even if some power plant in US uses Canadian NG. Another example can be a bunker fuel consumed and refueled by a crude oil ship-tanker in a US port and in a remote area port.

2.5 <u>Quantitative analysis of existing fuel/transportation LCIs</u>

Based on all the sections presented above one can realize the difficulty of matching a similar scenario and pathway to compare the existing studies results in a fair way. Similar problems will be found trying to create a composite result from existing studies. Mark (1998) did a comparison among the upstream emission results of some models for compressed hydrogen fuel, produced in a centralized steam reformation process, from natural gas. Figure 2-8 and Figure 2-9 show examples of his findings. A strong need for better comparative evaluation studies was clear, since no agreement was found among the models for either the total emissions or their detailed origins. Similar analysis was done at the beginning of this project, agreeing with the Mark (1998) findings. Figure 2-10 presents my result for natural gas recovering and processing for the gas used as feedstock in hydrogen fuel productions. Figure 2-11 shows another example of mine for methanol upstream activities in terms of total energy consumption. It is good to keep in mind that some adjustments are necessary in order to present all results in the same units, and that some differences in the scenarios are still present, but they serve well as examples for discussion.

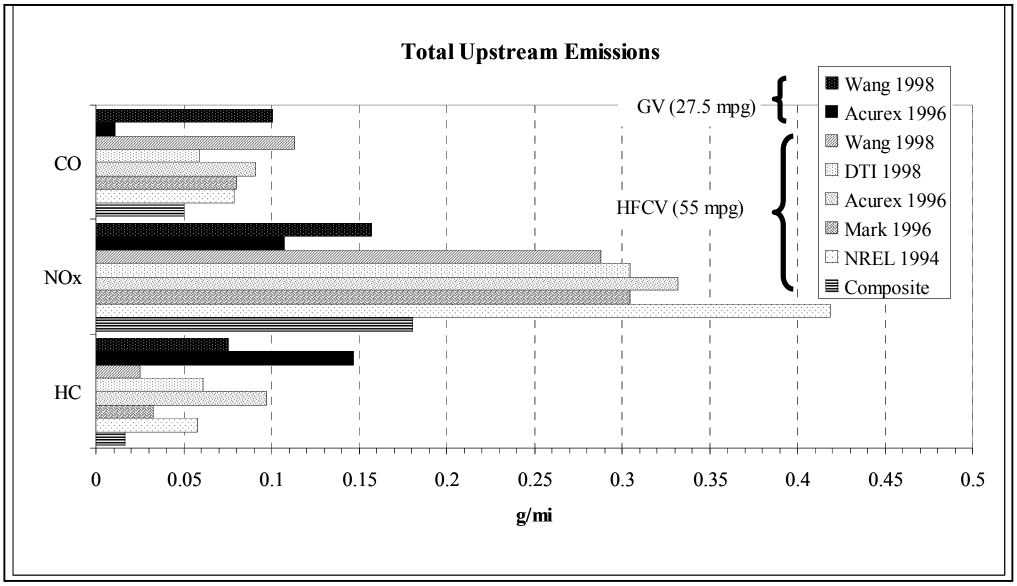
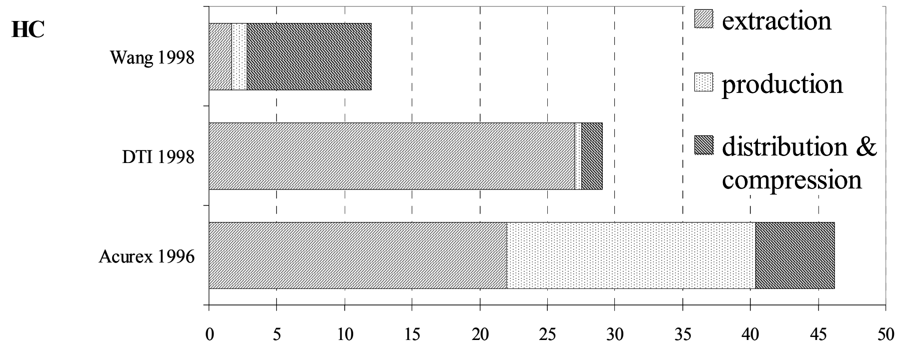


Figure 2-8: Mark (1998) comparison of the total upstream emissions for fuel cell vehicles in existing models

These result mismatches can be extrapolated to other fuels and pollutants as well, and some different examples were published in Contadini *et al.* (2000a). The paper also discusses the three main reasons for the result mismatches. The geographical differences are the first one. They are related to the initial study objective and, in general, can be found stated in the reports. Problems arise when they are put together for comparisons, such as the case of the Mark (1998) presentation, comparing a SCAB analysis with a US national analysis. Similar problems occur in the three figures presented in this section, and a good solution is to identify the geographical differences very clearly in the slides, as shown in Figure 2-11. Another situation where this problem arises is in the attempt to generalize the results. A classical example was the press release of the Pembina/Suzuki (2000) study. In the press release, some results were presented and discussed as universal but nowhere was the scope of the calculation done for Canadian scenarios clarified.



	Acurex 1996	DTI 1998	Wang 1998
▩ distribution & compression	5.8	1.5	9.2
▤ production	18.5	0.5	1.1
▨ extraction	22.0	27.1	1.7

g/mmBtu (CH2 delivered - LHV)

Figure 2-9: Mark (1998) comparison of the hydrocarbon emissions calculated by existing studies, for gaseous hydrogen fuel produced in centralized plants (SMR process).

A second problem is related to the technology composition scenario. Using the methanol analysis as an example, one can check that Delucchi’s results are based on a combination of coal and natural gas to methanol. Greet’s results are 100 % natural gas to methanol, but they are also a combination of 20 % of current technologies with 80 % of future technologies, and the Acurex results are the combination of 50 % advanced steam reformation plants and 50 % of advanced combined partial oxidation plants.

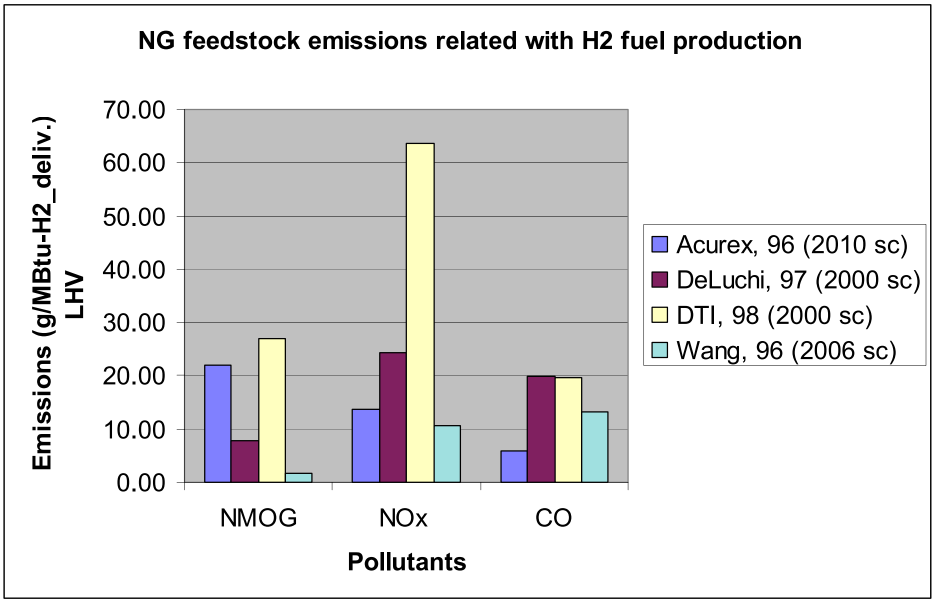


Figure 2-10: Total emissions associated with natural gas recovering and processing from existing models.

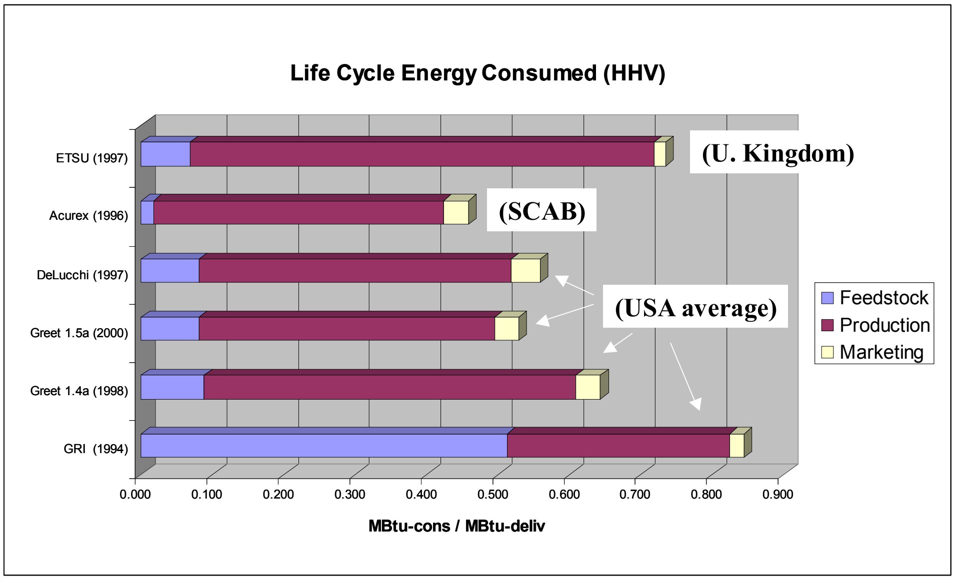


Figure 2-11: Life cycle energy consumption for methanol fuel from existing studies.

The level of the technology scenario composition goes as deep as the calculation detail performs. For example, for a very specific process such as the natural gas processing within the same area, different studies assume different combinations of equipment consuming the gas in the process (equipment share). Table 2-1 presents the values.

Table 2-1: Equipment share of US natural gas processing (%).

Study	Darrow (94)	Greet 1.5	Harrison 99	ADL(96)
NG Turbines		50	54	
NG Recip. eng.			46	67
NG Boiler	100	50		
Process Heat				33

The third level of disagreement, and also very important for this project, is the use of deterministic values to represent complex systems. For example, even considering a very specific technology, such as a typical-size (2,500 metric tons per day) production plant of methanol, using steam reformation process to produce the syngas, the efficiency numbers, without the consideration of extra steam for exportation (second column of Table 2-2), generate a lot of mismatches among the existing studies, going from 59 % to around 70 %. A reason for that is clear: the measurement over time of a single plant efficiency will vary according to the natural gas composition variation, operational adjustments, equipment malfunctions and maintenance, catalyst deactivation and so on. Trying to represent with a single number the average of several similar plants operated by different organizations and placed in different regions within the same country is not an easy task. It is hard to defend one study value as better than another one, especially because there is a lack of detailed information in the literature, such as operational pressures, catalyst load and life, etc. For example, EPA and CARB do not release emission factors of plants, such as methanol or hydrogen, and what the existing studies try to do is extrapolate them from boiler data and other equipment. In all these cases, the uncertainties behind each single number are also not apparent, and may contribute to eventual manipulation of the technological data, also generating mismatches.

Table 2-2: Analysis of existing data for methanol production plant.

Typical Size: 2,500 metric tons of MeOH per day – Steam reformation syngas						
HHV	Efficiency (%)		Electric. used (%)		NG used as fuel (%)	
Extra Steam/Electricity	Without	With	Without	With	Without	With
Greet 1.5a (2000)	69.6	71.6	0.2	-3.33	17	24
Acurex (1996)	-	68.3	-	-0.02	24.1	-
Delucchi (97, 93)	65	-	0.2	-	-	-
Greet 1.4 (1998)	65.6	-	0.2	-	-100	-
Darrow/GRI (1994)	-	66.1	-	-0.007	-	22.6
Ogden *et al* (1994)	67.4	-	1.8	-	-	-
DTI (1998)	64	-	-	-	-	-
Chem. Ecn. HB (96)	-	71.3	-	-	-	-
Dybkar (in Wang)	66	71.6	-	-	-	-
Islan (in Wang)	63	-	-	-	-	-
Borroni-Bird (96)	59	70	-	-	-	-
DOE (89)	61.1	70.4				
Sweeney (98)	65	-	-	-	-	-
AMI (98)	60	70				
Allard (2000)	64					
LeBlanc (in Cheng, 94)	69.4		0.81			
Leveton (2000)	64.0					
Pembina/Suzuki (2000)	61.8					

One way to represent these systems variation is by using distribution curves. This solution can be applied to all systems and even for values that everybody expects to be constant. As an example, Table 2-3 presents some physical parameters of hydrogen (H_2) used by existing studies. Of course, the study results are more sensitive to some variables modification than others.

Sensitivity analysis is an interesting approach to focus attention on the aspects that are important for the overall results of the assessment. One idea is to develop the LCI study in an interactive process starting with a simplified version of the product life cycle and after a sensitivity analysis concentrate the effort in the critical areas (EETP-EEE, 1996). The ISO 14041 (1998) suggests performing sensitivity analysis on significant inputs, outputs and methodological choices of the Life Cycle Inventory (LCI).

Table 2-3: Hydrogen physical parameters used by existing studies.

Analized Fuel	**Hydrogen - H2**							
Sources	DTI	DeLuchi	Ogden	Greet	Acurex	Pembina	MIT	Heywood
	1998	1993	1999	2000	1996	2000	2000	1988
Energy content (Btu/scf - HHV)	325	338	324	324	324	325		343
Energy content (Btu/scf - LHV)	273.4		274	274	274	274	290	290
Fuel density (g/scf)		2.52		2.40	2.40		2.546	2.549
Molecular Weight (g/mol)								2.015

What some of the existing studies do is to present different scenarios that are primarily variations of the system and/or pathway aggregations only. In this kind of analysis several inputs are changed at the same time and the significance of the changes is never discussed by any of the authors. The possible variation among the input data at the equipment level can also be critical but, in spite of its importance, this variation is not considered very seriously yet. Unnasch *et al*. (1996) is one of the studies that devotes some space to this kind of sensitivity analysis. Their report shows a huge variability of the individual NMOG emissions for the reformulated gasoline case, though the data and the methodology related to the calculation are unclear.

Greet 1.6 (2001), following early recommendations of this project, implemented as well the concept of uncertainty analysis in the model, using Monte Carlo simulation and probabilistic curve as input. In spite of the right direction adopted it is still suffering from several misunderstandings of the methodology proposed (section 3). Basically, Greet 1.6 uses triangular curves to represent bounding scenarios without realizing that by doing so it is accounting for zero probability of that scenario to occur. It also made no attempt to correlate the variables, and no regression sensitivity analysis – to understand the importance of each curve – was reported. In complement of that, unfortunately, the major problem of the model was, perhaps, the calibration of the curves with a very biased pool of experts. All of the experts were from only three oil companies that had explicitly engaged in pushing the gasoline pathway as the best solution for the future fuel cell fuel infrastructure problem.

In conclusion of this section, it is good to reinforce the difficulty of relying on one single value as input for the model or as the result of it. Based on that, it is almost impossible to do a fair comparison on the final results of existing studies. However, comparisons done at the detailed level are possible and very informative, as the examples presented here show. In fact, the comparison at the level of equipment and single stages is easier to perform and guarantees that only similar technologies and assumptions are present. This dissertation completed several of these detailed comparisons. They are incorporated in the database of the created FUEEM model and some of them are presented in section 4.

3 FUEEM METHODOLOGY

As described in section 1.3, this project and the development of the Fuel Upstream Energy and Emissions Model (FUEEM) was targeting to deal with uncertainties in life cycle assessment studies, in particular, in the analysis of fuel cell vehicles and their potential new fuels.

As explained in previous sections (2.3 to 2.5), some subjectivities and uncertainties will always be an inherent part of this kind of study and, therefore, the basic idea was to explicitly recognize the uncertainties and quantitatively include them in the model and analysis results. By doing that, my expectation was to generate richer information, minimize possibilities for future result mismatches, and create a higher level of credibility for a life cycle assessment study.

Three main necessities were recognized. First, the necessity to improve the analysis of data input trying to minimize situations described as “garbage in, garbage out,” thereby increasing the level of credibility of the study. A second necessity was to choose a variable format that better represents uncertainties than a single deterministic value. Finally, a third necessity was to create a model that combines and propagates the uncertainties through the calculation. I established as a parallel contribution the creation of a model that allows more flexibility for local analysis.

Working on the solution of these three necessities, this study generated two major original approaches. The first was the development of a methodology for the input data treatment for future technologies based on the concept of interested parties. The details of this methodology are presented in section 3.1. The second was the adaptation of economical risk analysis techniques into FUEEM to represent and propagate uncertainties into the calculation. The techniques involve the use of probabilistic curves, Monte Carlo simulation, and rank correlations. The details of these techniques are presented in section 3.2.1 and some details of the model are presented in section 3.3.

3.1 Input data treatment for future technologies

Most of the development of the FUEEM methodology to treat input data for the fuel cell vehicle analysis was based on the possibility of having an international panel of experts cooperating with the project goals. The objective of this section is to present the methodology adopted to take maximum advantage of the expert participation and to explain the rationale behind the decisions made. Several other methodologies exist to deal with the same necessity; therefore, this project solution is presented here as a case study. By doing that I hope and expect that future assessments involving interested parties participation will be able to benefit from this previous experience.

In pointing out some specific areas of this case study, I hope also to assist in future comparisons and extrapolations of this method. However, as a study case, there was no attempt to compare different methodologies at this point. Future attempts can be driven by Al-Alawi and Islam's (1996) statement that the best methodology is the one that accomplishes the project needs most effectively without compromising the quality of the project results. By interviewing the interested parties, I established the goal that the FUEEM results would be more realistic and acceptable by all parties. Incorporating the uncertainties into the calculation was one way to achieve a better representation of reality because of the common sense statement that 'the only thing we know about the future is that it is uncertain.'

The specific needs and the resources to achieve them are presented below, but, as a general comment, it can be said that the Fuel Cell Vehicle Modeling Program (FCVMP) is a five-year program (1997 - 2002) and that the FUEEM idea was created within the FCVMP one year later (1998). This "long-term" definition gave the FUEEM the opportunity to develop incrementally, using pilot models to establish the "final" calculation methodology and data treatment. The search to express real systems evolves from deterministic values, to ranges bounding a most probable case, to probabilistic curves, and finally to the dependency among curves. In this entire process, three types of general information could be identified:

Future scenarios: Several sections should be evaluated at the same time in order to forecast (for 2010) what may happen at different production sites and in the commercial activities that comprise a life cycle study. Possible variations of the current trends, public concerns, environmental laws, fuel and vehicle cost and market competition, new technologies, safety, and public perceptions are only a few examples of the complexity that the study faced.

Technical background: Air emission calculations deal, in general, with equipment emission factors associated with the activity level or equipment load. The equipment activities (work generated, fuel produced, energy consumed, etc.) constitute important information, and the "design" or interaction and balance among all the pieces of equipment in an industrial/commercial process is fundamental.

Literature adaptation: Almost all the data, such as emission factors and plant efficiencies, that are currently available in the literature are presented as deterministic values. The exception is Harrison *et al*. (1997), who present the values together with their associated errors. Since the FUEEM input data are probabilistic curves, an "adaptation" process was necessary.

Other important conditions were the participation of some of the major fuel companies (FCVMP sponsor donors), the involvement of some government agencies, and the UC Davis tradition in fuel analysis (Sperling, 1988; Sperling and Delucchi, 1989; Delucchi, 1991, 1993 and 1997 and others). These factors were fundamental in initiating and working with the concept of the expert network that became a very important part of the developed methodology. Other existing resources previously established in the FCVMP are the annual conferences and workshops. Both were incorporated into the FUEEM's assumption determination process.

3.1.1 The General Process

It was clear from the beginning that the best way to generate the input assumptions for the future was to split the task into two major problems:

A. To identify and understand the process values and their uncertainties in the present, and, based on that,
B. To estimate the values and their uncertainties for the future (year 2010).

A broad and comprehensive literature survey was identified as fundamental to analyzing the characteristics of the processes in the present. Eventually, complementing the data available in the published literature with industry surveys was expected to be plausible, depending upon the necessity, resources, and willingness of the companies to disclose their data. With the implementation of the methodology and the analysis of the existing data, the surveys became very important. The expert analysis was expected to complement these two data sources, since there is a lack of knowledge of data uncertainties in the current literature according to an EPA study of uncertainties in air emissions estimates (EIIP, 1996). This EPA report recommended using expert judgment as the preferred method to quantify the uncertainties of the existing data.

On the other hand, to extrapolate existing knowledge to the future, the technology forecast literature employs several techniques and they are classified in different ways (Sullivan and Claycombe, 1977; Armstrong, 1985; Porter and Rossini, 1987; Porter *et al.*, 1991 and Al-Alawi and Islam, 1996). Porter and Rossini (1987) present an interesting summary of five major techniques for forecasting:

A. <u>Monitoring</u>: To gather and organize information for use in forecasting (not a true forecast process but a support technique).

B. <u>Expert opinion</u>: To use when data are lacking and when modeling the situation is difficult or impossible. It is based on the idea that some individuals know more about a section than others.

C. <u>Trend analysis</u>: To apply statistical techniques when there is a significant amount of good data over a time period. It assumes that the past trend will be repeated in the future.

D. <u>Judgment-based models</u>: To reduce a complex system to a manageable representation when an acceptable theoretical framework is available.

E. Scenario construction: To integrate forecasts from various sources and techniques into a coherent picture, may encompass a plausible range of possibilities for some aspect of the future; can be a fantasy if a firm basis in reality is not maintained.

Porter *et al*. (1991) comment that these approaches should be neither exclusive nor exhaustive in a real inquiry. According to them, better inquiries result from using a combination of these techniques and the FUEEM inquiry and forecast tried to follow that advice. However, the reality is that the data are limited for a trend analysis, and disqualifies any possible theoretical framework (assuming one were available) to build a judgment-based model, since fuel cell vehicle development requires new conceptions of fuel. Porter *et al*. (1991) also describe different techniques to collect expert opinions, such as individual input; committees, seminars and conferences; the nominal group process; surveys; and the Delphi process. As explained below, all these techniques are used in some way in FUEEM.

3.1.1.1 The Expert Network

The FUEEM general process has a major component involving activities done by an expert network, and also contains activities done within the project only (but with a strong relation to the previous component). The expert network is an agreement among a panel of international experts to cooperate continuously with the project effort, based on their interest in the quality of the generated results. The expert network concept was introduced in the FCVMP agreements from the beginning of the program in the summer of

1997. Figure 3-1 shows a graphic representation of the adopted FUEEM participatory process.

The first step was to transform the early expert network idea, initially composed only of the project sponsor donor experts, into the concept of interested parties' participation. Experts from several other organizations were invited to participate. Around 25 to 30 experts have been involved in the process over the first two years. Organizations were invited to participate based on their industry membership (hydrogen, methanol, hydrocarbon fuels and equipment), involvement in previous modeling/analysis efforts and/or involvement in previous data generation, analysis of results or review process (universities, government agencies, national laboratories, NGOs and some private organizations). Two organizations required confidentiality and therefore are not listed among the participants presented here:

- Organizations participating full time since the beginning: Air Products, Methanex, Chevron, Exxon/Mobil, BP/Amoco, Acurex/ADLittle, California Air Resources Board, South Coast Air Quality Management District, Union of Concerned Scientists, Imperial College of London, Institute of Transportation Studies and University of California at Davis.
- Organizations participating part time (due to late entrance, specific interest or attrition): Aramco, Praxair, Hydrogen Burner Technology, Syntroleum, Directed Technologies Inc., National Renewable Energy Laboratory, Argonne National Laboratory, Environmental Protection Agency, Department of Energy and Princeton University.

The expert network activity details are discussed under the section 3.1.2.3. Two other activities in the general process that are not conducted by the expert network are discussed next.

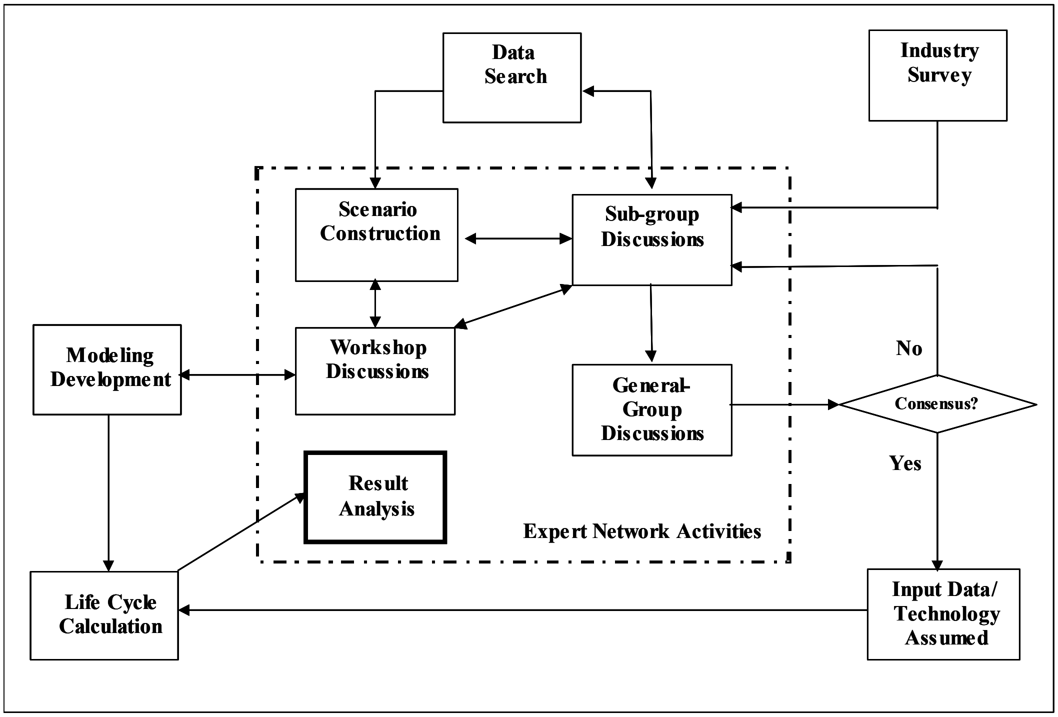


Figure 3-1: FUEEM Participatory Scheme for Future Technology Assessment

3.1.1.2 Data Search

The objective of this activity is to gather and organize the existing published data about the performance of current processes alongwith any published forecast of future performance. In general, the existing data for fuel upstream activities and emissions are a collection of single numbers from different studies that hardly represent a unique technology or time series data for an eventual trend analysis. A discussion of the data characteristics necessary for trend analysis can be found in Welch *et al.* (1998), Armstrong and Collopy (1993), and Armstrong (1985).

The existing fuel life cycle models and studies (Acurex, 1996; Wang, 2000, Delucchi, 1997; ETSU, 1998; Spath and Mann, 2000; etc.) apparently established their input parameters based only on a literature review. It is very common for one single source to be the basis for all input parameters on a given section within a study. On the other hand, in the FUEEM process, the result of the data search is very important but does not feed the model directly. Instead, it is used to feed an important discussion/consensus process that will generate the input assumptions to be used within the model.

In general, the results of this data search are presented to the expert network in table format. Table 2-2 is an example of this output format used for a specific methanol (MeOH) plant analysis.

Other important sources of information are the progress in Research & Development technology, the evolution of standards laws, evolution of policies and environmental public concerns. However, these sources of information are not considered here as part of the data search. They are mainly input into the discussions by each individual expert and become part of the scenario construction. According to the majority of the experts, their technical information is updated by news networks and conference participation. The FCVMP organizes an annual conference with this objective, where fuels and emission sections are always part of the agenda. Also, the project circulates some related fuel cell news for interested experts.

3.1.1.3 Industry Survey

During the project development, some discussions led to a sense that there was a lack of knowledge or a strong subjectivity in the analysis. It was more intense in the detailed technical issues and on the questions with little or no data availability in the literature, such as the correlation among some variables, and the emission factors for some processes. To minimize these problems, some companies agreed to open their operational data in such a way that probabilistic curves have been generated and correlation studies have been performed. A drawback to this technique is that using the data of a single plant or process to generalize the results is far from being an ideal situation. However, it is the first step for the consolidation of the methodology adopted by the project and a tutorial basis for future studies. The generalization process occured at the expert group discussion level and at least the industry data analysis has been addressing new questions and bringing new expert information to the pool of knowledge. One example of the industry survey results can be found in Contadini *et al*. (2000b). The ideal situation may occur when organizations such as EPA or CARB that have access to considerable data, start to publish more detailed information, such as the standard deviations or the probabilistic curves, details of the technologies aggregated into the same cluster, details about the equipment activities considered (efficiency, production, etc.) and eventual correlations with other parameters. The current qualitative level of information about the uncertainties in the data is very poor.

To obiviate the necessity of obtaining detailed technical information, the companies have also been identifying specific operational experts and allowing them to interact with the project on a one-to-one basis. The first step is to establish the doubts, the questions, and the network-expert initial solution tendencies. Based on this information, a semi-structured interview is conducted and the results, in terms of new questions, technical examples, data and/or statements, become input into the expert group discussion. A follow-up phase is performed with the technical expert originally interviewed, until the group reaches consensus on that issue. The follow-up was done, in general, over the phone or through e-mail but a second interview could occur if enough questions were still in place.

According to the classification of Porter *et al*. (1991), in general, the one-to-one process starts with a focused interview. The idea is to obtain subjective information about the study section. A typical example of questions of this phase could be "What advances do you see in the development of H_2-SMR (Hydrogen Steam Methane Reforming) plants in the next ten-year period?" In the second phase of the process, structured questions are asked regarding project necessities, such as "What is the typical operational hydrogen outlet pressure from the PSA (Pressure Swing Adsorption) installed in a H_2- SMR plant?" Finally, the final phase is a nonstructured interview where, based on the previous answers the expert is encouraged to express an opinion about some open issue in the expert network discussion. For example, the expert may be asked, "Do you think it is possible for a H2-SMR plant to release the hydrogen at 31 bars? And what whould be the benefits and drawbacks of doing that?" A summary of the interview is discussed with the expert before submission to the expert network. The expert is also invited to participate in the network for the discussion of the section correlated with the interview, creating a dynamic feedback most of the time.

This one-to-one method proved to be very efficient in solving some important technical questions that occurred in the discussion without solution. In the example above, the outlet pressure of the H_2-SMR dictates the compression requirement downstream. Some drawbacks here are the efforts and resources involved. It is necessary to interview at least two experts with different experiences (for example, operating/designing H_2-plants with pressures around 20 bars and 30 bars) and the method requires the physical presence of the interviewer. The success of the method is also dependent on the skill of the interviewer.

3.1.2 Expert network activity details

One idea of the expert network is to generate inputs for the model on which all interested parties can agree and to have them somehow help to build the inputs so that greater confidence in the final results can be justified. This decision was based upon the discussion of three alternatives:

1. A single modeler or single organization could decide on the inputs/methods of the analysis. Later on the interested parties could review it critically, as suggested by the ISO 14.040 (1997). The belief was that several details and pieces of information might be missed and that, in general, this approach would increase the risk that large modifications could be required at the end.
2. The interested parties participate in the entire process and the final decision could be based on a majority vote. In this case, however, a better representation of one industry sector over another in the expert network formation could bias the final result. This procedure could also block some information sharing.
3. The interested parties participate in the entire process and the final decision could be based on a consensus established with technical discussion and complementary information. This was the selected approach.

A second idea of the expert network is based on the hypothesis that some individuals know more about a section than others. For the same reason, according to Porter and Rossini (1987), forecasts made by a group of experts are safer than those produced by a single expert. The hypothesis for the statement is that a group engaged in a fruitful learning process can elicit the best idea from the most knowledgeable expert and even improve upon it. Figure 3-2 shows a graphical representation of this idea. However, it is not clear that researchers have produced enough evidence that group opinion is always superior to individual opinion. According to Rowe and Wright (1999), this idea has been accepted as common sense. The authors also suggest that some studies have concentrated on the comparison among group opinion techniques and criticize them, based on their failure to use a specific technique. Future studies are still necessary to prove this “many heads are better than one” hypothesis.

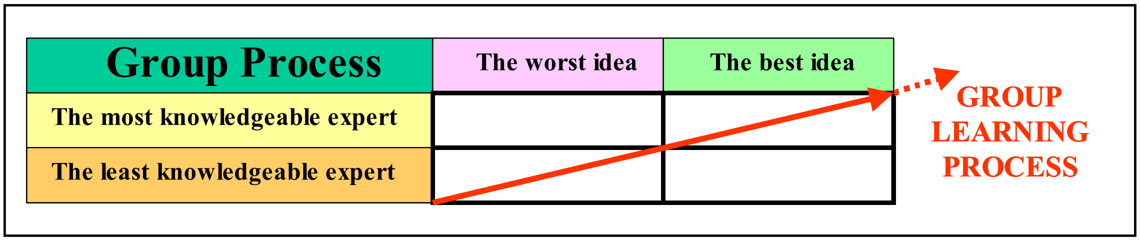


Figure 3-2: Graphical representation of the concept that group opinion can produce better information than the individual opinion.

3.1.2.1 Scenario Construction

Since the scenario construction within the expert network discussion has its own specificities, it is considered separately here. According to Porter *et al.* (1991) a scenario is a “descriptive sketch intended to produce a more or less holistic view of a future social state." Jones and Twiss (1978) contend that a comprehensive technology forecast must contain four elements:

A. Qualitative descriptions or scenarios,
B. Time,
C. Quantitative performance level and
D. Probability assessment.

Items (C) and (D) are the ultimate outcomes of the FUEEM technological forecast and they are discussed below. Time was pre-established early in the process, based on initial scenario discussions about fuel cell vehicle technology and fuel infrastructure. The qualitative description of what the model is considering and why it is considering it is then the major point here.

According to Porter *et al*. (1991), the innovation process is based on the interrelationships of the technological, economical, political, social and ecological environments. The uncertainties present in each of these issues are extremely high even when only a ten-year horizon is considered. Without a good discussion process, any scenario will be possible but the results will be meaningless. In agreeing with this idea, Sulivan and Claycombe (1977) state that a forecast is useful if it reduces the uncertainty surrounding an event. Based on this concept and because of the limitations of available resources a conservative scenario has been generated in the FUEEM forecast in order to select the "most feasible" technical options initially for a relatively stable, economic, political, social and ecological environment.

For example, hydrogen can be produced by a variety of processes (steam methane reformation - SMR, partial oxidation, electrolysis of water, gasification, biologically, etc.) and by a variety of feedstocks (natural gas - NG, oil, coal, biomass, electricity, sun, etc.). It is possible that each of these process-feedstock pairs may have some probability of being used by the year 2010, depending on conditions in the analyzed region. However, since most of these probabilities will be very small for the majority of the locations, the modeling priority chosen for FUEEM was the use of NG feedstock with SMR production process. This was considered to be the most likely to be used, based on costs, technology development, and other factors.

The scenario construction has an interactive relationship with the data discussion and model construction parameters. Using the same example above, a consensus was not reached on best plant size for NG/SMR. According to the experts, the most probable case should be the construction of centralized plants to supply the hydrogen. But because the demand for hydrogen is likely to be small in the introductory phase of FCV, a hydrogen pipeline is unlikely to be constructed on a large scale by 2010. It is possible that decentralized small plants, installed in fuel stations before 2010, could produce a considerable amount of hydrogen. Also, the discussions about the efficiency of the centralized plants show that enormous differences exist depending on the size of the plants and their co-production of extra steam. The model has now six options for hydrogen production: two decentralized and four centralized options (two sizes, with and without extra-steam generation). This approach reduces the uncertainty of each event considered, based on the fact that a specific technology can be analyzed more objectively and even be supported by available data. On the other hand, this approach transfers the subjective decision to the next step, where it requires the construction of a scenario establishing the possible distribution of regional hydrogen production across the six- modeled options.

This step was called “scenarios combination” and it generates most of the problems in reaching an agreement. The methanol scenario combination was a good, but most difficult, example. The new methanol plant designs are much more efficient than even the best existing ones but, on the other hand, there is now much more capacity for production methanol than there is demand for it in the world. It was barely possible to achieve a majority opinion on how many of the existing (and less efficient) methanol plants could be permanently decommissioned in the next ten years. Based on this decommissioning effort and on the new demand for fuel cell vehicles, a determination of how much of the new plant production could be considered also achieved barely majority opinion. The final solution was to use the majority (and not the consensus) to generate the combined scenario results but it was also necessary to present the results of the extreme cases as the “bounding scenarios.”

3.1.2.2 Workshop Discussion

The Fuel Cell Vehicle Modeling Program (FCVMP) conducts one conference and one workshop every year. The conferences are presented during the spring of each year, and are used to exchange information necessary for the scenario construction in FUEEM and to exchange news on R&D related sections. On the other hand, the workshops are organized every fall around the expert network and are used as a complementary part of the forecasting process. Four workshops have been conducted so far; and their main purposes were to discuss details about the methodology and the model effort and to identify options in the early stages of the problem definition for each fuel.

Basically, the techniques adopted in the workshops have been a mix of open discussions and the Nominal Group Process (NGP) developed by Delbecq and Van de Ven (1971). The technique combines a brainstorming process with some elements of the Delphi structure and it is known as the "estimates-talk-estimates" procedure. The idea is to alternate situations in which the group interacts with situations without interaction. According to Delbecq *et al*. (1975), when interaction does not occur the participants generate the most creative ideas and when they do interact they perform the best evaluation. For more details about the technique see also Roper (1988).

Martino (1983) defined two important characteristics of a working group. One is that the knowledge of the group is at least equal to that of any one member. The other is that a similar statement can be made for the number of factors considered. So the intent of a work group is to increase the knowledge base for a decision by at least identifying bad decisions. The group also has at least as much incorrect information as any member, so to be effective the group must cancel out misinformation. One drawback of a face-to-face meeting is that influence of power, status, or authority can suppress input, thereby minimizing the benefit of pooling knowledge. The anonymous vote process in the methodology tries to minimize this effect.

According to Porter *et al*. (1991), NGP is a "good technique for problem definition, to identify options and questions and also to build strong group identity." All of these sections were discussed in the first workshop (September 1998), when the expert team had just agreed to contribute to the fuel life cycle analysis effort and when the building of a new model was considered for the first time. After one year of working together in the expert network, the second workshop (September 1999) was conducted with the consolidation of the methanol and hydrogen fuel scenarios in mind, giving more emphasis to the group interaction and to the evaluation process. The third workshop (September 2000) concentrated on a detailed FUEEM software analysis in order to obtain agreement on the characteristics of the final version of the model. To do that, a more open discussion process was emphasized. A similar procedure was assumed in the last workshop (July 2001), when the final results were discussed.

Since the interested parties participation occurred over the span of the entire project, the final results brought no surprises and the reactions were very positive. This may be a good indication that the FUEEM method is on the right track to bring more confidence to life cycle studies. Similar reactions occurred even with the external public when the first results were published (Contadini *et al.*, 2000b and 2000c).

3.1.2.3 Group Discussions

The group discussions were the main activity for the expert network, which was divided into sub-groups. Allocation of the experts to sub-groups was conducted according to the expert's preference and his or her area of expertise. Initial discussions start in the sub-groups, and, after some results are reached, the summarized discussions and results are submitted for discussion to the general group. The sub-groups established are hydrogen, methanol, hydrocarbon, natural gas and methodology. Several experts decided to participate in more than one sub-group and they promised to get the opinion of another expert within their organization when the survey section necessitated an expertise different from their own. When this extra opinion was not obtained, the experts do not send any answers and express their inability to do so.

Several techniques exist to collect opinions from a group of experts. Examples include traditional surveys, the Delphi process, staticized groups, interacting groups, the nominal group technique, dialectic procedure, etc. An extensive literature can be found for each of these techniques and it is not the purpose of this paper to explain them.

Due to the limitation of available time for the project and to the international nature of the FUEEM expert network, all techniques that require the physical presence of the experts were rejected for this phase. The final technique adopted has most of the principles of the Delphi technique. This technique "is named after the ancient Greek oracle at Delphi, who offered visions of the future to those who sought advice" (Cassino, 1984 in Gupta and Clarke, 1996). Delphi is a special form of survey, designed to evaluate qualitative scenarios, to generate subjective probabilities, to obtain consensus, and to obtain more information (Sullivan and Claycombe, 1977). The Delphi process was developed by the Rand Corporation in connection with several defense-related studies that it made from 1948 to 1963. After Dalkey and Helmer (1963) published the technique it has become a widely used tool for measuring and aiding forecasting and decision-making in a variety of disciplines (Rowe and Wright, 1999). Gupta and Clarke (1996) conducted a comprehensive bibliographic survey of the Delphi Technique as it was used between 1975 and 1994. They identified 463 papers, indicating that Delphi has been applied to a large number of domains such as automotive engineering, environmental studies, transportation, and utilities, and has been used to address areas such as energy generation, project evaluation, productivity, technology planning, police analysis, the impact of legislation and tax reforms, and risk management.

The main idea of Delphi is to use questionnaires to collect the opinions of the panelists and build the most reliable consensus of the group, while avoiding the negative aspects of face-to-face interaction. A good definition is provided by Rowe and Wright (1999): "…the technique is intended to allow access to the positive attributes of interacting groups (knowledge from a variety of sources, creative synthesis, etc.), while pre-empting their negative aspects (attributable to social, personal and political conflicts, etc.)."

The four key features of the technique are the participants' anonymity, controlled feedback, interaction, and statistical aggregation of the group response. According to Porter *et al*. (1991) many variants exist for each of these features. Anonymity allows the experts to change their positions without any social pressure and reduces the tendency of the expert to defend an untenable position to preserve credibility or to maintain an institutional view. This feature helps in the creation of a final consensus. Two degrees of anonymity exist. The first is the identity of the participants and the second is the identity of the input. According to Sullivan and Claycombe (1977), the latter is far more important. In the FUEEM process, the feedback summary is always anonymous and the questionnaires are done by e-mail using the bcc (blind carbon copy) mode, thereby concealing the identity of the participants. However, since the project has also used the workshop technique, most of the participants know each other. According to Parent *et al*. (1984) a "groupthink" effect may occur when the experts share their opinion *a priori*. This possibility might constitute a limitation for discussions such as scenario construction, but this is a minor consideration, as discussed in Sullivan and Claycombe (1977). It can be compared with the experts participating in a conference where they need not necessarily agree or disagree with the presentations.

The group interaction occurs by a sequence of questionnaires called rounds, in which feedback from the previous round is provided. The occurrence of several rounds enables the group to build its own body of knowledge and find the best solution at the end. The interaction in FUEEM occurs at least three times, giving each participant (from the sub-groups and the general group) the opportunity to be involved at least twice. In the FUEEM process there is no interaction limitation, which means that the rounds continue until an open discussion is resolved. One solution adopted to resolve reasonable but conflicting positions was to include the alternatives in the model and analyze both situations. This transferred the decision to the regional analyses, where more information (from inventories) was available. Another approach is to delay the next round until new data (from an industry survey, for example) is available.

In spite of the fact that a final consensus is part of the process, the major focus in the FUEEM case is to obtain as many high-quality responses and opinions as possible. Jones and Twiss (1978) suggested avoiding too much emphasis on the achievement of consensus and Van Dijk (1990) showed with empirical experiments that Delphi could be used as a learning and research instrument tool. Based on these perspectives, the FUEEM emphases are on the expert comments and on the group learning process. Comment space is provided for every single section, in contrast to the classical Delphi process, in which comments are requested only for inputs falling outside of pre-specified limits or in the first round of the process. The feedback feature is the tool allowing this information flow among the experts through consecutive rounds. A summary of the comments was included in the feedback with every new set of data provided.

In the classical Delphi process, quantitative data is statistically summarized (mean and quartiles, in general) and reported, allowing the participants to check their initial positions in comparison to the group's current position. Each expert provides a judgmental response to each section and the result is an equal weight of the members, similar to a staticized group. Since most of the rounds in the FUEEM process are performed at the sub-group level, the number of experts participating is not high enough to generate a statistical curve from a single value input by each participant. Instead of a single value, each expert is required to provide what is essentially a probability density histogram, following Vose's (1996) suggestion. A minimum of three curves was established as an acceptable level in each round, and the composition of the judgments was done by Monte Carlo simulation. The resulting overall distribution is included in the feedback, not only the mean and quartiles. Figure 3-3 shows an example of expert opinion combination for the Delphi discussion round. A resulting curve with double (or more) modes indicates that more discussion rounds are necessary, even if the open comments are in agreement.

According to Vose (1996), for technical information a weighting procedure is preferred over a simple average of expert judgments. The FUEEM weighting factor is decided based on the expert's open-ended comments to support their judgments, on the expert's experiences and also on the expert's personal judgment of their level of confidence in their answers. According to Winkler and Makridakis (1983), a combined forecast obtained through weighted averages can be quite accurate and superior to an unweighted method. Dransfeld *et al*. (2000) have recently applied this method to a study of interactive television.

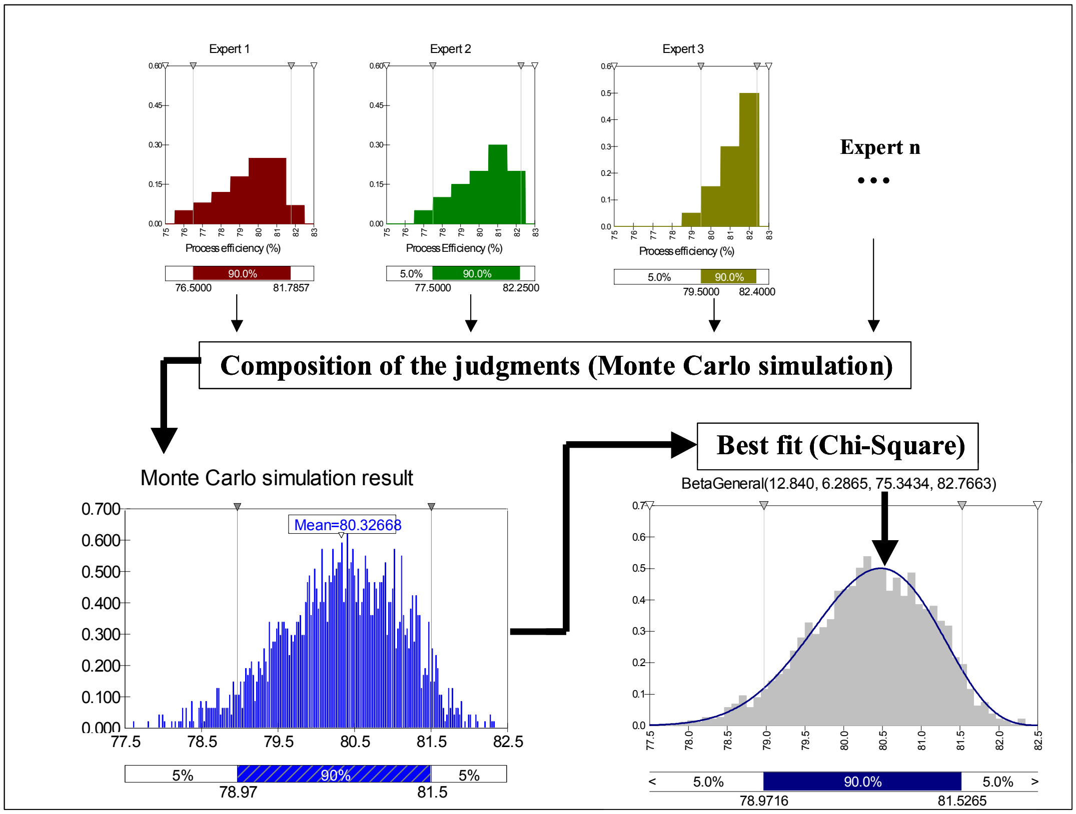


Figure 3-3: Expert opinion combination procedure for the FUEEM Delphi method.

Clemen’s (1985) idea of discarding the opinion of an “extraneous” expert (an expert who brings no additional information to the aggregated information) was also adopted in the FUEEM model. In a few cases, an expert provided technical information very different from the others’ and no comments about it were provided even after a new request to the expert do so. Table 3-1 summarizes the variant of the Delphi procedure adopted in the FUEEM process, according to the information type processed. The table uses the procedure names developed by Armstrong (1978).

Table 3-1: Summary of the procedures adopted in the FUEEM group discussion according to the type of information involved

FUEEM Delphi Procedures		INFORMATION TYPE		
Forecast Procedure	**Detail**	**Scenario Construction**	**Technical Design**	**Literature Adaptation**
Amalgamated	Each result's round is the composition of the majority's vote.	Ⓟ New scenarios may be generated to support conflicting opinions.	Ⓟ Modified by the weighting process and possible elimination of extraneous information.	✔
Polling	Several rounds. Each participant is polled at least twice.	✔	✔	✔
Feedback	The group consensus predictions are made known to the panel members prior to repolling.	✔ With extra focus on comments to support extreme opinions.	✔ With extra focus on the technical details of the comments.	✔ With extra focus on new data and examples provided.

✔ = Always used Ⓟ = Partially used

For the quantitative assumptions it is hard to discover whether the results follow the "pull of the median" or the "pull towards the true value" (Brockhoff, 1984). However, as a first step and first project of this nature (considering probabilistic curves for emissions and energy requirement calculations) the differences between the two pulls may be irrelevant, due to other uncertainties involved. One expectation of the FUEEM project is that it will motivate the future publication of emission factors and levels of activity of current equipment in statistical terms, bringing more objective information to the forecast panel.

The project did not attempt to compare the developed Delphi method with any other one. A qualitative analysis in the methodology group discussion pointed out that the method served the tasks well, eliminating or minimizing the agenda pushing from the results, bringing new information for the group learning process, and eliminating the problem of the distance among the experts. The cost, in terms of time, was pointed out as a major problem. On the other hand, over the first two years the project had very few losses by attrition. In fact, more and more organizations (interested parties) were willing to provide data and expert knowledge to the discussion. The sustained participation of a considerable number of experts in the FUEEM effort with no material gain can be a signal that the methodology was technically respected, participative, and motivational.

It should be pointed out that there is an ongoing debate about the value of the Delphi technique. Linstone and Turoff (1975) were concerned about the limited amount of controlled experimentation using the technique, compared with the number of applications. Several years later Rowe and Wright (1999) concluded that the applications have increased considerably and the limited experimentation done so far has suffered from several methodological problems. According to them, no conclusions about the right way to proceed can be made yet. To review this debate, see Armstrong (1999) and Ayton *et al.* (1999). According to them, there is a presumption that social pressures result in poor judgment. They also state that Delphi and other group techniques are still only "loosely connected to ideas and discoveries from social psychology and cognitive psychology."

In spite of these criticisms, several reports point out the benefits of using expert information and the fact that the choice of the experts is fundamental for a good forecast. The project did a careful selection of the organizations invited to participate in the effort and good representativeness can be claimed. However, some of the experts were not selected by the organization but were self-selected, because of previous contact with the project. Vose (1996) provides other sources of bias and errors in expert opinion, with references to other studies.

Finally, as in any survey, special care must be taken in the questionnaire design. The advice presented in Belson (1981) and in Sudman and Bradburn (1982) was always taken into consideration. Most of the time, a pre-test of the questionnaire was performed internally. Initially, some suggestions were provided in the questionnaires as examples and motivation for the beginners. This decision was based on Trommsdorff's (1982) statement that it should be irrelevant whether the information changing an expert opinion stems from an internal or an external source. However, to be conservative, and taking into consideration the findings of Vose (1996), this practice was stopped.

3.2 FUEEM uncertainty calculation

The decisions made in the model, about the best variable format to represent uncertainties, and the best propagation method in the calculation for the chosen variable format, did not occur separately. As stated earlier, FUEEM development and decisions occurred gradually based on some pilot project experimentations.

The first pilot project, late in 1998, used ranges for the initial data acquisitions, expert discussion, and calculation. The decision was made based on item-7 of the international standard ISO 14.041 (1998). This item discusses the limitations of the Life Cycle Inventory (LCI) and contains the following statement:

"…uncertainty is introduced into the results of an LCI due to the cumulative effects of input uncertainties and data variability. Uncertainty analysis as applied to LCI is a technique in its infancy. Nevertheless it would help to characterize uncertainty in results using ***ranges*** *and/or* ***probability distributions*** *to determine uncertainty in LCI results and*

conclusions. Whenever feasible, such analysis should be performed to better explain and support the LCI conclusions."

The minimum, maximum, and most probable values for the ranges were not so difficult to establish. They were very intuitive for the experts and with little data the experts provided their input with confidence. The calculation was done using vectors and it fairly closely reproduced the traditional deterministic models running for three different scenarios. The only special care that was necessary was to understand in the calculation when the smallest value was going to generate the smallest result and correct the orientation of the vector in the opposite case.

From this first pilot experiment, I learned that bounding the most probable value with the two extremes provides a better sense of the uncertainties involved in the analysis but gives no idea of the importance of the extremes and how concentrated the possibilities are around the most probable value. Based on this, a decision to move to the probabilistic distributions alternative was made for the second pilot project, in middle of 1999.

With probabilistic curves as the variable format to express uncertainties, some alternatives existed to propagate the information through the calculation. The traditional approach uses point-valued probabilities characterizing uncertainty due to stochastic variability. An entire statistic area has been developed based on expert opinion and point-value probabilities. This statistic area is called Bayesian because it started from Bayes's theory and it is an analytical process that does not consider the dependences among variables. According to Vose (1996), a drawback using this kind of analytical approach for simulation is the difficulty of performing changes in the model. This point was considered a critical limitation and this option was eliminated. For more information about Bayes's methods see Braun (1988) and Carlin *et al*. (1996). Later in the process, Yu and Park (2000) point out that in the Bayesian approach the problems, such as cognitive imprecision or vagueness in determining the probability, have been recognized but their uncertainties are not considered. For an expert opinion, instead of point-value probabilities, Yu and Park (2000) suggest the use of a "possibility distribution of probability," which according to them represents an imprecise probability by means of a subjective possibility measure associated with judgmental uncertainty. The idea of possibility distribution of probability was exactly what was done in the second pilot project by requesting from each expert a histogram kind of probability curve (See section 3.1.2.3). For simplicity the "possibility distribution of probability" is referred to here as probabilistic curves or distributions only.

The second pilot project worked with the assumption of independency among the variables. By assuming probabilistic curves and independency among variables, two computational approaches could be used: one was Monte Carlo Simulation, developed since the beginning of the digital computer development, and the other one was the Fuzzy technique. Details about Monte Carlo simulation method are presented in section 3.2.1, but, since its beginning, Monte Carlo simulation has being associated with high computational requirement (Morgan and Henrion, 1990), and, because of that, some authors have been proposing and using Fuzzy set techniques (Smith, 1994; Lipman, 1999 and Yu and Park, 2000).

More information about Fuzzy techniques can be found in Zimmermann (1990), but, in a very simple way, it is a graphical calculation simulating very accurately the composition of single triangular or trapezoidal curves. The final result is close to the Monte Carlo simulation result. On the other hand, the computational requirement for Monte Carlo simulation is not a barrier any more, considering the current capabilities of regular personal computers. In fact, the use of Monte Carlo simulation has been increasing in economic risk analysis (Vose, 1996), as well as in cost-benefit analysis (Morgan and Henrion, 1990). In complement of that, Short *et al*. (1995) compare and favor Monte Carlo simulation over several other techniques to characterize uncertainties in economic evaluation of energy production. Using this information, Monte Carlo simulation was chosen for use in the project.

Considering independence among variables, a model was developed in Matlab® language using the histogram-kind of curves and matrices representation. The model worked very well, but, in further discussions, some experts expressed their wish for the project to go a step further and include at least the possibility of considering the dependence among input variables.

The Emission Inventory Improvement Program of the US Environmental Protection Agency has a study (EIIP, 1996) about uncertainties in emission estimates. After some consideration of the limitations of qualitative and semi-quantitative analysis, they suggested three preferred quantitative analysis method alternatives presented as: the preferred option, the intermediate option (Alternative 1), and the last option (Alternative 2). Alternative 2 is the use of the Delphi Method or other survey of experts to generate upper and lower bounds in estimates. It is exactly what the FUEEM project did in the first pilot analysis described earlier. Alternative 1 is to use expert judgment (based on as much data as available) to estimate standard deviation (or coefficient of variation) and distribution for the key variables of each source type (or category), to assume independency, and to use error propagation to estimate uncertainty limits.

The error propagation method is referred to by Benkovitz (1985) and it is the suggestion of the International Panel on Climate Change (IPCC, 1995) to combine uncertainties. The percentage uncertainties U_T is given by:

$$U_T = \pm\sqrt{(U_E^2 + U_A^2)} \text{ ; } |U_E| \text{ and } |U_A| < 60 \text{ \%.} \qquad \text{Equation 3-1}$$

where, U_E is the percentage uncertainties associated with the emission factor and U_A with the activity data. It is important to reinforce that this method assumes independency among the variables. This method was used by Balentine *et al*. (1994) to analyze the uncertainties in the inventory study of the Grand Canyon visibility associated with emissions from transportation.

Finally, the EIIP (1996) preferred option is to conduct a probabilistic modeling (e.g., Monte Carlo simulation) accounting for dependencies among variables using expert judgment as in Alternative 1. The assumption of independence could be a serious limitation according to the study and the possibility of considering the dependence among the variables was the main reason for their classification of Monte Carlo simulation as a preferred method for evaluating uncertainties in emission inventory calculation.

After some consideration, the experts in the early 2000 study accepted the idea of considering dependence among variables. Because Monte Carlo simulation is currently the only simulation methodology that allows the dependence consideration, its use was reconfirmed. The matrix approach was then replaced by the traditional point-by-point interaction and as far as I know this study was the first and is still the only Life Cycle study to use probabilistic curves, Monte Carlo simulation, and correlations among variables.

3.2.1 Monte Carlo simulation technique

The objective of this section is to provide a general overview of the basic mathematical technique used to accomplish the Fuel Upstream Energy and Emissions Model (FUEEM) requirements. The methodology is known as Monte Carlo simulation or method. The general comments presented here are a compilation of information from several books: Shreider (1966), Hastings (1975), Rubinstein (1981), Ross (1985), Kalos and Whitlock (1986), Vose (1996), Mooney (1997), Ross (1997) and Law and Kelton (2000). This discussion can also be used as an initial compilation of references for readers who want to study the issue in more detail.

The Monte Carlo simulation can be defined as the “new technique” of investigation based on the possibility of simulating random processes on a computer, and can also be referred to as the method of statistical trials. By definition Monte Carlo simulation is a stochastic model since it uses at least one probabilistic input component. On the other hand, it works best when time is not an important component of the modeled system, as in FUEEM; therefore, it is a static simulation. Another class of problems solved by the Monte Carlo method is deterministic problems, when a numerical solution is constructed in the form of statistical estimators. Deterministic solutions of complex equations will not be covered here. For more details see Mikhailov (1991) and Mikhailov (1995)

The Monte Carlo simulation works by randomly sampling the input variables and performing all the operations established in the model using these sampled values. The process is repeated *n* times, with each time being called a run or interaction. As a result of the simulation each output parameter will be a frequency table (histogram type) containing the values of all interactions. The statistics of these data can then be analyzed.

3.2.1.1 Short history

In the above definition, the use of quotation marks (“) around the expression new technique is due to the fact that most of the authors refer to a 1777 text as the earliest documented use of random sampling. In this text the Comte de Buffon set out a mathematical analysis to figure out the probability of a needle (thrown at random) intersecting straight lines on a horizontal plane. In 1886 Laplace suggested that Buffon’s idea could be used to evaluate π. In 1901 Lord Kelvin used random sampling to solve some time integrals in the kinetic theory of gases. Several developments in the probability theory occurred up to the Second World War in the 1940s, when the beginning of digital computers and the development of the atomic bomb consolidated the use of the method. The method was used to simulate the random neutron diffusion in fissionable material, and Von Neumann and Ulam introduced the term “Monte Carlo” as a code word for the secret work at the Los Alamos laboratory.

From there, with the advance of computational speed and memory, it became a powerful tool to analyze complex problems and to solve certain integral and differential equations. The method has been used in different fields such as statistical mechanics, radiation transport, economic modeling, etc., and at least two specialized softwares have been developed to perform Monte Carlo simulation (i.e., @Risk ® and Crystal Ball ®).

3.2.1.2 The probability theory basis

Consider a variable “*X*,” for example the efficiency of some engine or the emission factor for some technology, and also consider that a cumulative distribution function “*F(x)*” can be defined as the probability that (“*X*”) takes on values less than or equal to “*x*.” Or:

$$F(x) = P(X \leq x), \text{ for all } x \qquad \text{Equation 3-2}$$

Note that the cumulative distribution function is always non-decreasing $\left(\frac{d}{dx}F(x) \geq 0\right)$ and that $F(-\infty) = 0$ and $F(+\infty) = 1$.

If “X” is a discrete random variable defined over the integer values k = 1, 2, …, n with non zero probabilities (e.g., when a coin is tossed), then

$$p(x) = P\{X = x\} \qquad \text{Equation 3-3}$$

p(x) is the probability mass function, where

$$F(x_k) = \sum_{1}^{k} p(x) \quad \text{and} \quad \sum_{1}^{n} p(x) = 1 \qquad \text{Equation 3-4}$$

If “*X*” is a real continuous random variable, the probability of it having any precise value within a range is very small. Instead of looking for a probability mass associated with “X,” a probability density function “*f(x)*” is defined representing the rate of change of the cumulative distribution function. According to the definition:

$$f(x) = \frac{d}{dx} F(x) \qquad \text{Equation 3-5}$$

Also, we can define the probability of lying between any two exact values (*g, h*) as:

$$P\{g \le x \le h\} = F(h) - F(g) = \int_{g}^{h} f(x)dx \qquad \text{Equation 3-6}$$

where $h > g$. See Figure 3-4 for a graphical representation of these definitions. See also in Table 3-2 some examples of density functions and cumulative functions.

<u>Pseudo-Random Number Generators</u>:

In the following sections we will see that a basic necessity of the Monte Carlo approach is the generation of random numbers. It is impossible to generate a “pure” random process by computer that is equivalent to throwing dice in a Monte Carlo casino. Computer random generator methods will always be deterministic and will repeat themselves at some point in time. However, it is possible to generate random numbers by computer with good statistical properties using the so-called pseudo-random numbers generators. Von Neumann and Metropolis first proposed this idea in the 1940s with the “midsquare method.” This method was proposed because the previous alternatives required the use of established tables or mechanical devices limiting the simulation speed and/or length. From there several methods were developed looking at length, statistical uniformity, statistical independence, reproducibility, and economical generation speed (Barry, 1996).

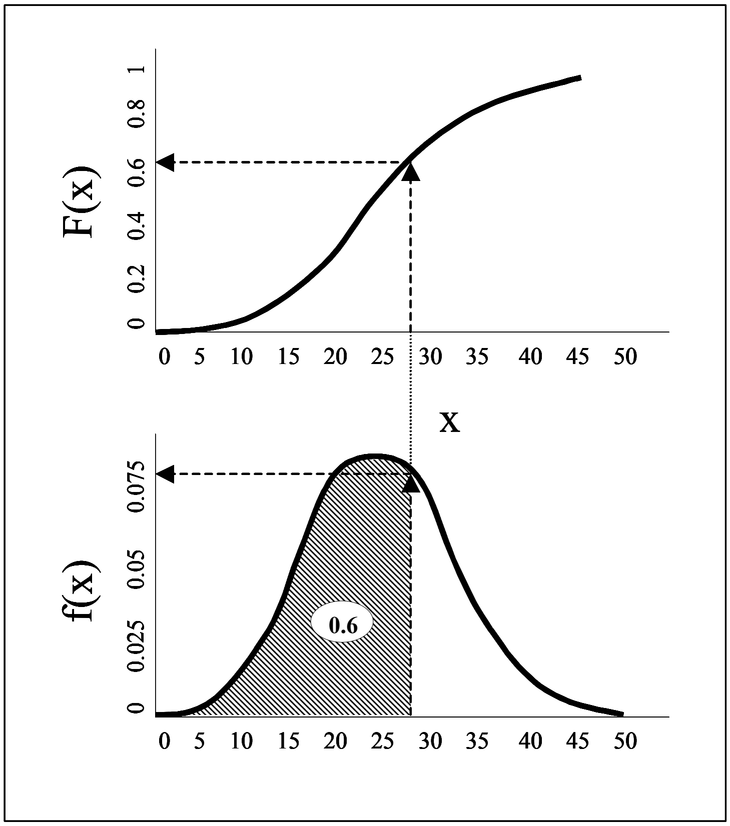


Figure 3-4: Relation between F(x) and f(x).

The most popular and well-studied method is the Linear Congruential Generators (LGC) introduced by Lehmer (1951, in Law and Kelton, 2000). As an example, the software Crystal Ball ® 3.0 uses a LGC called the Park and Miller generator described by:

$$X_i = 16{,}807\, X_{i-1} \bmod(2^{34} - 1) \qquad \text{Equation 3-7}$$

In general, LGC works with four nonnegative integers: *m* (the modulus, $2^{34} - 1$ in the above example), *a* (the multiplier, *16,807* in the above example), *c* (the increment, *zero* in the above example) and X_0 (the seed, an integer bigger than zero and smaller than *m* chosen by the analyst to reproduce the same sampling when necessary). It is based on the modulus of a linear relation provided by the following recursive formula:

$$X_i = (a\, X_{i-1} + c)\ mod(m) \qquad \text{Equation 3-8}$$

Table 3-2: Examples of probabilistic distribution functions.

Functions	Density	Cumulative
Exponential (β)	$f(x) = \dfrac{e^{-x/\beta}}{\beta};\ x \geq 0 \text{ and } \beta > 0$	$F(x) = 1 - e^{-x/\beta}$
Log-logistic (γ, β, α)	$f(x) = \dfrac{\alpha\left(\dfrac{x-\gamma}{\beta}\right)^{\alpha-1}}{\beta\left[1+\left(\dfrac{x-\gamma}{\beta}\right)^{-\alpha}\right]^{2}};$ $x > \gamma$ $\alpha > 0$ $\beta > 0$	$F(x) = \dfrac{1}{1+\left(\dfrac{x-\gamma}{\beta}\right)^{-\alpha}}$
Weibull (α, β)	$f(x) = \alpha\beta^{-\alpha}x^{\alpha-1}e^{-(x/\beta)^{\alpha}};\ x > 0,$ $\alpha > 0$ and $\beta > 0$	$F(x) = 1 - e^{-(x/\beta)^{\alpha}}$
Triangular (a, b, c)	$f(x) = \dfrac{2(x-a)}{(b-a)(c-a)}\ if\ a \leq x \leq b$ $f(x) = \dfrac{2(c-x)}{(c-a)(c-b)}\ if\ b < x \leq c$ $a \le x \le c\ and\ a \le b \le c$	F(x) = 0 if x < 0 $F(x) = 1 - \dfrac{(x-a)^2}{(b-a)(c-a)}\ if\ a \leq x \leq b$ $F(x) = 1 - \dfrac{(c-x)^2}{(c-a)(c-b)}\ if\ a \leq x \leq b$
Normal (μ, σ)	$f(x) = \dfrac{1}{\sqrt{2\pi c^{2}}}e^{-(x-\mu)^2/2\sigma^2};\ c > 0$ $and\ -\infty < x < \infty$	No closed form
Beta (α1, α2)	$f(x) = \dfrac{x^{\alpha_1-1}(1-x)^{\alpha_2-1}}{\int_0^1 t^{\alpha_1-1}(1-t)^{\alpha_2-1}dt};$ $0 \le x \le 1,\ \alpha_1 > 0\ and\ \alpha_2 > 0$	No closed form

A sequence of integers (X_i) between 0 and *m-1* is generated with the "remainders" (fractional part) of $(a\, X_{i-1} + c)/m$ and the desired random numbers $U_i(0,1)$ are generated by the normalization:

$$U_i = X_i / m \qquad \text{Equation 3-9}$$

where, $0 < m$, $a < m$, $c < m$ and $X_0 < m$. If one decides to generate his/her own pseudo-random numbers, special care should be taken by testing the randomness and uniformity of them (See: Rubinstein, 1981; Barry, 1996 and Law and Kelton, 2000).

3.2.1.3 Monte Carlo Sampling

Several methodologies exist to randomly sample probabilistic functions. The inverse transformation method, the rejection method, and the polar method are the most common and are well reported in the literature. Each method works differently (some are more computational efficient) for different situations such as the function shape and composition, the existing analytical representation, the necessity for stopping rule in the simulation, etc. Most of the existing simulation packages use the inverse transformation method.

The Monte Carlo sampling is based on the inverse function of $F(x)$ called $F^{-1}(x)$ defined as:

$$F^{-1}(F(x)) = x \qquad \text{Equation 3-10}$$

A uniform random number "U" can be generated in the interval between zero and one using the uniform probabilistic function $F(x)$ in such a way that,

$$F(X) = U \quad or \quad F(x) = u \quad (0 \leq u \leq 1) \qquad \text{therefore,}$$

$$F^{-1}(U) = X \quad or \quad F^{-1}(u) = x \qquad \text{Equation 3-11}$$

Figure 3-5 shows this idea for five samples. Here are some examples of inverse functions:

- Exponential distribution with mean β: $F^{-1}(u) = -\beta \ln(1-u)$
- Weibull: $F^{-1}(u) = -\beta[-\ln(1-u)]^{1/\alpha}$
- Log-Logistic: $F^{-1}(u) = \gamma + \beta[u/(1-u)]^{1/\alpha}$
- Triangular [0, 1, c] where 0 < c < 1: $F^{-1}(u) = \begin{cases} \sqrt{cu} & \text{if } 0 \le u \le c \\ 1-\sqrt{(1-c)(1-u)} & \text{if } c < u \le 1 \end{cases}$

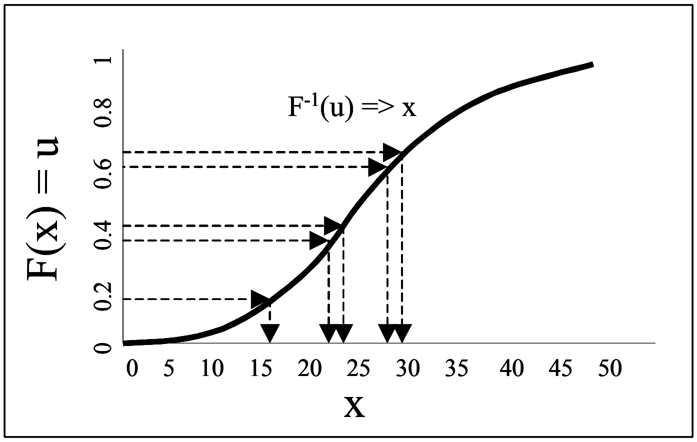


Figure 3-5: Monte Carlo sampling idea

The inverse transformation method has the advantage of facilitating the implementation of variance-reduction technique, the correlation among variables, the use of truncated distributions, and the generation of order statistics. One disadvantage of this method is the limitation of writing a formula for F^{-1} in closed form expression for distributions like normal and beta. Numerical methods such as power-series expansion are in general used to evaluate F^{-1} in these cases. A comprehensive survey of numerical methods to generate the inverse functions can be found in Press *et al.* (1992) and

Kennedy and Gentle (1980). According to Law and Kelton (2000) numerical methods can yield machine accuracy, and they may also make more difficult specifying acceptable stopping rules for the simulation when necessary.

3.2.1.4 Output data analysis

The most interesting characteristic of the Monte Carlo simulation is the random nature of its output. For most cases it can be assumed that each run output is independent[2] of others since random samples from probability distribution are typically used to drive the simulation. Also, assuming that the result has a finite mean (μ) and a finite variance (σ^2) bigger than zero, some statements can be made. First, the sample mean ($\hat{\mu}$) and the sample variance ($\hat{c}^2$) can be used as unbiased estimators if a very large number of experiments is performed.

$$\hat{\mu} = \frac{\sum_{i=1}^{n} X_i}{n} \qquad \text{Equation 3-12}$$

$$\hat{c}^2 = \frac{\sum_{i=1}^{n} [X_i - \hat{\mu}]^2}{(n-1)} \qquad \text{Equation 3-13}$$

Second, a confidence interval for μ can be constructed and the hypothesis that $\mu = \mu_0$ can be tested to guarantee that n is sufficiently large. Using the classical central limit

---

[2] This may not be true if the model is not a static simulation and time is an important parameter. Simulations of manufacturing systems and queuing systems are common examples. Even in those cases, it is often possible to group simulation output data into new "observations" and apply the techniques developed for independent and identically distributed random variables. Law and Kelton (2000) present a detailed explanation of these techniques and provide many of other references to this topic.

theorem and the idea that $\hat{c}^2$ will converge to σ^2 for large samples, an alternative confidence interval expression can be used, according to Law and Kelton (2000):

$$I(n, \alpha) = \hat{\mu} \pm t_{n-1,1-\alpha/2}\sqrt{\hat{\sigma}^2 / n} \qquad \text{Equation 3-14}$$

where, $t_{n-1,1-\alpha/2}$ are the critical points of the "*t distribution*" with "*n-1*" degrees of freedom and $\sqrt{\hat{\sigma}^2}$ is the standard deviation of X_i. Using μ_0, a hypothesized value for the mean (μ), and assuming the level of satisfactory coverage α (e.g., α = 90 %), the null hypothesis H_o that $\mu = \mu_0$ can be tested. If H_o is true, the statistic below (t_n) will have a *t distribution* with *n-1* degrees of freedom:

$$t_n = \frac{[\hat{\mu} - \mu_0]}{\sqrt{\hat{c}^2 / n}} \qquad \text{If } |t_n| \begin{cases} > t_{n-1,\alpha/2} \rightarrow reject H_0 \\ \le t_{n-1,\alpha/2} \rightarrow "accept" H_0 \end{cases} \qquad \text{Equation 3-15}$$

Simulation software packages, like @Risk 4.0 ®, test the convergence of the standard deviation of each interaction until it reaches the satisfactory level established by the modeler. The idea is if at the end of the simulation the convergence is not reached then another simulation set (with more interaction runs) should be performed.

3.2.1.5 Latin Hypercube Sampling

In recent years several techniques have been developed to reduce the variance of the outputs and get statistical convergence sooner. These methodologies are very important to save computational time. The Latin Hypercube Sampling (LHS) is the most used variance reduction method by now, and, similarly to the others, it works as a variation of the original sampling method. However, recent studies are proposing to go even beyond the use of pseudo-random numbers (see: Fox, 1999). LHS is a technique developed by McKay *et al*. (1979) that produces, with fewer interactions, a better sampling response than simple random sampling when the output is a monotonic function of the input. The computational LHS algorithm to generate the samples was presented by Iman *et al*. (1980). It basically divides the range of the variable into exactly *n* intervals in such a way that the probability of the variable falling into each interval is *1/n*. Then *n* randomly selected numbers (u_i) from a uniform distribution (0,1) are sampled and scaled to Pn_i according to the following equation:

$$Pn_i = u_i * (1/n) + (n_i - 1)*(1/n) \qquad \text{Equation 3-16}$$

This will ensure that the entire range of intervals has been covered. Figure 3-6 shows the graphical representation of this idea. This process will be repeated until all interactions of the simulation are performed. Since this process will generate an undesirable repetition of incremental probabilities at *n* multiple sampling, the input vector is finally randomly mixed ($Pn_i \Rightarrow F(x)$).

According to Iman *et al* (1981) LHS has the following properties:

a) the full range of each input variable is sampled.

b) no variable is emphasized over another.

c) unbiased estimates of cumulative distribution functions and means for model output are obtained and

d) biased estimates of variances occur but such estimates have a smaller mean square error than estimates obtained with random sampling or stratified sampling.

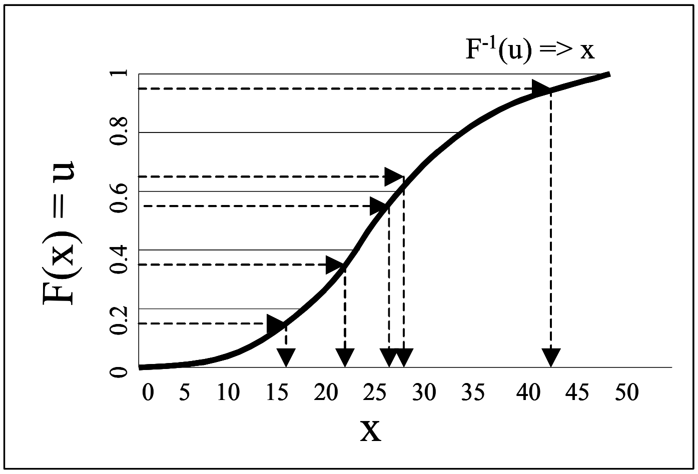


Figure 3-6: Latin Hypercube sampling idea

3.2.1.6 Dependencies among variables

The term *dependency* is used in probabilistic models when a variable “Y” has a statistical relationship with another variable “X,” and “Y” will be generated influenced by the relationship with “X.” The variables are called respectively *independent (X)* and *dependent (Y)* and a causal relationship is presupposed. On the other hand a *correlation coefficient* is a value used in statistics that describes the degree of linear relationship between variables. In general, a *correlation* is used in regression analysis and Pearson’s [3] correlation coefficient is a well known example. There is no causal relationship associated with *correlation* and this is the major difference from the term *dependency*.

It is still common to assume of independence for the input variables in probabilistic simulations. However, in the “real world” the dependences do exist and failing to consider them on the simulation may not be appropriate. There are two major approaches to consider the variable dependences on computer simulation models. One is called by Vose (1996) the “Envelope Method” that uses the logic of the independent variable statistically determining the dependent variable value. The other one was developed by the Sandia National Laboratory scientists in the early 1980's and it is called "Rank Order Correlation."

The Envelope Method

The Envelope Method tries to consider linear combinations of variables to achieve a desired correlation structure. The basic idea of this method is to use a large number of observed correlations to draw the lines of the relationship using a scatter chart[4]. Depending on the original distribution of the dependent variable, a line equation representing a distribution parameter must be identified. For example, if a uniform distribution is the original representation for the dependent variable, two bounding lines can represent the minimum and maximum observed values. For each interaction a randomly chosen independent value will generate the limits for the dependent variable value random selection. If a triangle distribution is considered then the line that defines the most likely value must be defined too. See Figure 3-7 for details.

Following the example presented in Figure 3-7, if the first simulation interaction selects the independent value of x = 23 then the dependent value for this interaction will be randomly selected from a triangle distribution curve with the minimum value equal to 3.29 ($y_{min} = -0.17*23+7.2$), the most likely value equal to 4.03 ($y_{most} = -0.19*23+8.4$), and the maximum value equal to 4.89 ($y_{max} = -0.22*23+10$). For each interaction the minimum, most likely, and maximum values for the dependent variable sampling are

---

[3] Pearson's coefficient is defined by: $\rho = Cov(X,Y)/\sigma(X).\sigma(Y)$, where Cov(X,Y) is the covariance between X and Y and $\sigma(X)$ and $\sigma(Y)$ are the standard deviations of "X" and "Y".

[4] The independent variable values are plotted in the x-axis and each correspondent value of the dependent variable is plotted in the y-axis.

established again. A similar idea can be applied for the normal distribution where, using the data values, one can establish the least squares line and the standard error running a regression analysis. In the same way, after the simulation has selected the independent value then the dependent value will be selected from a normal distribution having the mean calculated from the least squares line and the standard deviation equal to the statistic error.

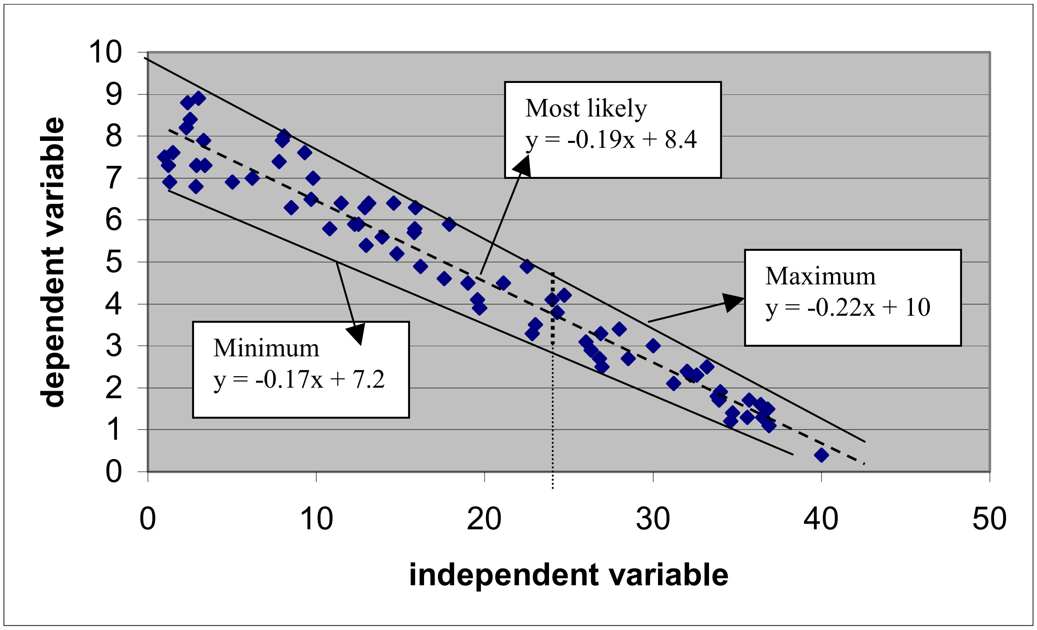


Figure 3-7: An example of the Envelope Method application

<u>The Rank Order Correlation Method</u>

In 1906 C. Spearman introduced into his psychological work the concept of rank correlation known as "footrule." The evolution of his work generated the so-called Spearman's rho coefficient of rank correlation (r_s) calculated as:

$$r_s = 1 - \frac{6\sum d^2}{n^3 - n}$$ Equation 3-17

where "*n*" is the number of existing correlation pairs and "*d*" is the difference between the rank score attributed to each datum for the same pair. Perfectly positively correlated data sets have $r_s = +1$, perfectly negatively correlated data sets have $r_s = -1$, and values between -1 and $+1$ will represent the tendency towards one extreme or the other with $r_s = 0$ representing no correlation [5].

Iman and Conover (1982) developed a method to induce rank correlation among input variables for use in simulation studies. They were trying to solve the problem of using linear combination of non-normal random variables in a study of geologic disposal of radioactive waste at Sandia National Laboratories. Because the method can be applied to all types of probabilistic distributions it has been adopted by the recently developed software packages for Monte Carlo simulations (i.e., @Risk ® and Crystal Ball ®).

Iman and Conover (1982) discovered that using van der Waerden scores (a_i) [6] on Spearman's correlation, the plots of input variables appear very "natural." According to them "resulting bivariate normal scatter plots formed elliptical patterns" instead of having a "pinched in the middle and spread out in the tails" appearance when single ranks are used (Iman and Davenport, 1982). One example of their plot is presented in Figure 3-8.

Using the defined coefficient of rank correlation ($r_{s\text{-}def}$) and the defined number of interactions (n) the simulation model goes over several operations. First, "*n*" randomly

---

[5] Only on the extremes (+1 and –1) will the Pearson's product-moment coefficient be equal to Spearman's coefficient. In fact, both are special cases of a general correlation coefficient (Γ) equation defined as: $\Gamma = \frac{\sum a_{ij} b_{ij}}{\sqrt{\left(\sum a_{ij}^2 \sum b_{ij}^2\right)}}$. Where a_{ij} is the score of the variable *A* and b_{ij} is the score of the variable *B* to any pair " *ij*". For more details on rank correlations see Kendall and Gibbons (1990).

[6] The Van der Waerden score is defined by $a_i = \Phi^{-1}\left(i/(N+1)\right)$, where Φ^{-1} is the inverse function of the standard normal distribution function and $i = 1,\ldots N$.

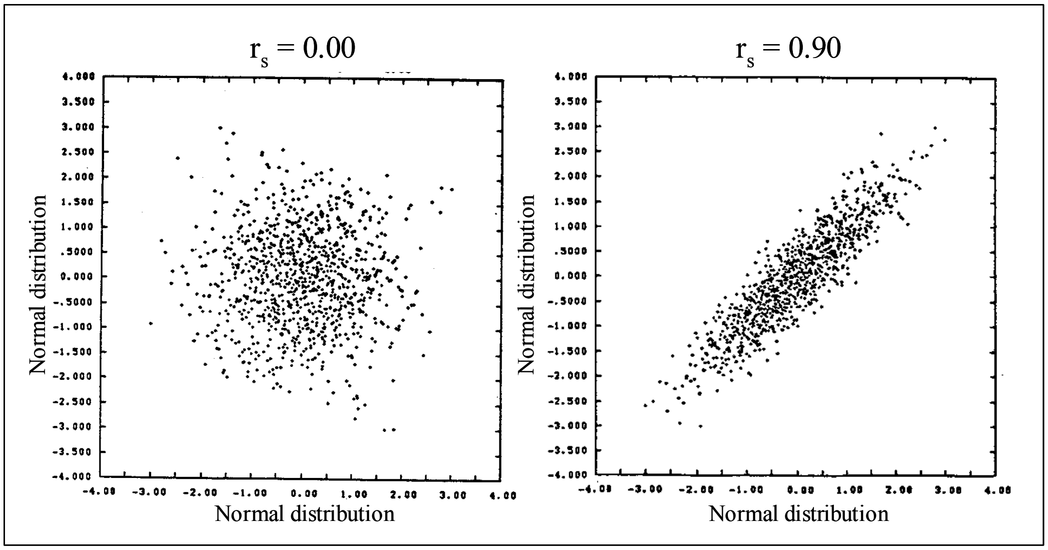


Figure 3-8: Graphical format of two different rank order correlation degrees of normal distributions. (source: Iman and Davenport, 1982).

distributed van der Waerden scores are generated for each variable (independent and dependent). The scores are ranked and a new Spearman's coefficient is calculated ($r_{s\text{-}cal}$) using the equation (4.1). Then, the "*n*" score pairs are rearranged until the coefficient of rank correlation calculated matches the defined coefficient ($r_{s\text{-}cal} \cong r_{s\text{-}def}$). They are rearranged using the Cholesky factorization scheme of Scheuer and Stoller (1962). This computational algorithm is presented in appendix-A of Iman *et al* (1980). Then sampling numbers are randomly generated for the independent and dependent variables and ranked. Finally, the sampling numbers are rearranged in pairs following the same rank-pairs defined by the final Spearman's ($r_{s\text{-}cal}$) pair arrangement.

Rank order correlation method versus envelope method.

When a large initial data set is available the correlation can be directly extracted from it without a problem. When no large data is available and expert opinion is necessary, Vose (1996) states that the rank correlation coefficient has no intuitive format to the experts, even if they are exposed to graphical format, as suggested by Iman and Davenport (1982). Vose's opinion is that one should use rank order correlation only when the results elasticity is small for the correlated variables and one can test that by changing the rank correlation coefficient and checking the resulting variation.

On the other hand, Iman and his colleagues at the Sandia National Lab. developed the rank correlation method because, among other things, it preserves the shape of the original distribution function. With a closer look at the envelope method one can figure out that this method just preserves the shape of the original curve if it has a uniform distribution. For the normal and triangular distribution the envelope method will, in fact, sample a lot of small curves with the same format of the original one, instead of sampling a small piece of the larger original curve.

3.3 FUEEM Characteristics

The objective of this section is to present some of the characteristics of the Fuel Upstream Emissions and Energy Model (FUEEM) and explain how it incorporates all the information and techniques presented above.

3.3.1 Scope, boundaries and time frame.

Similarly to existing models like Unnash *et al* (1996 and 2000), ETSU (1996, 1997 and 1998), Greet (1998, 1999 and 2000), or Delucchi (1991 and 1997), FUEEM focuses on major criteria pollutants (NO_x, SO_x, CO, NMOG and PM_{10}) and major greenhouse gases (CO_2, CH_4 and N_2O). It also assesses the greenhouse gases' impacts in terms of $CO_{2\text{-equivalent}}$ by using the deterministic values of one-hundred-year global warming potentials, as suggested by the International Panel of Climate Change (IPCC, 1995) or, as an option, by using probabilistic curves of the economic damage index.

$PM_{2.5}$ is still in a very early stage of understanding and data measurement. The great difficulty is to identify a way of forecasting these emissions, since the majority of them come from secondary formation in the atmosphere, involving complex reactions and ambient conditions. An EPA study (EIIP, 1999) suggests, for introductory purposes, a rough assumption that $PM_{2.5}$ is a composition of 20 % of the PM_{10} plus 25 % of the SO_x plus 25 % of the NO_x plus 20 % of the NMOG emissions. FUEEM considers only the primary emissions as, roughly, 60 % of the PM_{10} emissions. This is assumed just to have an option of including this pollutant in the model, and has no scientific basis. This should be revised as soon as better data are available and until then $PM_{2.5}$ will not be considered in any analysis.

At this point the scope is limited to air emissions, which are the main concern for the transportation sector. Water and solid waste are going to be a matter of future improvements in the model. Similar to most of the other models, the boundaries here include the operational phase of the activities from feedstock extraction to the vehicle operation. The activities or stages include the feedstock extraction, processing, storage, and transportation as well as the fuel production, storage, transportation/distribution, and fuel consumption at the vehicle. The secondary fuels and electricity consumed in each activity are also considered from the feedstock extraction to the final use. Future improvements may also include the emissions associated with the pre-operational phase (site development, construction, and life cycle of the necessary materials like steel, concrete, etc.) and post-operational phase (decommissioning, dismantling, and recycling).

Delucchi (1991 and 1997) includes in his CO_2 calculation the emissions associated with steel used in the car-assembling phase, showing that they are not negligible and should be considered. However, for comparison purposes of similar vehicle system technologies the assumption that the vehicle bodies will consume similar amounts of material is reasonable and acceptable.

Since Fuel Cell Vehicles (FCVs) are a new technology in development, the time frame of 2010 was discussed and adopted as the referential for the technology to be in place, in circumstances similar to a well-established market. Or in other words, if it becomes a reality by that time all the life cycle businesses associated with fuel cell vehicles are going to be in place with more solid technologies (in economic terms) than may occur in a transitional period. This scenario will depend on the analyzed region but the main point is that much earlier than 2010 FCVs will be unlikely to have a high market share and a fuel infrastructure consideration, and much later than 2010 the uncertainties in forecasting the fuel upstream business become very big and unproductive to analyze.

As explained earlier, the project made the decision to conduct a more detailed analysis of the considered activities, rather than include several pathways with a more superficial analysis. The project is concentrating the resources in the natural gas (NG) pathway scenario because it provides the necessary and most probable fuels for Fuel Cell Vehicles in 2010. These fuels are hydrogen, methanol, and Fisher Tropsch naphtha, which is a clean (sulfur and aromatics free) and unsaturated hydrocarbon fuel produced from NG. Future development of this project should include other pathways like crude oil, coal, biomass, etc.

Circular calculation is introduced in the model to deal with interactions among pathways, but unlike the existing studies such as Greet (1998, 1999 and 2000) and Delucchi (1991 and 1997) that perform this calculation in an aggregated level, FUEEM generates this calculation for each specified area. The FUEEM circular calculation correlates the natural gas feedstock and natural gas power electricity generation in each area considered.

FUEEM treats the following cycles:

- Natural Gas (NG) feedstock: extraction of the raw NG, processing of the raw NG into the marketable gas, bulk storage, transmission, centralized distribution, and decentralized distribution.
- Hydrogen: hydrogen production from NG, bulk storage, transportation and distribution (if necessary), compression and storage at the fuel station, and the vehicle refueling.
- Methanol: methanol production from NG, bulk storage, transportation, fuel terminals, distribution, and vehicle refueling.
- Fisher Tropsch Naphtha (FTN): FTN production from NG, bulk storages, transportation, fuel terminals, distribution, and vehicle refueling.
- Electricity: Electricity production from NG, transmission, and distribution.

Since electricity, in general, is a mix of different technologies and feedstock pathways, FUEEM is incorporating the existing results from other studies for pathways different than NG. The other pathways are oil, coal, biomass, nuclear, hydropower, geothermal, wind, and solar energy.

The operational unit of the complete study is milligrams of pollutant per kilometer (grams per km for the CO_2 case) or energy required in mega Joule (MJ) per kilometer. The fuel upstream analysis is accomplished in terms of grams of pollutant per energy content, Giga Joule (GJ), of the fuel delivered to the vehicle (kg of pollutant per km for the CO_2 case) or energy requirement (GJ) per energy content of the fuel delivered for the vehicle (GJ). All energy content assumes high heating values (HHV).

3.3.2 The software

The Fuel Upstream Emissions and Energy Model (FUEEM) has been designed to assess the air emissions generated by all life cycle activities in the fuel production chain (from feedstock extraction to refueling process) plus a complementary module for the vehicle operations and another for the assessment of the greenhouse gases emissions.

The model works in @Risk® environment, which contains all the necessary statistical features, such as the best curve fit, Latin hypercube sampling for different probabilistic curves, rank correlations, etc. As a default, all the FUEEM simulations use Latin hypercube sampling with the seed fixed on “1” to facilitate reproduction of the results. A large sample size of 3,000 interactions was used and, for an established convergence factor of 1.5 %, the most complicated component model converged around 1,100 interactions.

FUEEM incorporates several formats developed by several previous studies and by doing so is currently the most updated design. Unnash *et al*. (1996) introduced the interesting feature of correlating the emissions with the geographical area of occurrences (emissions generated in SCAB, California, USA and the rest of the world). Similarly, FUEEM gives the option for the analyst to specify three different areas in the results. Consequently, it requires information inputs for each area. In the same way Greet (1998) introduced the idea of providing the energy result disaggregated in terms of petroleum, fossil fuel and total energy consumption and this idea was incorporated in FUEEM as well.

A unique FUEEM characteristic is the possibility of getting the information in a more detailed form than the existing studies. This information includes the amount of pollutants generated by combustion processes, the accounted amount for fugitive emissions, and the amount of pollutants considered by the second order calculation approach. Table 3-3 and Table 3-4 show the details of the information flowing through the model.

Table 3-3: Energy data output format

energy-required MJ / km or GJ / energy-fuel delivered GJ				
	Process	Fugitive	Secondary	Total
Petroleum	r(1)	r(2)	r(3)	r(1) + r(2) + r(3)
Fossil Fuel	r(4)	r(5)	r(6)	r(4) + r(5) + r(6)
All sources	r(7)	r(8)	r(9)	r(7) + r(8) + r(9)

r = probabilistic function generated as result.

Table 3-4: Emissions data output format (per pollutant considered)

milligrams / km or grams / energy-fuel delivered GJ				
	Process	Fugitive	Secondary	Total
Area - I	r(1)	r(2)	r(3)	r(1) + r(2) + r(3)
Area - II	r(4)	r(5)	r(6)	r(4) + r(5) + r(6)
Everywhere	r(7)	r(8)	r(9)	r(7) + r(8) + r(9)

r = probabilistic function generated as result.

FUEEM contains three levels of calculation type. The first level is called component models or component worksheets. Wherever possible, the calculation at this level attempts to incorporate physical parameters and achieve a level of calculation and discussion that promote a better understand of the activity in terms of process design and technology used. Most of the input variables are included on these worksheets. This level of detail also increases the flexibility for local analysis by having optional features like different levels of emissions rates for a high enforcement air control area, medium enforcement area and uncontrolled area. Twelve component worksheets were established in FUEEM:

1. Fuel characteristics
2. General equipment characteristics
3. Hydrogen fuel marketing
4. Liquid fuels marketing
5. Hydrogen production
6. Methanol production
7. Fisher-Tropsch production
8. Natural gas industry
9. Electricity
10. Rank correlations among variables
11. Fuel cell vehicle operations
12. Global warming assessment

The second calculation level is the pathway definition where pathway scenarios are put together by connecting the chosen chain activities from the component worksheet “library” that makes sense for the analyzed area. Basically, this calculation level sums the results of the component models and accounts for the fuel downstream own-use. At this level some of the geographical characteristics are also required, such as the pipeline lengths, the natural gas reservoir characteristics, the electricity mix generation, etc. The pathway worksheets also make possible calculation of combined scenarios from four selected pathways. Five worksheets currently exist in FUEEM, representing each of the fuel cycles specified in the project scope (section 3.3.1):

1. Hydrogen pathway
2. Methanol pathway
3. Fisher-Tropsch Naphtha pathway
4. Natural gas feedstock pathway
5. Electricity pathway

Finally, the third calculation level is the result worksheet where the vehicle operation result is combined with the fuel upstream pathway results, and where a life cycle comparison is made possible. At this level the assessment of the greenhouse gases occurs by transforming all greenhouse gas emissions into $CO_{2\text{-equivalent}}$ and summing them. The calculation levels two (pathway scenarios) and three (results) are the "bookkeeping process" specified earlier.

3.3.3 FUEEM Calculation Example

In this section I present the basic calculation performed in the FUEEM software. After the Latin Hypercube sampling and correlations treatment, the basic calculation in FUEEM is similar to the existing models' approach presented in section 2.4. The idea here is to present a calculation example for easier understanding, and show it with more mathematical notations than graphical presentations. It is necessary to reinforce again that what FUEEM is doing differently is investigating in a more detailed level each activity represented in the component worksheets. The calculation details of the component worksheets are case specific and some details of them are discussed in section 4.

Monte Carlo simulation randomly samples all the input variables per interaction and then the calculation at each interaction is performed as a deterministic calculus. The result of several interactions restores the curve configuration. To preserve the information that each input is a probabilistic curve to be sampled, and each result (even the intermediate ones) has a characteristic curve, I have represented them in brackets [ ]. To check the probabilistic curve of intermediate results, one should identify them as an output format in the @Risk software and run the simulation again.

3.3.3.1 Fuel upstream pathway composition

Let's assume that we have selected for the hydrogen fuel a combination of three pathways, or, in other words, that all the hydrogen delivered as compressed fuel at the fuel stations located inside of the area of interest are a mix of hydrogen produced decentralized at the fuel stations (let us say around 15 %), with some hydrogen produced centralized in 27 MTPD-metric tons per day plant capacity located inside of the area (assuming around 35 %) and that the rest of the hydrogen (around 50 %) is produced outside of the area in bigger plants with 270 MTPD capacity.

Having calculated the emissions and energy requirement for each pathway, the final answers are the weighted composition of the individual results. This operation can be described as:

$$\textbf{[Upstream-result]}_{\mathbf{F}} = \sum_{p} [\text{Pathway-mix}]_{F,p} * [\text{Pathway-result}]_{F,p} \qquad \text{Equation 3-18}$$

where, the uppercase subscript “F” is the fuel delivered at the fuel station being considered in the life cycle calculation. “F” represents the hydrogen fuel in the example. The lowercase subscript “p” is the pathway. In our simple example “p” assumes three values (1 to 3) depending of the hydrogen production plant scenario. “[*-result]” are the probabilistic functions generated by the pathway worksheet calculation. In both cases the result refers to the fuel delivered at the fuel station (end use). “[Pathway-mix]” are functions for the fuel mix assumed (e.g., normal distribution with mean equal 0.50 and standard deviation equal 0.05, for p = 3). Note that $\sum_{p} [\text{Pathway-mix}]_{F,p} = 1$ (or 100 %).

To calculate the result of a single pathway all the major activities performed in the specified boundaries are divided in component or activities calculations. In our example, the activities represent the vehicle refueling process at the fuel station, the hydrogen compression, and storage at the fuel station, the hydrogen pipeline transportation from centralized production (if it is the case), the hydrogen production, the feedstock, and other secondary fuels pathways for each area.

The composition of the results of each stage or activity generates the pathway results. The necessary amount of fuel delivered by each stage is dependent on the fuel own-use in the downstream activities. To exemplify this idea, let’s assume that we use pipelines to transport the gaseous hydrogen and that we lose (fugitive emissions) more hydrogen transporting it in larger quantities from outside of our area than in the other pathways. Based on that, to deliver at the fuel station the same amount of hydrogen, we need to produce more hydrogen in the big plant located outside of the analyzed area (pathway 3 in the example).

The description of this consideration can be written as:

$$\textbf{[Pathway-result]}_{\mathbf{F,p}} = \sum_{s} [\text{Downstream-own-use}]_{F,p,s} * [\text{Stage-result}]_{F,p,s}$$

Equation 3-19

where, the lowercase subscript "s" represents the stages or activities, for example, the refueling process, storage, transportation, etc. The "[Stage-result]" are the probabilistic functions generated by the model calculation at each stage. The result refers to the fuel delivered for the next stage in the same pathway. The "[Downstream-own-use]" are the factors representing the fuel (F) demanded by all subsequent stages in the pathway until the end use. The own-use is related to the fuel (F) being consumed as fuel in combustion processes, as feedstock of some activities, and also representing losses (fugitive emissions) in the stages. The following equation represents its calculus for the stage (n):

$$[\text{Downstream-own-use}]_{F,p,s(n)} = [\text{Ouf}]_{F,p,1} * [\text{Ouf}]_{F,p,2} * \ldots * [\text{Ouf}]_{F,p,n-1} \qquad \text{or}$$

$$\textbf{[Downstream-own-use]}_{\mathbf{F,p,s(n)}} = \prod_{s=1}^{n-1} [\text{Ouf}]_{F,p,s} \qquad \text{Equation 3-20}$$

where, "$[\text{Ouf}]_{F,p,s}$" are the own-use factors of the fuel (F) at each stage (s). Let us assume in our hydrogen example ($F = H_2$) that we are calculating the pathway three ($p = 3$) representing the hydrogen production outside of the analyzed area in a 270 MTPD plant capacity. Let us assume also that all the hydrogen consumed in the pathway is related to fugitive emissions at each stage only (other energy consumptions are related to natural gas and electricity). For easier comprehension, one single interaction in the Monte Carlo simulation is shown in Figure 3-9. For the example, the results of the random sampling of the own-use variables are the loss of 0.005 MBtu per 1 MBtu of hydrogen delivered at the fuel station ($[\text{Ouf}]_{H2,3,FS}$ = 0.5 %), the loss of 0.015 MBtu per 1 MBtu of hydrogen transported to the fuel station ($[\text{Ouf}]_{H2,3,Pipe}$ = 1.5 %) and loss of 0.01 MBtu per 1 MBtu of hydrogen saved in a high pressure bulk storage tank before reaching the pipeline ($[\text{Ouf}]_{H2,3,\ St}$ = 1.0 %). Following the example, the amount of hydrogen necessary to be produced at the plant for each MBtu delivered at the fuel station is 1.03 MBtu.

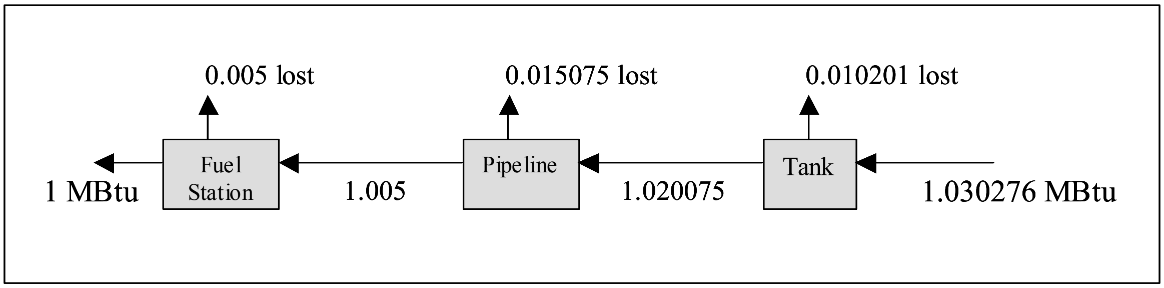


Figure 3-9: An example of the fuel own-use calculation.

or, $[\text{Downstream-own-use}]_{H2,3,s(4)}$ = 1.005 * 1.015 * 1.01 = 1.030276 = 1.03.

Therefore, $[\text{Ouf}]_{F,p,s} = [\text{F-in}]_{p,s} / [\text{F-delivered}]_{p,s}$ or

$$\mathbf{[Ouf]_{F,p,s}} = ([\text{F-delivered}]_{p,s} + [\text{F-consumed}]_{p,s}) / [\text{F-delivered}]_{p,s} \qquad \text{Equation 3-21}$$

where, "$[\text{F-delivered}]_{p,s}$" is the amount of fuel (F) delivered from the stage (s) and "$[\text{F-consumed}]_{p,s}$" is the amount of fuel (F) consumed at the stage (s), or

$$\mathbf{[F\text{-}consumed]_{p,s} = [F\text{-}in]_{p,s} * [Ouf]_{F,p,s}} \qquad \text{Equation 3-22}$$

It is interesting to point out that when a different fuel is consumed in a particular stage the life cycle result of that particular fuel is corrected by the downstream own-use of the analyzed fuel ([Downstream-own-use]$_{F,p,s(n)}$). For example, the contribution of the natural gas consumed at the hydrogen plant is related to the hydrogen losses in our example. This calculation is shown in detail later.

Another point is the interactive (or circular) calculation performed to account for the fuel use in other cycles (see section 2.4.4). FUEEM solves this problem by creating an intermediary result file where the first interaction uses the default input and the other interactions uses the results of the previous one until they match each other.

Having defined all the parameters related to the pathway composition in the life cycle analysis, the rest of the calculations are done inside blocks representing each stage or activity (component worksheets). To exemplify these calculations let us keep using the 270 MTPD hydrogen production example and assume that the plant uses a natural gas steam reformation process, no extra steam production for exportation, and a selective catalytic reactor (SCR) for NOx emission control.

One of the first requirements of these calculations is to locate the activity geographically in one of the three areas defined in the model. A code is established for each area and a name can be placed for them; for example, area 1 is equal to California South Coast Air Basin (SCAB), area 2 is equal to California State and area 3 is the rest of the world. Some characteristics of the area are also requested like electricity mix generation, emission law enforcement, etc. Let us assume that we are analyzing compressed hydrogen fuel cell vehicles running in SCAB and that our hydrogen plant is built outside SCAB but within California.

3.3.3.2 Stage energy requirement

The life cycle energy requirement of a stage is a sum of the regular energy used by the process plus the energy content of any possible loss (fugitive emissions) plus the life cycle energy requirement of every fuel consumed in the process. Or,

$$\mathbf{[Life\text{-}cycle\_total\_energy]_{s,A,c}} = [regular\_process\_energy]_{s,c} + \ldots$$
$$[fugit\_emiss\_n\_accounted\_energy]_{s} + [associated\_life\text{-}cycle\_energy]_{s,A,c} \quad \text{Equation 3-23}$$

where, the lowercase subscript "s" is the stage or activity. In the example it represents the hydrogen plant for the specified characteristics (270 MTPD, no steam exportation and NG steam reformation process). The uppercase subscript "A" is the area where the stage is located (e.g., California outside SCAB). The lowercase subscript "c" is the air emission control device assumed (e.g., SCR).

Two data inputs are necessary to calculate the regular energy requirement of the process. The first one is the efficiency of the uncontrolled process (s) and the second one is the efficiency factor for the air control device (c) used. Both data are in terms of percentage and the efficiency factor indicates the efficiency reduction of the uncontrolled process using the control device. Based on that, the regular energy requirement per energy delivered (H_2 in our example) by the activity is:

$$\mathbf{[regular\_process\_energy]_{s,c}} = 1 / ([eff\_uncontrolled]_{s} - [eff\_factor]_{s,c}) - 1 \quad \text{Equation 3-24}$$

where, $[\text{Efficiency}]_s = [\text{energy\_out}]_s / [\text{energy\_in}]_s$. Note that in the case of our example there is no co-product in the process (steam) and the [energy_out] is already the energy delivered that applies to the calculation (energy content in the H_2 produced). In the case where co-products are present a share portion (credits) is established according several methods (see section 2.4.2) and the "new" efficiency will reflect that:

$$\mathbf{[Shared\_efficiency]_{s,pr}} = [\text{energy\_delivered}]_{s,pr} / [\text{energy\_in}]_s \qquad \text{Equation 3-25}$$

where,

$$\mathbf{[energy\_delivered]_{s,pr}} = [\text{energy\_out}]_s * (1 - [\text{co-products\_share}]_{s,pr}) \qquad \text{Equation 3-26}$$

and the lowercase subscript "pr" is a single product or fuel considered (e.g., hydrogen).

Three steps are necessary to calculate the energy associated with losses that in general are not accounted for in the day-to-day efficiency of a process, such as losses in maintenance, operation fails, accidental spills, etc. The first step is to identify the type and amount of fuel used in the process (energy_in composition for the efficiency formula). The second step is to calculate the fugitive losses for each fuel and finally to identify the amount of these losses that are not incorporated in the process efficiency accountability.

The process information is analyzed previously, and the energy share input data is established. The share will represent all the associated energy of fuels and feedstock necessary for the process. All compounds together make the regular energy imported in. In our example only natural gas (NG) and a small amount of electricity is utilized to produce hydrogen. The general equation can be written:

$[\text{energy\_share}]_{s,f(1)} + [\text{energy\_share}]_{s,f(2)} + \ldots + [\text{energy\_share}]_{s,f(n)} = 100\ \%$ or

$$\sum_{1}^{n} [\text{energy\_share}]_{s,f(n)} = 1 \qquad \text{Equation 3-27}$$

where, the lowercase subscript "f" are the fuels and feedstocks utilized by the stage (s). Therefore, the calculation of the regular energy requirement of each fuel per energy delivered at the end of the stage can be calculated as:

$$\mathbf{[Reg\_energy]_{s,c,f(n)}} = [\text{regular\_process\_energy}]_{s,c} * [\text{energy\_share}]_{s,f(n)} \qquad \text{Equation 3-28}$$

A fugitive emission rate per fuel and per activity (stage) is the necessary data input for the second step. What this assumption tells us is that a percentage of the fuel utilized will be considered lost as fugitive emission (leaks, purges, valves, maintenance, etc.). Eventually, a previous calculation can be made using the emission factor available for inventories and a more detailed design for a typical process (including number of valves, flanges, purges, etc.). The result of this previous calculation is in terms of energy lost per regular energy consumed.

The thirtieth step will require an input data associating a percentage of the fugitive emission that is not accounted for in the regular process efficiency. Based on that, the following equation applies:

$$\mathbf{[fugit\_emiss\_n\_accounted\_energy]_{s}} = \sum_{1}^{n} [\text{Reg\_energy}]_{s,f(n)} * [\text{Fug\_emiss\_rate}]_{s,f(n)}$$

$$* \ldots [\text{n\_accounted\_rate}]_{s,f(n)} \qquad \text{Equation 3-29}$$

Since the energy output of the model splits the energy required in terms of fuel derived from petroleum (diesel, residual oil, etc.), from fossil fuel (petroleum plus NG and coal), and from all sources (fossil fuel plus nuclear, biomass, etc), the result level identifies the fuel (f) and adds it when necessary (see Table 3-3).

Up to this level this operation is done only with the result of the calculation. However, in the next operation, responsible for including the life cycle energy requirement of secondary fuels, the input data come in the same format as the output and therefore three operations are necessary (for the petroleum, fossil fuel, and total energy requirement calculation). Note that these input data are assumptions for the first interaction in the circular calculation but for the other interactions and for the pathways that already exist in the model they are intermediary results. The area allocation of the stage plays a role at this level when the geographical specificities (distances, power generation mix, etc.) are determinant of the life cycle pathways. The secondary calculation is,

$$\mathbf{[\text{associated\_life-cycle\_energy}]_{s,A,c}} = ([\text{fugit\_emiss\_n\_accounted\_energy}]_{s} + \ldots$$

$$[\text{Reg\_energy}]_{s,c,f(n)}) * [\text{Pathway-energy-result}]_{f(n),A} \qquad \text{Equation 3-30}$$

3.3.3.3 Stage emissions

The emissions are calculated at the equipment level using emission rates per pollutant in terms of amount of pollutant emitted (e.g., grams) per amount of fuel consumed by the equipment. Based on that, the first information necessary to the calculations is the amount of fuel consumed per equipment type. To do that an equipment share variable is assumed for each fuel used in the process. These variables identify the major equipment in the process and quantify the percentage of the total energy associated to the fuel consumed by them.

$$\sum_{1}^{n} [\text{equipment\_share}]_{s,f,eq(n)} = 1 \quad (\text{or } 100\ \%) \qquad \text{Equation 3-31}$$

where, the lowercase subscript "eq" represents the equipment type utilizing fuel (f) in the activity or stage (s). Following our example, the NG consumed by the hydrogen plant is partly utilized as feedstock in the steam reformation process and partly utilized as furnace fuel. Therefore, the calculation of regular energy requirement of each equipment type per fuel per energy delivered at the end of the stage can be calculated as:

$$\mathbf{[Reg\_equip\_energy]_{s,c,f,eq(n)}} = [\text{regular\_energy}]_{s,c,f} * [\text{equipment\_share}]_{s,f,eq(n)}$$

Equation 3-32

Note that:

$$\sum_{1}^{m} \sum_{1}^{n} [\text{Reg\_equip\_energy}]_{s,c,f(m),eq(n)} = [\text{regular\_process\_energy}]_{s,c} \qquad \text{Equation 3-33}$$

The emission per equipment is calculated as:

$$\mathbf{[Equip\_emissions]_{s,c,f,eq(n)}} = [\text{Reg\_equip\_energy}]_{s,c,f,eq(n)} * [\text{Emission\_factor}]_{s,c,f,eq(n)}$$

Equation 3-34

and, finally, the process emission is:

$$\mathbf{[Process\_emissions]_{s,c,f}} = \sum_{1}^{n} [Equip\_emissions]_{s,c,f,eq(n)} \qquad \text{Equation 3-35}$$

Of course, what is presented here is a generic example. In a real calculation, one needs to take into account the available data for each case, and then do the proper calculation based on those. For example, the emission factor for hydrogen production can be expressed in terms of grams of pollutant per amount of hydrogen produced, or grams of pollutant per amount of NG burned in the reformer. See Contadini *et al* (2000a) for more discussion of this point.

Finally, in the case of CO_2 emissions and SO_x emissions, the calculation is done by mass balance based on the composition of the fuel burned. In other words, the amount of carbon or sulfur in must be equal to the amount of carbon out. The sulfur is, in general, assumed to be in the form of H_2S and the sulfur out in the form of SO_2.

4 FUEEM COMPONENT MODELS

4.1 Hydrogen marketing activities

Direct hydrogen is the simplest and most efficient design for fuel cell vehicles. The hydrogen storage and the fuel infrastructure are the major uncertainties for the success of this technology. Through lack of better choices, compressed gas was chosen as the most reliable option to be considered in the model since the cryogenic option presents a lot of concerns in terms of safety, energy requirement in the liquefaction process, and boiling off losses. Trucks can transport hydrogen in liquid form; however, a high-energy cost must be paid in the liquefaction process and all this cost is lost in the vaporization process at the fuel station. Compressed gas can also be transported by truck but again this option is very expensive due to the low energy density of the gaseous hydrogen. Storage solutions such as metal hydrides have been studied for more than 20 years and show no sign of major breakthrough. Nanostructures are still in very initial stages of development to be considered in the market in the next 10 years.

Based on these facts, two options can be considered in the case of a larger demand of hydrogen: pipelines and hydrogen production at the fuel station. A hydrogen pipeline can be considered as an intermediate process to move hydrogen from the hydrogen plant or plant bulk storage to the hydrogen fuel station.

The approach adopted in this study focuses on pipeline design parameters that contribute to the final efficiency and emission rates. It also focuses on the year 2010 as the time frame.

In general, hydrogen pipelines are more expensive than natural gas pipelines. Ogden (1999) estimated the pipeline cost per mile of around $ 1 million in a heavily populated area like Los Angeles. It is possible that some improvements may occur; for example, according to Socolow (1997) a new low-cost metal pipe can safely be used. Most of the FUEEM experts agreed that the highest cost to install a new pipeline is the land price (including permissions). The eventual possibility of placing the hydrogen pipeline next to the existing natural gas pipeline may reduce the costs. For a larger hydrogen market, our previous discussion and other studies (Shelef *et al*. (1994); Mark (1996); Ogden (1998) and others) tend to conclude that hydrogen transportation by pipeline may be the cheapest pathway and therefore should be included as an option in the FUEEM. This study discusses the major sections for the energy requirement calculation of possible hydrogen fuel pipeline transportation and compression at the fuel stations.

According to Pottier and Blondin (1995) the engineering design of pipelines for hydrogen gas is similar to those for natural gas (NG). However, the existing emission models have been treating the issue at a very aggregated level leaving some room for a better treatment of the assumptions.

For example, Greet (1998) uses a 1980's NG data where 250,000 miles of transmission lines (32" diameter) plus 900,000 of main distribution lines (12") and 520,000 miles of service lines (2") were used nationwide to transport 22 trillion cubic feet (TCF) of natural gas. Mixing all diameters and using a single linear relationship he came up with the requirement of 76,000 miles of pipeline to transport 1 TCF of hydrogen fuel. The rest of his assumptions are that the same NG pipeline length and size can carry the same amount of H_2 using bigger compressors (3 to 3.5 times). Assuming that 98.6% of the consumed energy occurs in NG compressors and turbines and 1.4 % in electric compressors with no feed losses, he came up with the pipeline efficiency of 94 %. In August of 1999 he published another report (Greet (1999)) where he assumes feed losses of 13 %, which bring down the NG energy consumption to 86 % and electricity consumption of 1% to come up with a different pipeline efficiency of 97 %. Finally by January of 2000, a new report (Greet (2000)) assumed a pipeline efficiency of 95 % only stating a comparison with the NG pipeline efficiency of 97 % (all in LHV).

Bentley *et al.* (1992) and Harvey (1995) assume an efficiency of 97 % and Delucchi (1991) and (1997)) assumes that hydrogen pipelines will use compressors powered by hydrogen internal combustion engines. Based on that and without any other statement, Delucchi assumes that 0.10 Btu of H_2 is consumed per Btu of H_2 delivered by the pipeline (efficiency of 90.9 %). Acurex (1996) assumes only liquid hydrogen transportation.

4.1.1 Energy Requirement and Pipeline design

To calculate the energy requirement and emissions associated with the hydrogen transportation process it is important to take into account parameters like the length and other technical characteristics of the transportation process. As discussed below, the gas is transported by pressurization at compression stations over distance to compensate for the pressure drop in the pipe due to friction. Figure 4-1 illustrates this concept. To have a flexible geographical analysis capability in the model, it is our goal to generate all off the transportation data per distance or in other words the pipeline distance is one input parameter in the model. The lack of association of the input assumptions with the distance was pointed out as one of the major difficulties of using Wang's model (1999) for local analysis.

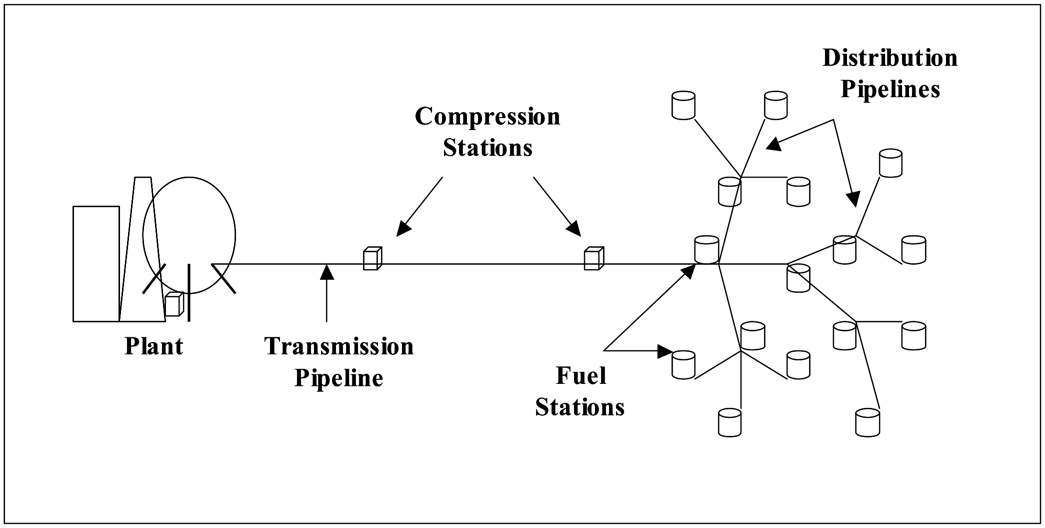


Figure 4-1: Schematic of a hydrogen fuel pipeline design

One of the main concerns is the selection of the pipeline materials since hydrogen may cause embrittlement in some kinds of steel used for NG transmission (Leeth, (1977); Mathis, (1976); Shelef *et al*, (1994); Pottier, (1995) and others). Embrittlement is defined as a decrease in the strength of certain steels caused by hydrogen. The problem occurs mainly in high strength steels and at high temperatures. For more details see Thompson (1979). Plastic pipes (PVC - Polyvinyl Chloride and HDPE – High-density Polyethylene) normally used for NG distribution pipes cannot be used for hydrogen pipelines since their porosity is too large for the hydrogen molecular size (Socolow, 1997). Based on this material information and mainly on the lack of natural gas pipeline system availability to delivered hydrogen in major urban areas, it is our assumption that it will be necessary to construct new dedicated hydrogen pipelines. The option considered by Ogden *et al.*

(1994) of using the existing NG pipeline system to transport a blend of 15 % to 20 % of H_2 by volume with NG will not be considered, since this design requires a separation process at the end of each line.

4.1.2 Pipeline Pressure

The assumption of dedicated hydrogen pipelines is important because the characteristics of the outlet pressure for the fuel station can be designed according to that. Using this argument Arthur D. Little (1996) assumes as 1,000 psi (6.89 MPa) the pressure of the hydrogen delivered at the fuel station, minimizing the compression requirement there and transferring it to a more centralized pipeline compression station. With this design they come up with the pipeline efficiency of 99.2%. According to Socolow (1997) the existing American and European pipelines operate at pressures up to 1500 psi (10.34 MPa). Other studies (Ogden, (1995) / (1998) and Mark, (1996)) assume the pressure of the hydrogen delivered at the fuel station as 200 psi (1.38 MPa) and Moore *et al.* (1998) assume a variable pressure between 220 and 441 psi (1.52 to 3.04 MPa). In our study we generated various scenarios with hydrogen being delivered at different pressures, including 200 and 1000 psi, at the fuel station.

The pipeline inlet pressure is another variable in the calculation and it is related to the pressure of the hydrogen released by the PSA (Pressurized Swinging Adsorption) at the hydrogen plant. According to Patel *et al.* (1994) this hydrogen flow pressure can vary between 420 and 450 psi (2.9 to 3.1 MPa) for a centralized plant. Our expert network advised us to use a distribution curve to determine this pressure with a minimum of 250 psi and a maximum value of 420 psi with a major tendency towards the minimum value.

The main reason for this is that high-pressure operation implies thicker catalyst tubes, increasing the cost. Also, low pressures favor the synthesis reactions and increase the efficiency. Using the @Risk software we determined a distribution curve and the main values can be seen in Table 4-1. If the plant works with bulk storage, the inlet pipeline pressure will be the pressure of the bulk storage vessel.

4.1.3 Bulk Storage

None of the existing models that deal with the distribution of gaseous hydrogen mentions or gives details about having incorporated bulk storage in the calculation (Greet, DTI and Ogden). Regular pipelines directly connect the centralized production plant to the fuel stations, but for this design two considerations must be taken into account:

- The pipeline will directly transmit the demand oscillations into the production characteristics. According to Thomas *et al.* (1997) a production surge factor must be considered in this case to establish the necessary plant size. Also, McAuliffe (1980) suggests that a non-constant output of hydrogen decreases the efficiency of the production plant and this has not been considered in the models. Increasing the storage volume at the fuel station and synchronizing the supply time schedule may solve this problem, and this option is included in this study. However it is important to point out that a bigger storage tanks at the fuel station implies a higher capital investment and the decentralized marketing network may not accept it. The capital cost increase is due to bigger storage tanks and the necessity of a reliable information network among the hydrogen plant and the all fuel stations.

- Mathis (1976) states that line-pack storage can be used on a daily basis. It may be feasible for a long transmission line; however, it does not apply for a distribution network. For example, a 50-mile long pipeline holding hydrogen at 1,000 psi (6.90 MPa) should have a 4 ft (1.22m) diameter to store 30 MBtu of H_2 (28 x 10^3 GJ), the necessary amount to refuel approximately 80,000 vehicles a day (supporting a fleet of approximately 700,000 vehicles @ 33 miles/day and 90 miles/gallon-gasoline-equiv.).

The solution of large volume hydrogen storage has been studied mostly in the late 70's and early 80's, immediately after the petroleum crisis. Underground storage using natural or specially created cavities has been recommended as the alternative. Pottier (1982) and Pottier and Blodin (1995) give various examples of underground gas storage in France. Deep aquifers with porous and permeable geological layers, in general, are used for very high volumes (0.1 to 1 x 10^9 m^3) on an annual basis. McAuliffe (1980) identifies the regions within the USA that contain this geological formation in the strata, and a great part of Southern California and Central Valley fits this classification. Pottier and Blodin (1995) also point out that the output gas may contain hydrogen sulfide (similar to NG) requiring a processing station to eliminate this compound.

In regions where salt layers exist, special cavities can be created by controlled dissolution. A single cavity can have a volume capacity of approximately 1 x 10^6 m^3 and several cavities can be built for weekly or daily storage purpose. According to Pottier and

Blodin (1995) the working pressure may vary from 0.6 to 1.8 times the hydrostatic pressure at the cavity roof, translating to 60 to 180 atm (881.76 to 2645.27 psi) for a 1,000-meter deep cavity. Taylor *et al.* (1986) compared five different alternatives for storing hydrogen and determined that salt caverns have the lowest cost even though they involve a considerable initial capital investment. One of the disadvantages of salt caverns is that the working fluid must be saturated brine.

According to the FUEEM expert network variable output at the centralized hydrogen production plant should not be used. Efficiency loss, plant reliability and safety concerns were pointed out as motives for considering bulk storage. They considered pipeline-pack storage unfeasible due to the pipe diameter limitation in urban areas, transforming it into a high-cost option with low benefits. On the other hand, salt cavities are a viable solution, although they are geographically limited due to geological formations and may be prohibited in certain urban areas.

Carpetis (1988) provides some data for high-pressure storage vessels including the operational pressure of 3336 psi (23.0 MPa). According to him this is the most economical aboveground short-term storage (less than 30 hours) for hydrogen. Based on all this information it was decided to include the option to work with high-pressure bulk storage in the range between 2,900 and 3,627 psi (20 to 25 MPa). The distribution curve is shown in Table 4-1.

4.1.4 Flow Rates x Pipeline Diameters

Other very important variables in the pipeline design are the gas flow rate in the pipe and the diameter considered in the design. The gas flow rate for transmission lines is related to the hydrogen plant output capacity and the flow rates for the distribution lines are related to the fuel station gas demand.

The FUEEM model works with two centralized hydrogen plant capacities: 27 MTPD (0.3125 kg/s) and 270 MTPD (3.125 kg/s). One factor to be considered is the percentage of the overall capacity of which the plant is expected to operate. Moore *et al.* (1998) assume that the production for a 300-MTPD and a 30-MTPD-plant capacity will be 270 MTPD and 27 MTPD (90 % of the plant capacity), respectively. We have checked a specific plant's operation (35 MTPD) data for two months and found that it operated those particular months in the range between 99.5 % and 100.5 % of its nominal capacity. For the pipeline design we are considering 100% of the plant capacity.

Another point that should be considered is the fuel station hydrogen demand, which will depend on the fuel station capacity. Ogden *et al.* (1998) and (1999) consider a fuel station demand of 1 Mscf/day (2,400 kg/day) to be sufficient for a fleet of 9,220 vehicles or a refueling of 654 vehicles per day. They consider the typical Los Angeles mileage traveled to be 11,000 miles per year per car and the car fuel efficiency to be 106 mpgg_{eq} (miles per gallon of gasoline equivalent). Moore *et al.* (1998) designed a Fuel Station for 500 cars per day considering the average hydrogen demand of 2.7 MTPD (2,700 kg/day). Thomas *et al.* (1998) in their cost analysis study looked at different fuel station capacities from 100 vehicles per day to 1000 vehicles per day with each vehicle refuel at 5.6 kg of hydrogen per time (560 to 5,600 kg/day). Patel *et al.* (1999) suggested a fuel station design for delivering 6,000 kg/day of hydrogen. Finally, Mark (1996) considered 267 fuel stations to deliver 606 MW of hydrogen or 1,377 kg/day per fuel station (HHV) on average. The FUEEM expert network decided to work with values between 350 and 500 cars per day and an average hydrogen demand of 4 kg of hydrogen per vehicle per refueling. The curves can be seen Table 4-1.

Another important variable for the flow rate definition is the number of pipes transporting the hydrogen plant production and the connection between the transmission line and the distribution lines. Figure 4-2 shows two different approaches to the connection assumptions. In the first approach the calculations for transmission line and distribution line are done independently and the flow rate is constant in both line types. In the second approach, the flow rate in the transmission line decreases over the distance. Apparently all the detailed studies for this section have been done independently (approach “a”). For example, for a 606 MW (368 MTPD – HHV) hydrogen demand, Mark (1996) assumes 4 bulk-transmission lines to the cities, which translate into the transportation of approximately 92 MTPD per line. From the end of each transmission line, 17 local distribution lines (16 km each) delivered the hydrogen to approximately 67 fuel stations. Using the approach “a,” for the calculation, the underlying assumption is that approximately 4 fuel stations (67/17) are placed at the same location. Patel *et al.* (1999) have suggested the approach “b” as a more realistic design for a large regional gaseous hydrogen plant distribution. For a 30-MTPD plant a transmission pipeline of 30 miles has a connected distribution pipeline every 3 miles. For a 10 times larger plant capacity, 10 similar transmission pipelines were considered. No further details were explored. The approach “b” is considered in this study.

For the definition of the number of pipes transporting the hydrogen plant production, the experts suggested that we adopt a similar Patel *et al.* (1999) design for the distribution process, or in other words a main distribution line for every 27-MTPD demand. For remote transportation (assuming a 270 MTPD plant outside of cities, for example) they suggested 2 transmission lines.

Leeth (1977) reported some diameters of existing hydrogen transmission pipelines. According to him there is a 203 mm (8”) hydrogen pipeline in Texas and a hydrogen pipeline system in Germany which mostly consists of 300 mm (11.8”) pipeline. Pottier (1995) also reports that L’Air Liquide Company pipelines in France and Belgium are mostly 100 mm (3.9”) diameter. Ogden (1995) and Mark (1996) assume in their studies 3” for distribution pipelines and Mark (1996) assumes 6” for transmission pipelines. After discussion and after calculations, we decided to use 8” for the transmission lines, 4” for the main distribution lines, and 2” for the secondary distribution lines.

4.1.5 Pipeline Length

Depending on local conditions, there is an option of varying the length of the pipelines. Three different options were established for the distribution lines (20 to 30 miles, 34 to 46 miles, 48 to 62 miles). Another three options were established for the transmission lines (35 to 65 miles, 80 to 120 miles, 125 to 175 miles). All were treated as normal distribution curves.

Greet (1999) assumed just one scenario in his model. He considers the hydrogen plant located at the natural gas fields and pipelines to transport the hydrogen from there into the market place. This design requires transmission lines longer than the maximum option in the FUEEM. However, the consensus of the FUEEM expert network is that natural gas is easier and costs less to transport than hydrogen and the natural gas pipelines are already in place in developed countries. Therefore, new hydrogen plants should be built as close as possible to the market area.

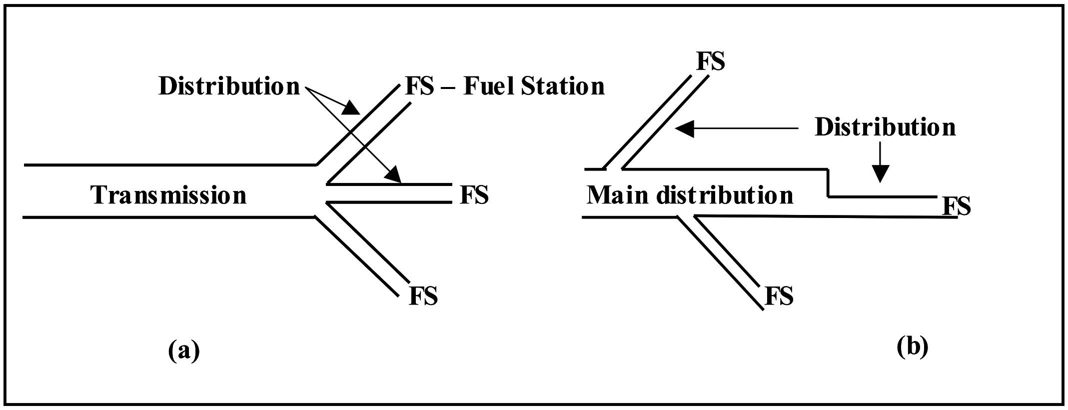
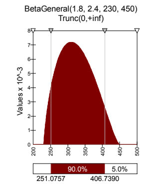
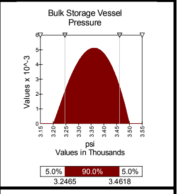
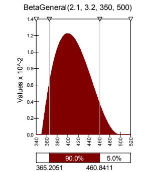
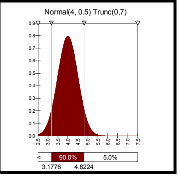


Figure 4-2: Two possible approaches for the flow rate assumption

Table 4-1: FUEEM input assumptions for the hydrogen marketing activities

<table>
<tr><th>Parameters</th><th>Unit</th><th>Min/Max
(90% Confidence)</th><th>Mode</th><th>Mean</th><th>Curve Shape</th></tr>
<tr><td rowspan="2">Pipeline Inlet Pressure</td><td>psi</td><td>251 / 407</td><td>309.7</td><td>324.3</td><td rowspan="2">
</td></tr>
<tr><td>MPa</td><td>1.73 / 2.81</td><td>2.14</td><td>2.24</td></tr>
<tr><td rowspan="2">Bulk Storage Vessel Pressure</td><td>psi</td><td>3230 / 3470</td><td>3356</td><td>3356</td><td rowspan="2">
</td></tr>
<tr><td>MPa</td><td>22.27 / 23.92</td><td>23.14</td><td>23.14</td></tr>
<tr><td>Vehicles per day</td><td>cars</td><td>365 / 461</td><td>400.0</td><td>407.4</td><td>
</td></tr>
<tr><td>Hydrogen demand per vehicle</td><td>kg</td><td>3.2 / 4.8</td><td>4.0</td><td>4.0</td><td>
</td></tr>
</table>

4.1.6 Hydrogen Compression

Once all the parameters, such as diameter, flow rates, pressures, etc. are defined, the model is able to calculate the compressor power required to take hydrogen through the pipeline. According to Leeth (1977) the gas industry has been using the isothermal flow of a compressible fluid as the basis for pipeline analyses. Pipe diameters, distance between compressor stations, pressure ratio, compressor power, etc. are usually the parameters of interest. Various equations have been used to describe the gas flow relationships among these parameters and many formulations have been developed in order to simplify calculations and answer specific questions (Leeth, (1977); White, (1994); Pottier, (1995); Ogden *et al.*, (1995)). These equations are quite similar and are fairly basic equations of fluid dynamics. One of the equations used in the model is:

$$W = \frac{1}{\eta} mCpT \left[\left(\frac{P_2}{P_1} \right)^{\frac{(\gamma - 1)}{\gamma}} - 1 \right] \qquad \text{Equation 4-1}$$

where, W is the compressor power (kW); η is the compressor efficiency (%); m is the mass flow rate (kg/s); Cp is the heat capacity (kJ/kg.K); T is the gas temperature (K); P_1 and P_2 are the inlet and outlet pressures (Pa) and γ is the ratio of heat capacities (C_P/C_V) of the gas.

Mathis (1976) compared the two major types of compressors used in the natural gas industry to boost the pressure along the pipelines: reciprocating and centrifugal compressors. According to him reciprocating compressors will have a serious sealing problem due to the rapid diffusion of relatively small hydrogen molecules and the attack by hydrogen on sealing materials in non-lubricate designs.

On the other hand centrifugal compressors will not produce the required pressure rates without extensive multi-staging; since pressure rise is the product of density and head rise, a lower density gas requires a higher head machine.

In a complementary report, Pottier (1995) presented a more updated study of compressors for hydrogen in which he also concluded that there are two compression technologies available for hydrogen: reciprocating compressors and centrifugal compressors. The latter are used extensively in natural gas compression stations for medium and large flows. For hydrogen, use of centrifugal compressors certainly creates more problems than the use of reciprocating ones. In fact the recompression rate for hydrogen is one-fourth that for natural gas, for the same given tangential speed of the rotor. This requires a larger number of stages. Also hydrogen tends to return to the inlet, due to its low specific gravity, thus decreasing centrifugal compressor efficiency. On the other hand, reciprocating compressors used for natural gas can be used for hydrogen without major design modifications. However, since hydrogen diffuses more readily, special attention must be given to sealing.

Also, Ogden *et al.* (1995) suggested that to compress hydrogen a positive displacement reciprocal compressor would be needed. Centrifugal compressors cannot achieve these high pressures because of leakage, and piston compressors have too high losses due to friction. Based on the information above we are considering only reciprocating compressors in our analysis. The necessary compressor power can be provided by different sources such as electric motor, hydrogen internal combustion engine, or natural gas internal combustion engine. In the model we are considering the electric and natural gas motors as options. The assumed efficiency curves for the compressors and for the motors were taken from the literature and confirmed by several compressor manufacturers. These values are presented in Table 4-2.

4.1.7 Turbo-compressor at the bulk storage

FUEEM gives the option of restoring part of the energy of the compressed hydrogen gas stored in a high-pressure tank located at the hydrogen centralized plant, by including a turbo-compressor in the design. The energy recovered by the expander (W) is calculated in a very similar way to the energy to compress the gas.

$$W = \frac{1}{\eta} mCpT \left[1 - \left(\frac{P_2}{P_1} \right)^{\frac{(\gamma - 1)}{\gamma}} \right] \qquad \text{Equation 4-2}$$

where, m is the mass flow rate to the expander and the efficiency (η) is the product of the expander mechanical efficiency and the expander isentropic efficiency. The assumed values for these efficiencies are presented in Table 4-2.

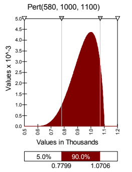
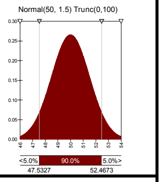
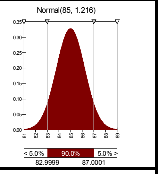
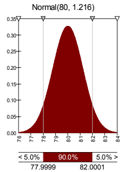
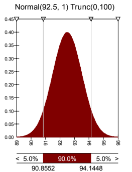
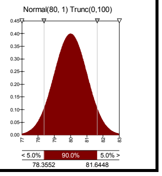
4.1.8 Hydrogen Refueling Station

A few gaseous hydrogen-refueling stations have been implemented so far to serve the demonstration program of fuel cell buses in cities like Chicago and Vancouver. The cost and complexity of fuel stations were always a subject of discussion but for the purpose of this study the compression requirement and the fugitive emissions are the only variables necessary to be considered. Most of the existing complexity of the fuel stations is related to safety concerns and the high cost is expected to be reduced with mass production. Ogden (1999) estimates the cost of about US$1.7 million per station but a multi-stage compressor is specified to compress the gas from 200 psi to 8000 psi. Higher inlet pressure from the pipelines and lower final pressure in the storage vessel may reduce her figure.

The fuel station efficiencies assumed by the existing studies are: 92.8 % for Arthur D. Little (1996) considering an inlet pressure of 1,000 psi. Initially Wang *et al.*(1997) assumed 90 % but later changed that to 92 % (Greet, 1999). Hart and Bauen (1998) present the figure of 92.3%, but to compress H_2 from 1.0 bar (14.696 psi) to 250 bars (3627 psi) only. Delucchi (1993) considers in his model gaseous hydrogen stored on board the vehicles in metal hydrides tanks. To pressurize the gas to 500 psi he considers that 0.03 Btu of electricity is consumed per each Btu of hydrogen compressed, or in other words a compressor efficiency of 97.09 %.

An interesting DOE study (1997) of hydrogen refueling thermodynamics shows the relation among the gas temperature in the vehicle vessels, the refueling time, and the final pressure of the vessel (after temperature stabilization). According to the study an overpressure of 800 psi is required to achieve the final pressure of 5000 psi in a 5 minute refueling. Based on that, a suggested total pressure of 5800 psi is the storage pressure at the fuel station vessel. Greet (1999) and Thomas *et al.* (1997) work with the overpressure of 1000 psi, and Mark (1996) states that this figure should be between 500 and 1000 psi. The assumed overpressure curve in the FUEEM model is approximately 950 psi as shown in Table 4-2.

Table 4-2: FUEEM input assumptions for the hydrogen marketing activities

Parameters	Unit	Min/Max (90% Confidence)	**Mode**	**Mean**	**Curve Shape**
Refueling over pressure	psi	780 / 1071	1000.0	946.7	
	MPa	5.38 / 7.38	6.89	6.53	
Compressor efficiency	%	47 / 52	50	50	
Expander mechanical efficiency	%	83 / 87	85	85	
Expander isentropic efficiency	%	78 / 82	80	80	
Electric motor efficiency	%	91 / 94	92.51	92.5	
NG motor efficiency	%	78 / 82	80	80	

4.1.9 Emissions

It should be noted that hydrogen is not considered as a pollutant and therefore the fugitive emissions related to it count only as energy losses. The only emissions considered in this model occur when natural gas is used as a fuel for the compressor motors. The assumed emissions rates were based in EPA-AP42 (1995), Acurex (1996), Workman Jr. *et al.* (1996) and Greet (1999) and treated as normal curves. The parameters for these curves are shown in Table 4-3. The life cycle emissions for electrical energy generation are calculated as secondary fuel emissions.

Table 4-3: Emission rates for small stationary NG reciprocating engines

Pollutant	mean	standard deviation
	(g/GJ of NG consumed)	
NOx	55.00	7.75
CO	250.00	44.71
NMOG	20.01	6.03
CH_4	300.00	60.61
N_2O	1.80	0.06
PM_{10}	9.00	1.20
$PM_{2.5}$	19.61	3.07
SOx	0.25	0.03
CO_2	49000.00	2409.5

4.2 Hydrogen production

Hydrogen has been extensively produced worldwide to serve basically two kinds of industries. The chemical industry consumes 53 % to 55 % of the total 31 to 32 billion standard cubic feet of hydrogen produced per day (scf/d), and the majority of this hydrogen is used to produce ammonia for soil fertilization (Shanley and Ondrey, 1996). The refinery processing industry consumes 9.8 to 10 scf/d of this marketable hydrogen. A similar amount is also internally produced in catalytic reformers and consumed by the refinery but it is not included in the total figure presented. All the hydrogen in the refinery is utilized by the residuum hydrocracking process; the residuum, heavy oil and distillate hydrotreating process; and the naphtha hydrodesulfurization process (Radler, 1996). The FUEEM expert network expectation is that environmental concerns and pressure for low-sulfur fuels will increase the demand for hydrogen and new plants will be built over time. Eventual over-demand due to the use of hydrogen fuel for fuel cell vehicles in the year 2010 is therefore assumed to be supplied by new plants also.

Hydrogen can be produced by different processes and feedstocks. Existing processes can be chemical, such as steam reforming, partial oxidation, and the combination of both called autothermal reforming and gasification; or electrochemical, such as water electrolysis. Their main reactions are presented below:

- General steam reforming:……..……… $C_nH_m + n\,H_2O \leftrightarrows n\,CO + (n + m/2)\,H_2$
- Partial oxidation:……………..………… $C_nH_m + n/2\,O_2 \leftrightarrows n\,CO + m/2\,H_2$
- Autothermal reforming:…… $C_nH_m + p\,O_2 + (n\text{-}2p)\,H_2O \leftrightarrows n\,CO + (n\text{-}2p{+}m/2)\,H_2$
- Gasification:………………………………….. $C + H_2O \leftrightarrows CO + H_2$
- Water electrolysis:…………………………… $H_2O + e^- \leftrightarrows H_2 + ½\,O_2$

According to the comments provided by the FUEEM expert network (FEN), steam reforming works very well for gaseous and light liquid hydrocarbons such as natural gas and naphtha. Compared with other hydrogen production processes it has a modest cost (around 1.90 to 2.70 $/Mscf). Gasification is the preferred process for heavier liquid hydrocarbon feedstocks as well as for solid feedstocks such as coal and biomass. Partial Oxidation (POX) has been considered for gas-to-liquids fuel production due to its H_2/CO ratio and high syngas production rates for moderate plant size. Gasification, as well as POX, can be utilized for gaseous, liquid, and solid feedstocks; however, their higher cost limits their application (3.00 to 4.30 $/Mscf). Finally, water electrolysis produces oxygen (O_2) and hydrogen (H_2) by splitting the water molecule with electricity. Electricity can be produced many different ways and the regional cost of the electricity associated with a moderate cost of the electrolyzer may limit the process use only for some market niches (12.00 to 20.00 $/Mscf).

Basically the major cost for chemical hydrogen is a combination of the feedstock cost with the capital cost for the syngas production. Syngas is the primary gas produced by hydrocarbons that is mainly composed of percentages of H_2 and CO. In general, the syngas characteristic is expressed in terms of its H_2/CO ratio and the ratio requirement varies from one product to another (hydrogen, methanol, ammonia, etc.). In the hydrogen case the highest ratio is better. To increase the ratio a shift reaction is performed after the steam reformation reaction. Currently, steam methane reforming (SMR) is the most utilized process for hydrogen production. The cost, abundance, availability, low-sulfur content of natural gas (methane) associated with its relatively easy and low cost processes and highest final H_2/CO ratio, drive this option. Based on all these characteristics the expert opinion (FEN) is that SMR will be the technology of choice in the following 20 years or so. The overall SMR reactions are presented below:

$CH_4 + H_2O \leftrightarrows CO + 3\,H_2$ reforming

$\underline{CO + H_2O \leftrightarrows CO_2 + H_2}$ shift

$CH_4 + 2\,H_2O \leftrightarrows CO_2 + 4\,H_2$ overall

4.2.1 The plant design

A detailed understanding of the overall process was required due to the level of discussion and data collection for the model. As stated before most of this information comes directly from the expert panel; however, to initiate and complement the discussion sections, data from Patel *et al*. (1994), Ogden *et al*. (1995), Wang (2000), and Spath and Mann (2000) were used. A summary of the discussion results is presented here and Figure 4-3 shows a simplified scheme of a typical plant configuration.

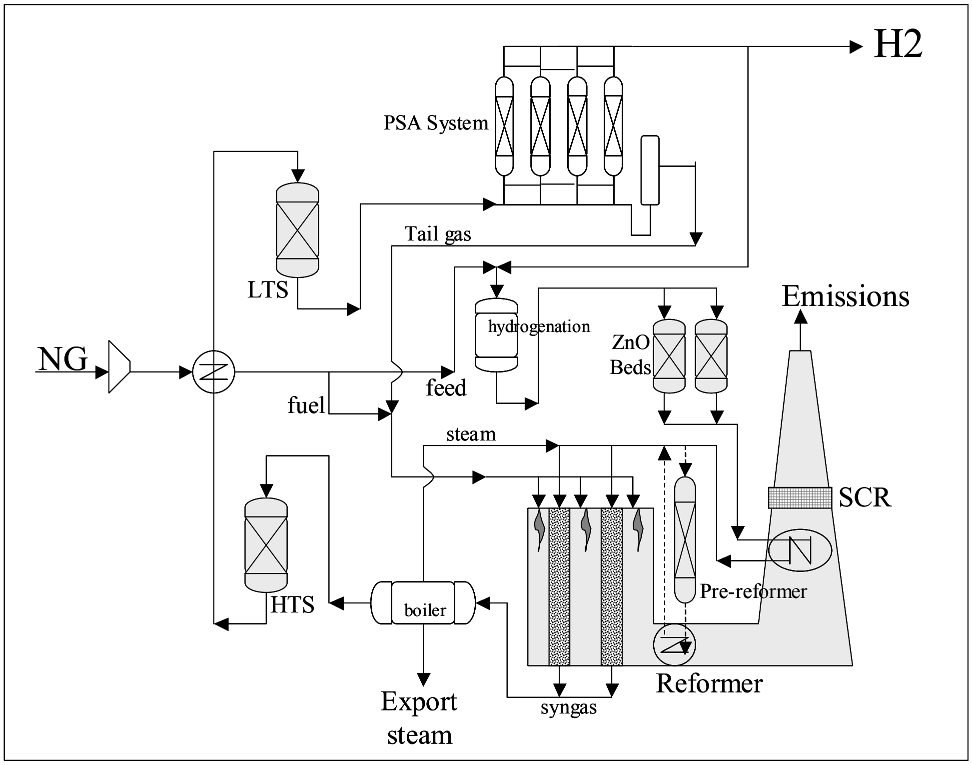


Figure 4-3: Simplified scheme of a typical new SMR hydrogen plant

In general, natural gas (NG) is acquired by hydrogen plants at about 1 to 2.1 MPa (150 to 300 psi). Part of this NG is burned as fuel in the reformer furnace. The percentage of the NG utilized as fuel can vary from 3 % to 20 % depending on the plant design and operation parameters (see discussion below). The majority of the NG that is used as feed in the reformation process is then pressurized at about 3.1 to 4.1 MPa (450 to 600 psi) using single-stage reciprocating compressors powered by electric motors. Lower pressures favor the synthesis reactions increasing the efficiency of the plant. Also, higher pressures require thicker reformer catalyst tubes increasing the capital cost of the plant and provoking higher leakages. However, local conditions such as the pressure of the feedstock gas and the desired product characteristics may change these economics. The typical reforming pressure is around 2.41 to 2.76 MPa (350 to 400 psi).

Basically, the steam methane reforming (SMR) technology accommodates the endothermic reforming reaction inside of high-alloy tubes filled primarily with nickel catalyst. Conventional catalysts are refractory like alumina containing 10 to 20 % of nickel. The tubes are fire heated inside of larger furnaces providing the necessary reaction energy. Since nickel is highly vulnerable to sulfur poisoning a desulphurisation process is added upstream. This process accomplishes two steps; first organic sulfurs are hydrogenated to H_2S (hydrogen sulfide) by preheating the natural gas to about 360 to 380 ^oC (680 to 716 ^oF) and adding a small amount of H_2 before the hydrogenation vessel. Then all the H_2S is removed in zinc oxide beds (ZnO) following the reaction below:

$$H_2S_{(g)} + ZnO_{(s)} \leftrightarrows ZnS_{(s)} + H_2O$$

It is important to point out that zinc sulfide (ZnS) is a solid waste and therefore the only air SOx emitted is from the NG burned as fuel. This emission is calculated by mass balance in the FUEEM component model assuming that all H_2S is oxidized to SO_2.

$$H_2S + 3/2\ O_2 \leftrightarrows SO_2 + H_2O$$

Superheated steam at 265 to 280 ^oC (510 to 535 ^oF) and 2.41 to 2.65 MPa (350 to 385 psi) is added to the desulphurized feedstock on a steam-to-carbon ratio of between 2.5 to 3.5. This amount of steam that is greater than the stoichiometric amount necessary (2.3 times) is used to minimize thermal cracking and coke formation. An optional pre-reformer may be installed to deal with the coke formation and also to produce an equilibrated mixture of carbon oxides, with methane and hydrogen performing shift and reforming reactions simultaneously. Since the pre-reforming limits the extra-steam generation by using some of the waste heat, other options for the coke formation have been developed like changing the catalyst composition at the end of the reforming tubes using “hydrotalcites” or adding potassium or uranium oxide (Bhattacharya, 1995). Before the pre-reformer the NG/steam mixture is pre-heated to 480 to 510 ^{o}C (900 to 950 ^{o}F) and after it the kind of syngas mixture (20 to 25 % of H_2, 65 to 70 % of CH_4 and traces of C_2H_6) is pre-heated again to 600 to 650 ^{o}C (1110 to 1200 ^{o}F) before it reaches the primary reformer.

After the reformer the hot syngas (870 to 950 ^{o}C or 1600 to 1740 ^{o}F) is cooled down to 340 to 360 ^{o}C (645 to 680 ^{o}F) in preparation for the exothermic shift reaction. A higher reforming temperature increases conversion and better accommodates thermal recovery; however, the severity of the operations requires different reactor metallurgy. The cooling process is done in boilers generating steam from 1.72 to 4.8 MPa (250 to 700 psi) depending of the plant configuration. Extra steam for exportation can be an important co-product of the plant allowing for better integration in the plant design and increasing the overall thermal efficiency.

The next step for the syngas is the high temperature shift reactor (HTS) utilizing iron-based catalyst and operating around 350 ^{o}C (660 ^{o}F). The syngas is cooled down again and the final CO conversion is performed around 205 ^{o}C (400 ^{o}F) in a low temperature shift reactor (LTS) containing a copper-based catalyst. By this time 90 to 95 % of the CO has been “shifted” to CO_2 increasing the hydrogen concentration.

In modern plants the hydrogen purification has changed from CO_2 removal using chemical absorption and methanation processes to pressure swing adsorption (PSA). PSA is a physical separation process based on the capacity of certain solid adsorbents to selectively remove certain components (CH_4, CO_2, CO, etc.) from multi-component gas streams. Activated carbon, carbon molecular sieves, silica gel, activated alumina and zeolites are normally used in the beds (Peramanu *et al*., 1999). PSA units work with up to 12 coupled vessels. While one vessel is adsorbing the components from the hydrogen stream (syngas), the other one is desorbing the components and regenerating the bed by reducing the pressure to about 0.014 to 0.035 MPa (2 to 5 psi) and purging the desorbed gas with some hydrogen. This process generates a pure hydrogen stream (+ 99.8 %) at high pressure since the pressure drop in the system is only approximately 0.07 MPa. On the other hand, since hydrogen is necessary to regenerate the beds, the recovery of it can vary from 65 to 90 % with small variations in the tail gas pressure, making this variable the biggest operational controlling point (Peramanu *et al*., 1999). This high-energy content tail gas is burned in the reformer furnace providing most of the energy necessary to the reforming reactions. The composition of the tail gas varies widely depending on the PSA operational sets. One example of this composition is presented by Spath and Mann (2000):

H_2 (27 % mol), CH_4 (14 % mol), CO (3 % mol), N_2 (0.4 % mol) and some water vapor.

Finally, the burned gas (stack or flue gas) can be treated before vent at the gas waste-heat recovery session. The best available technology for air emissions control in this case is coupling a Selective Catalytic Reduction unit (SCR) with a Continuous Emission Monitoring System (CEMS) that continuously monitors the oxygen concentration, flow rate, temperatures and some emissions to adjust the process. The SCR unit contains catalytic layers including titanium dioxide, tungsten trioxide and others where the injected aqueous ammonia (NH_3) reacts with NO_x to generate inert gases. For example:

$$2/3\ NH_3 + 1/5\ NO_2 \leftrightarrows 7/12\ N_2 + H_2O$$

Other costless options for NOx reduction are the Selective Non-Catalytic Reduction (SNCR) and low-NO_x burners. Even the tail gas recirculation (the uncontrolled situation) will generate less thermal NO_x than a natural gas furnace due to the presence of inert gases and hydrogen in the fuel composition (see Mark *et al*, 1994 and Spath and Mann, 2000).

4.2.2 Data search

The expert discussion initiated with the existing data collected from the literature. Some proprietary data provided to me (the mediator) as support in the discussion are not included in the paper. The following Table 4-4, Table 4-5 and Table 4-6 summarize the survey results of the most comprehensive studies of gaseous hydrogen SMR production plants. Initially the idea was to understand the existing plants (and data) and later forecast the technology (and data) for the 2010 time frame.

An identified source of disagreements over the future plants' data was the size or production capacity of the new facilities. Some experts believe that new plants are going to be much bigger than the existing ones, while others do not. According to Shahani *et al.* (1998) the majority of the existing SMR plant sizes are from 20 to 80 Mscf/d (million standard cubic feet per day) and the largest ones are from 210 to 230 Mscf/d. The plant scale favors thermal efficiency and cost but requires a bigger hydrogen market and that, for certain regions, may not be the case considering the fuel cell vehicle's fuel demand in 2010 or so. Based on that the FEN decided to create two centralized plant size alternatives, a 27 metric tons per day (MTPD) and a 270 MTPD, equivalent to a 30 and 300 MTPD (72 and 720 Mscf/d) operating at 90 % capacity (10 % of the time with operation zero for maintenance, etc.). The sizes were based on Moore and Raman's (1998) report.

Table 4-4: Existing values for centralized hydrogen plants using SMR and no extra-steam produced.

HYDROGEN PRODUCTION SMR – NO EXTRA STEAM	**GREET 1.4** [a]	**GREET 1.5**	**Acurex** [b]	**Ogden** [c]	**DTI** [d]	**Air Products** [e]
Efficiency (%)	68	73	61.1	85/90	69	75 / 77.6
Input energy as electricity (%)	0.2	0.2	0	0	2.9	0.5 / 1.0
NG used as fuel (%)	100	17	52.8	17.6	17	10

a: Wang (1998), only the combustion process is taken into account.

b: Unnasch *et al.* (1996) from Table 5-34, calculated using 100,000 Btu NG/lb H2 for feedstock, 52,830 Btu NG/lb H2 for combustion and 61,100 Btu/lb H2 (HHV). For fuel processing it gives efficiency of 61.1 % that means 61,100 / 100,000. For the boiler (combustion) breakdown 52,830 / 100,000 = 52.8 %. In fact, these numbers do not appear in the report.

c) Ogden *et al.* (1995). On page 11 they talk about 85 % efficiency. From Table 6A-5 it can be calculated as 90 %. The other variables were calculated from the same table using 135 Btu-HHV per gram of H_2 and 50.29 Btu-HHV per gram of NG. The numbers are closer to plants with extra-steam production (see Table 4-5) but no extra-steam appears in table 6A-5. So far, the newest studies being done at Princeton University are still using the same values.

d: From Table D-1 – Thomas *et al* (1998).

e: Patel, Nitin (1999). Personal communication.

Another possible alternative for introducing of hydrogen fuel may be the installation of smaller units at the fuel station for decentralized hydrogen production. Studies done by Thomas *et al.* (1998), Ogden (1999) and Lipman (1999) agree that this alternative can be competitive if the small units are mass-produced. This alternative takes advantage of using the existing NG infrastructure and the production volume of the units can be compared to similar reformers for small stationary fuel cells. There are still some concerns about safety and staff expertise to operate the “small chemical plant” in every fuel station. FUEEM is considering this option with two plant sizes, one with a flow rate of 2.7 MTPD and the other with a flow rate of 1.0 MTPD operating with a catalytic burner.

Table 4-5: Existing values for centralized hydrogen plants using SMR and producing extra steam for exportation.

Studies	Plant size (MTPD)	total effic. (%)	steam energ. (%)
Dybkjar [a]	23.81	85.86	23.78
Greet 1.5a [b]	-	83.0	14.46
Shahani-c1 [c]	120	80.9	6.66
Shahani-c2 [c]	120	85.1	24.27
Shahani-c3 [c]	120	86.8	30.44
Patel -H-N2 [d]	60	86.4	7.25
Patel - L-N2 [d]	60	85.2	7.28
NREL-2000 [e]	136.8	89.0	7.91

a: In Wang (2000)
b: Wang (2000) in low heating values.
c: Shahani *et al.* (1998). c1 = basic case, c2 and C3 = case 2 and 3.
d: Patel *et al.* (1994). L-N2 = typical natural gas composition and H-N2 = high amount of nitrogen in the NG composition
e: Spath and Mann (2000). According to the authors 198.041 MBtu of exported steam per hour was used.

Table 4-6: Existing values for decentralized hydrogen plants (small units for fuel stations)

HYDROGEN PRODUCTION SMR – DECENTRALIZED	**Air Products**	**Praxair**	**BOC**	**Praxair**	**BOC**
Size (MTPD)	2.72	2.72	1.36	0.45	0.18
Efficiency (%)	66.6	70.5	64.3	69.3	77.6
Input energy as electricity (%)	0.7	2.4	0	3.4	0
NG used as fuel (%)	17.1	-	13.6	-	2.5

source: Thomas *et al.* (1998).

The Environmental Protection Agency (EPA) is the American organization that has access to most of the equipment emission measurements and they provide a compilation of emission factors per level of equipment activity (EPA-AP42, 1995).

Unfortunately, the report provides only the factor (perhaps the mean) and a letter rating the reliability, or robustness, of the factor that has no statistical meaning. Particularly, in the hydrogen production case, no emission factor is provided, and what most of the studies did was to use the emission factors from natural gas boilers and somehow scale them down (mainly thermal NO_x) compensating for the inclusion of the PSA tail gas in the fuel composition. Table 4-7 presents the values. Van Der Drift (1996) reports NO_x emissions from burners operating with a mixture of hydrogen and methane but the composition of the mixture has an always-high hydrogen content (~ 80 %). To complicate this lack of data the AP-42 report (1995) provides burner emission factors for uncontrolled equipments only and special care must be taken to adjust the data for the inclusion of emission control devices such as low-NO_x burners or SCRs.

Agreements as to the technologies assumed are very important and they are not always clearly stated in the reports for purposes of future comparison. FUEEM assumes three levels of air control technologies to be selected according to the area's air quality enforcement. A plant in a high-control area may use SCR, CEMS and low-NO_x burners. For an intermediate-control area the plant may only use SNCR and low-NO_x burners. Finally, an uncontrolled option is available for areas with lack of enforcement. The most controlled option was defined first and the others were scaled based on expert experience and, in some, values provided by the report EIIP (1998). The report presents the emission reduction level when a utility emission control is used. For a SCR (gas) NO_x is reduced by 80 % related to the uncontrolled equipment, CO by 8 % and N_2O by 60 %. The report also presents the efficiency loss as a percentage of the total efficiency due to the addition of the emission control technology. For the SCR the loss is 1 % and this has been incorporated into FUEEM energy requirement calculations.

Table 4-7: Reformer Emission rates assumed by existing models to calculate the emissions of hydrogen production plants

EMISSION RATE **(g/MBtu-NG burned -HHV)**	Acurex [a]	Mark *et al* [b]	Greet 1.4 [c]	Greet 1.5 [c]	NREL [d]
NO_x	45.44	31.75	23.339	35.19	58.6
CO	15.90	15.42	17.614	36.99	5.42
CH_4	1.33	-	0.128	0.99	0
NMOG	1.33	1.22	0.617	2.43	0
PM 10	-	-	1.321	3.33	1.48
SO_x	-	-	0.278	0.278	0
N_2O	-	-	0.189	0.99	0

a: From EFAC9.XLS (Unnasch *et al*., 1996). The numbers were calculated using H2 density of 0.53 lb/100scf and energy content of 32,400 Btu/100scf (HHV). Process efficiencies of 61.1 % and 52.8 % of energy share of NG combusted are used in the calculation also. The numbers in the report (grams of pollutant per lb of H2) are: NOx (2.4 g); CO (0.84 g); CH4 (0.07 g), and NMOG (0.07 g).

b: Mark *et al.* (1994) the original values are in terms of lb per MBtu of fuel burned. The values 0.07 (NO_x), 0.034 (CO) and 0.0027 (NMOG) are assumptions based on the 1993 version of the AP-42 (1995) for NG combustion. The tail gas was considered to scale down the emission factors in terms of the amount of NG burned as fuel.

c: Wang (1998 and 2000). The emission factors are related to future devices and they are converted to HHV using the factor of 90%. The model considers industrial boiler emission factors in terms of NG burned as fuel.

d: Spath and Mann (2000). Apparently the plant only uses low NO_x burners as an emission control device. The numbers in the report are 0.084 g of CO/Kg of H_2, 0.023 g of PM_{10}/Kg of H_2, 20 ppm of NO_x translated into 0.9072 g/Kg of H2 (Table 4), 8,892.2 g of CO_2/Kg of H_2 and zero for CH_4, N_2O, NMOG and SO_x (Table 4). The factors used in the transformation were 127 Mg of H_2/day and 82 MBtu of NG_{fuel}/hr.

4.2.3 Industry survey

The emission factors and equipment activities values, such as efficiency, must encompass the variations of technologies that naturally occur in reality even when some boundaries are delineated. Two very similar plants can operate at different PSA outlet pressures, different maintenance levels, catalysts compositions, etc. Therefore, the establishment of these emission factors must be performed by organizations such as EPA that for mandatory reasons already have a great deal of data. One of the objectives of the FUEEM project is also to sensitize such data-collector organizations to for the importance of and need for better and more complete outputs.

The FUEEM project does not have enough resources to generate these factors properly even though I decided to realize a survey in an industry to contribute to the general data collection process and to provide some input for the expert panel discussion. In the hydrogen case the main reasons for the industry survey were: the lack of emission data on hydrogen reformers and the rough and somewhat subjective solution adopted so far; the necessity of investigating eventual correlations among variables since the FUEEM calculus is not deterministic; and the expert interest in investigating the shape of some probabilistic curves since this type of data discussion was new for most of them.

The investigated hydrogen plant has a production capacity close to the 27 MTPD alternative and extra-steam exportation. Data was collected for two different months. One month was in winter (December, 1999) and the other was in summer (May, 2000). An existing continuous emission monitoring system (CEMS) reports the NO_x and CO emissions hourly, and also information about plant activities such as natural gas consumed, natural gas energy content (HHV), amount and energy content of the steam imported and exported, amount of hydrogen produced, etc. was collected daily.

One interesting occurrence was the variation in the NG composition between the two sets of data. In winter the plant used around 10 Mscf (Million standard cubic feet) per day of an available NG with a high level of nitrogen and therefore lower energy content. Since the mean of the plant total efficiency (energy out/energy in) was slightly different (83.37 % and 83.89 %) a graphical correlation study was done to generate an example of the envelop-method proposed by Vose (1996). Figure 4-4 shows the study.

The expert efficiency values for the 2010 plant alternatives were generated in terms of triangular distribution curves. The minimum, most probable, and maximum values in the triangular curves are established in the FUEEM calculus after the NG composition is sampled and the energy content of it is calculated. Lines having the same slope as the lines presented in Figure 4-4 with the origins adjusted to match the expert efficiencies consensus define the input curves. The origins values assumed are presented in Table 4-8. The NG energy content is calculated according to the method proposed by Van der Lugt (1986) considering non-ideal gas relations. The components summation factors necessary for the compressibility factor calculation in the method were assumed to be the same ones proposed by the author.

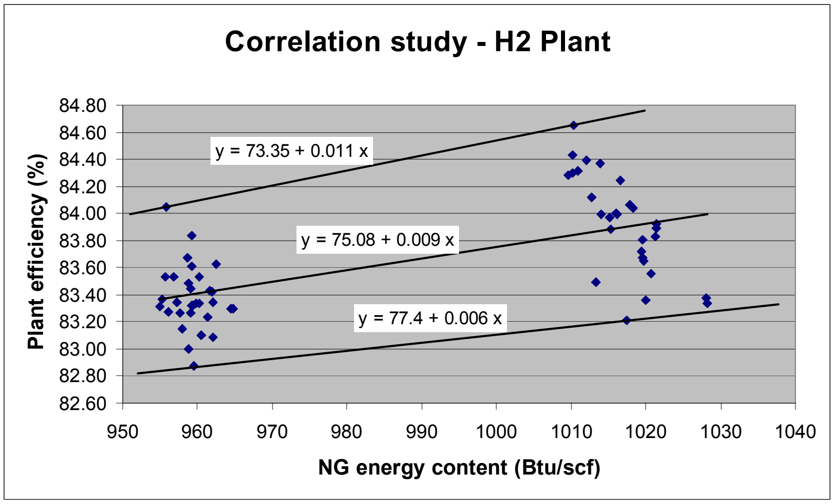


Figure 4-4: Correlation study between hydrogen plant efficiency and utilized NG energy content (HHV).

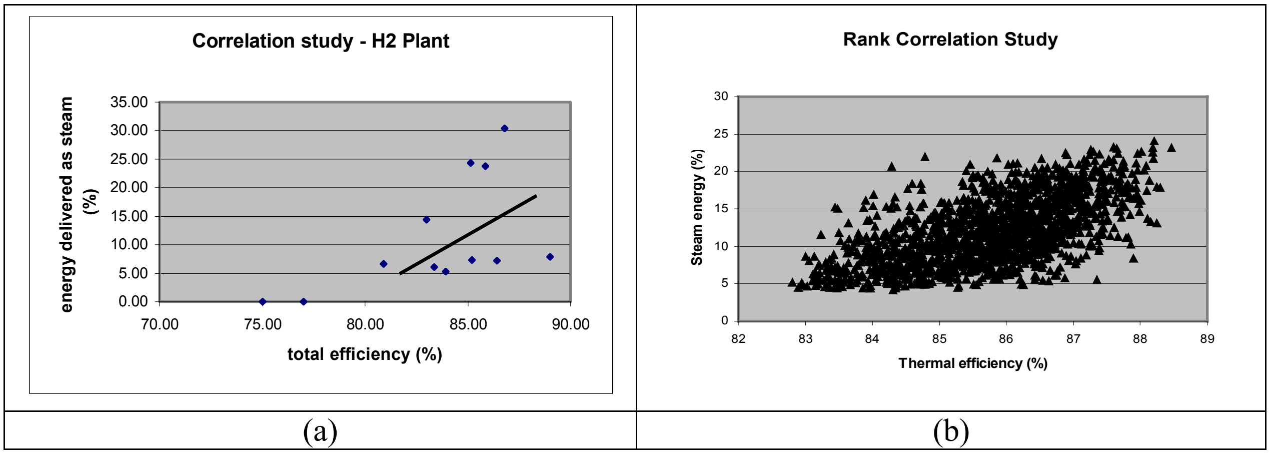
A Natural Gas composition study was completed to understand the variations of the gas in different regions and it is important to point out that from that study two NG gas composition curves were adopted in this component model, one called typical NG with the energy content mean of 37,738 KJ/m^3 (1013 Btu/scf) and standard deviation of 359.3 (9.64), and the other with a higher content of N_2 and an energy content mean of 34,720 KJ/m^3 (931 Btu/scf) and standard deviation of 342.9 (9.20).

Table 4-8: Origin of the lines used for the efficiency calculation

Plant configuration		Line origens		
size (MTPD)	extra-steam	minimum	most probable	maximum
270	yes	79.19	78.50	77.70
270	no	68.19	67.89	67.70
27	yes	76.71	77.08	79.19
27	no	66.19	65.99	65.70
2.7	no	59.19	58.09	58.70
1.0	no	57.09	55.99	56.60

Another interesting occurrence was the modification in the PSA operational parameters (among others parameters) to produce more or less steam. In winter an average of 6 % of the total energy produced was steam, while in summer this figure was 5.3 % on average. Based on that we decided to investigate the correlation between the extra-steam produced and the plant efficiency. After an interview with the engineers it was clear that not only does the efficiency change by manipulating the steam production, but also, more importantly, the designs of the plants are different for different steam production capacities because the manipulation of the operational parameters in a plant is, in general, limited. Spath and Mann (2000) state, “The hydrogen plant efficiency changes if the excess steam can not be utilized by a nearby source. However, this does not change the amount of hydrogen produced by the plant,” but this is not correct. It assumes that first a plant is built and then the extra-steam is offered to the market, but in reality if the market does not already exist the plant design will be different. Shahani *et al.* (1998) are clear on this point.

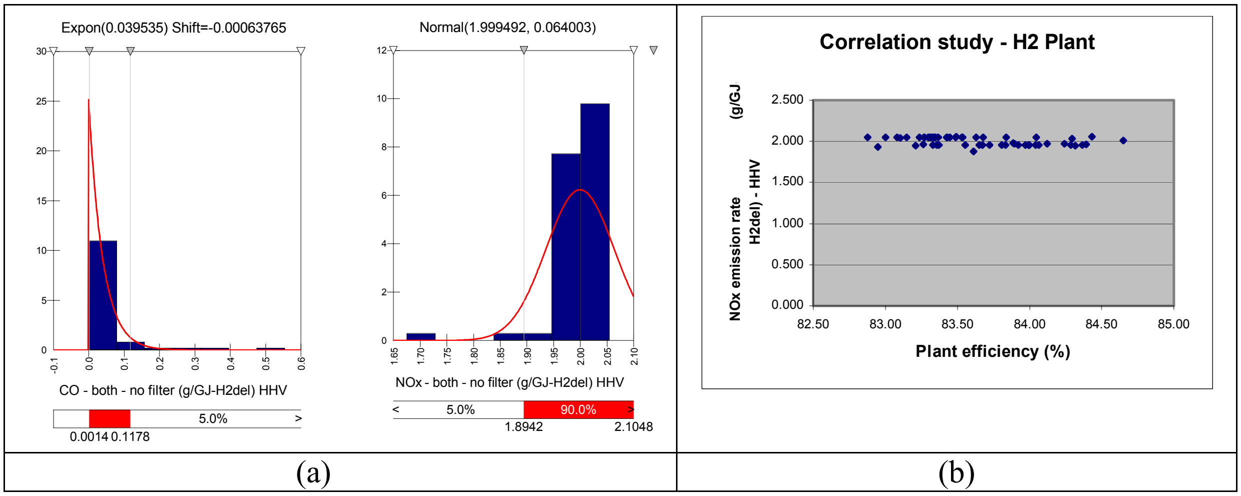
Trying to solve this correlation problem, the Table 4-5 data, complemented with the industry survey results (seasons average data), were used to generate Figure 4-5a. A necessary decision was to accept or not the correlation and it was clear that much more data would be necessary for a reasonable level of confidence. However, based on the engineers position we decided to accept it. As an example we decided to use in this case the rank order correlation method developed by Iman and Conover (1982) that is already developed into the software utilized. Based on that, a discussion was held to establish the right rank coefficient to use in the model since it is not an intuitive task. Several rank coefficients were tested and the graphics were analyzed by the experts to come up with the assumption of 0.6. Figure 4-5b shows the sampling values of the first 2000 interactions.



(a) (b)

Figure 4-5: Rank order correlation study between the extra-steam produced by a hydrogen plant and its total thermal efficiency.

By changing the operational parameters of the PSA, the tail gas composition varies and therefore the amount of NG necessary to be used as a fuel varies too. When the emission factors are based on the amount of NG burned as fuel such as in Wang (2000) and Mark *et al*. (1994) this variable becomes an important input. From the existing literature one can find values from 10 % to 18 % (Table 4-4), but in this industry survey values as low as 3 % were found and therefore coupling the emissions with the NG fuel variable was not a good solution because it would incorporate a huge uncertainty and a correlation with the efficiency through the extra-steam. The emissions were coupled with the amount of hydrogen produced and also some amount of the emissions was attributed to the extra-steam generated according to the energy content on both products. Since FUEEM is dealing mainly with fuels, the co-products credits based on the energy content (HHV) were adopted as the single method to use. Figure 4-6a shows the CO and NO_x emissions of the hydrogen plant in the survey and the data present no correlation with the plant efficiency. Figure 4-6b shows one example of this.



(a) (b)

Figure 4-6: CO and NOx emission rates from hydrogen production plant (HHV)

Finally, most of the existing studies assume the fugitive emissions in the plant to be natural gas or sometimes methane only. Trying to improve this assumption somewhat, some percentage of the fugitive emissions was assumed as syngas based on a study of the pipe lengths, valves, flanges, etc. carrying syngas and NG. It assumed a normal curve with a mean of 0.125 % of NG leaking per NG used (std. dv. = 0.065) and 0.291 % of syngas leaking per NG used (std. dv. = 0.15), assuming the conversion of approximately 0.228 moles of syngas per mol of NG.

4.2.4 FUEEM inputs

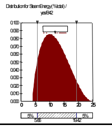
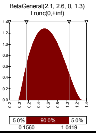
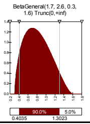
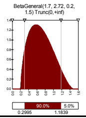
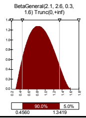
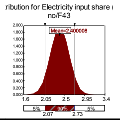
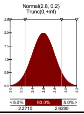
Other major inputs are discussed in this session. The emission rates for the reformer in a high controlled area are presented in the results since they were assumed in terms of grams of pollutants per Giga Joule of hydrogen produced. For the intermediate air control enforcement area alternative NO_x is assumed to be reduced 50 % of the uncontrolled scenario, CO reduced 4 % of the uncontrolled scenario, and N_2O reduced 30 %. For the small-decentralized plant there are some uncertainties related to the constant steady state operation of the plant. A CARB report (Unnasch and Drunert (1999)) analyzes some vehicle reformer emissions and the majority of the emissions occur in the start up regime. Based on that and on the fact that there are some uncertainties about the kind of air control technology that should be used in the small-decentralized plants, the intermediate scenario was assumed.

Table 4-9 presents the inputs related with the extra-steam produced and electricity share adopted.

4.2.5 Results

As stated before the objective of this component model is to calculate the energy requirement and emissions generated by hydrogen plant alternatives. Table 4-10 presents the natural gas (NG) requirements and electricity requirements for all alternatives. In Table 4-11 the reformer and fugitive emissions are presented for the 27 MTPD plant, which produces extra-steam and uses a typical NG composition. Finally, in Table 4-12 the results for the 1.0 MTPD decentralized plant are presented.

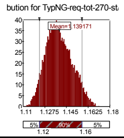
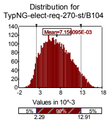
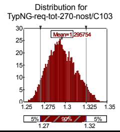
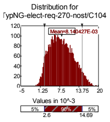
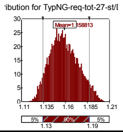
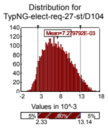
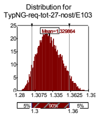
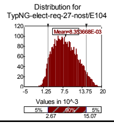
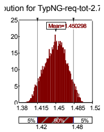
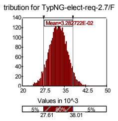
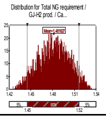
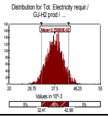
Table 4-9 : Other major inputs for the energy requirement in hydrogen plants.

Variable	Units	Min/Max (90 % conf.)	Mode	Mean	Curve Shape
Extra-steam	%	5.66 / 19.42	9.88	11.88	
Electricity share 270 MTPD - steam	%	0.15 / 1.04	0.53	0.58	
Electricity share 270 MTPD – no steam	%	0.4 / 1.3	0.69	0.81	
Electricity share 27 MTPD - steam	%	0.3 / 1.18	0.58	0.7	
Electricity share 27 MTPD – no steam	%	0.46 / 1.34	0.83	0.88	
Electricity share 2.7 MTPD	%	2.07 / 2.73	2.4	2.4	
Electricity share 1.0 MTPD	%	2.27 / 2.93	2.6	2.6	

At the component level the emissions and energy requirement associated with the natural gas life cycle activities and with the electricity life cycle activities are not included yet. It makes the comparison with other studies somewhat more difficult because some reports present their numbers only at aggregated levels (including all activities from the "well to the plant"), especially the fugitive emissions. However, some conclusions can be reached considering the plant efficiency, the amount of NG used as fuel, the emission factors used in other models (e.g., Greet 1.5a (2000), Acurex (1996) and NREL (2000)) and the appropriate unit conversions. The factors used to convert other model results are:

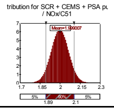
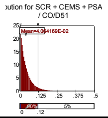
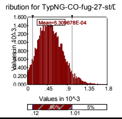
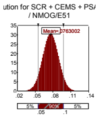
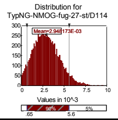
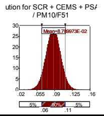
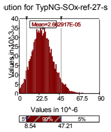
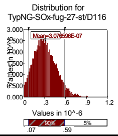
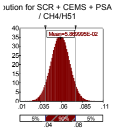
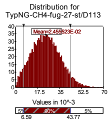
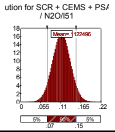
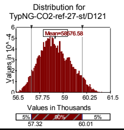
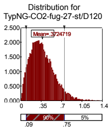
- 0.2389 MBtu of NG consumed as a fuel per MBtu of hydrogen produced by the plant (with steam exportation) in Greet 1.5a (2000),
- 15.505 lb per GJ of hydrogen to transform Acurex (1996) numbers, and
- 142 MJ per kg of hydrogen in the NREL (2000) data.

Table 4-10: Fuel requirements of hydrogen plants using typical NG composition (GJ_{fuel} / $GJ_{H2\text{-}produced}$ - HHV)

Plant Characteristics	Total NG requirement				Total Electricity requirement **(x 10^{-3})**			
	Min / Max[a]	Mode	Mean	Shape	Min / Max[a]	Mode	Mean	Shape
270 MTPD extra-steam	1.12 / 1.16	1.128	1.135		2.29 / 12.91	4.2	5.1	
270 MTPD no extra-steam	1.27 / 1.32	1.278	1.286		2.6 / 14.69	6.1	8.9	
27 MTPD extra-steam	1.13 / 1.19	1.124	1.153		2.33 / 13.14	3.9	6.6	
27 MTPD no extra-steam	1.30 / 1.36	1.285	1.319		2.67 / 15.07	9.3	10.0	
2.7 MTPD decentralized	1.42 / 1.48	1.427	1.439		27.6 / 38.0	33.2	33.4	
1.0 MTPD decentralized	1.45 / 1.52	1.486	1.482		32.4 / 42.9	37.6	37.5	

a: At 90 % confidence.

Table 4-11: Calculated emissions for a 27 MTPD hydrogen plant with extra steam exportation and typical natural gas used (grams / GJ-$H_{2\text{-produced}}$ - HHV)

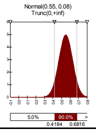
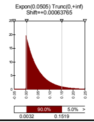
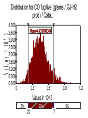
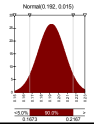
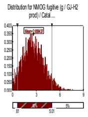
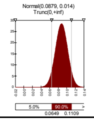
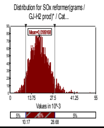
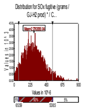
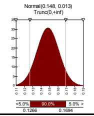
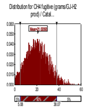
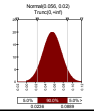
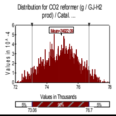
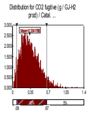
Pollutants	Reformer emissions				Fugitive emissions			
	Min / Max[a]	Mode	Mean	Shape	Min / Max[a]	Mode	Mean	Shape
NO_x	1.89 / 2.10	2.00	2.00		-	-	-	-
CO	0.003 / 0.12	0.004	0.0008		0.12 / 1.01 x 10^{-3}	0.50 x 10^{-3}	0.53 x 10^{-3}	
NMOG	0.05 / 0.10	0.076	0.076		0.65 / 5.6	2.21	2.95	
PM_{10}	0.16 / 0.21	0.187	0.188		-	-	-	-
SO_x	8.5 x 10^{-3} / 47.2 x 10^{-3}	19 x 10^{-3}	26 x 10^{-3}		0.00007 / 0.00059	0.16 x 10^{-3}	0.31 x 10^{-3}	
CH_4	0.14 / 0.18	0.158	0.159		5.42 / 42.7	24.6	23.3	
N_2O	0.07 / 0.15	0.113	0.112		-	-	-	-
CO_2	57321 / 60015	58363	58577		0.09 / 0.74	0.32	0.37	

a: At 90 % confidence.

* To transform to lb/MBtu multiply by 2.326 x 10^{-3}

The conclusions of the analysis are, first, Acurex (1996) greatly overestimates all the reformer emissions. It looks as though an external calculation was previously done, including the fugitive emissions in the reformer emission rates. However, checking the fugitive emission results (Table 4-11) we could see that this was not the case because NMOG and especially CH_4 emissions should be higher and not the NO_x and CO.

Table 4-12: Calculated emissions for a 1 MTPD decentralized hydrogen plant with catalytic burner, SCR and typical natural gas used (grams / GJ-$H_{2\text{-produced}}$ - HHV)

Pollutants	Reformer emissions				Fugitive emissions			
	Min / Max[a]	Mode	Mean	Shape	Min / Max[a]	Mode	Mean	Shape
NO_x	0.42 / 0.68	0.55	0.55		-	-	-	-
CO	0.003 / 0.152	0.003	0.05		0.22 / 0.70 x 10^{-3}	0.42 x 10^{-3}	0.44 x 10^{-3}	
NMOG	0.17 / 0.22	0.19	0.19		0.61 / 5.01	2.50	2.66	
PM_{10}	0.06 / 0.11	0.09	0.09		-	-	-	-
SO_x	0.0102 / 0.0287	0.020	0.019		0.0007 / 0.00054	0.003	0.002	
CH_4	0.13 / 0.17	0.15	0.15		5.08 / 38.1	18.4	21.0	
N_2O	0.02 / 0.08	0.06	0.06		-	-	-	-
CO_2	73060 / 76070	75037	74922		0.08 / 0.67	0.30	0.33	

a: At 90 % confidence.

* To transform to lb/MBtu multiply by 2.326 x 10^{-3}

Based on the industry survey FUEEM assumes smaller emission rates for NO_x (1.9 to 2.1 g/GJ-H_2 in this study versus 8.0 and 6.4 g/GJ-H_2 for Greet 1.5a (2000) and NREL (2000) respectively) indicating that more measurements would be necessary than just extrapolating the data from NG boilers. A similar conclusion can be reached for CO where very few emissions were found in the industrial survey. While our maximum value is 0.12 g of CO/GJ-H_2 with a very small probability to occur, the NREL (2000) value is 0.59 g/GJ-H_2 and the Greet (2000) value is 8.4 g/GJ-H_2.

On the other hand, for NMOG and especially for CH_4 the fugitive emissions that are an important parameter, where apparently not considered by NREL (2000) and Acurex (1996). The small differences in CO_2 emissions are mainly due to the differences in the assumed efficiencies.

4.3 Liquid Fuels Marketing Activities

The major benefits of liquid fuels are the higher energy density compared to gaseous fuels and the relative ease with which one can transport and store them. The benefits in the transportation and storage of liquid methanol and Fisher-Tropsch Naphtha (FTN) qualify them as possible hydrogen carrier fuels for FCVs. The rationale for marketing these liquid fuels closely parallels that for gasoline. Since most of the data and studies available in this area are related to gasoline, the strategy adopted was to assess the figures for gasoline and then extrapolate them to the other liquid fuels. The details of this extrapolation are explained in the sections below, but basically it uses the fuel vapor pressure differences together with the fuel densities and energy content differences. From the existing fuel life cycle studies in the literature only Unnasch *et al*. (1996) has the level of detail used in the FUEEM calculation and therefore most of comparison is done using it.

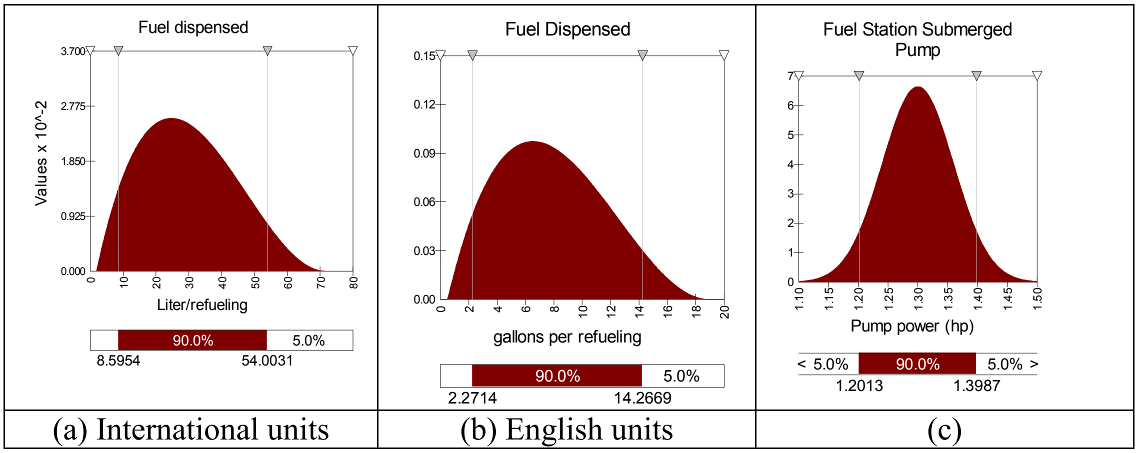
4.3.1 Retail Activities

4.3.1.1 Vehicle refueling:

This study assumes the boundary of the fuel upstream activities as the vehicle refueling process. This activity consumes some electricity to pump the fuel from the fuel station storage tank, in general an underground tank, into the vehicle tank. The air emissions associated with the vehicle refueling process are the ones related to the displacement of the fuel vapor in the vehicle tank and the ones evaporated from eventual fuel spillage and retention of the fuel in the nozzle. Evaporative emissions from the vehicle tank other than at the refueling process should be considered at the vehicle operation activity.

Part of the refueling emissions, such as spillage and nozzle retention, are related to the frequency of the activity and in some sense to the vehicle range design. According Unnasch (1996) the average gasoline fill-up in the US is 8.8 gallons but the range is from 1/2 to 18 gallons. In his study he assumes 9.0 gallons for gasoline and 15 gallons for methanol. In a subsequent study (Unnasch, 2000) he assumes 9.0 gallons for methanol as well. In the FUEEM discussion one of the companies (called here Company A) presented an internal study done in 1999. The assumption in that study was 10 gallons as the average for gasoline refueling. A study done by API (1989) observed more than 2,500 vehicle refuelings looking into conventional systems (without any kind of emission control) in the Baltimore area and systems equipped with balance recovering devices (Stage 2 facilities, in the EPA denomination) in the District of Columbia. In both cases they found a bi-modal curve with one mode about 5 gallons and the other one about 9 gallons. The average refueling in the District of Columbia was 7.8 gallons and in the Baltimore metropolitan area was 8.6 gallons. For passenger cars in 2010 the FUEEM experts decided to assume a single mode curve, since the methodology developed for the Monte Carlo simulation does not support a bi-modal one. The shape of the curve is based on the Baltimore data (Fig 3-5 of the API report) assuming that more efficient future vehicles may use smaller tanks to have more space available for the FC system. The assumed probabilistic curve is a Beta General distribution with a minimum of 0.5 gallons (1.89 L) and maximum of 19 gallons (71.9 L) using α_1 equal to 2.00 and α_2 equal to 3.07. The probabilistic curve is presented in Figure 4-7(a and b) and it is important to point out again that for a 90 % confidence level (the level considered in the study) the 5 %

percentile (minimum) is 2.27 gal. (8.6 L) and the 95 % percentile (maximum) is 14.27 gal (54.0 L).



(a) International units

(b) English units

(c)

Figure 4-7: First set of assumptions for the vehicle refueling calculation

The energy requirement at the fuel station (ER_{FSP}) for the refueling process (pump) is calculated by the following Equation 4-3:

Equation 4-3:
$$ER_{FSP} = \frac{PP}{FR}$$

where,

PP is the submerged pump power in terms of horsepower (hp) converted to Btu/min by using the factor of 42.42. The assumed curve is a normal distribution with mean equal to 1.3 hp (970 W) and standard deviation of 0.06 (see Figure 4-7c), and

FR is the fuel flow rate in terms of gal/min (or L/min) that is calculated by using Equation 4-4.

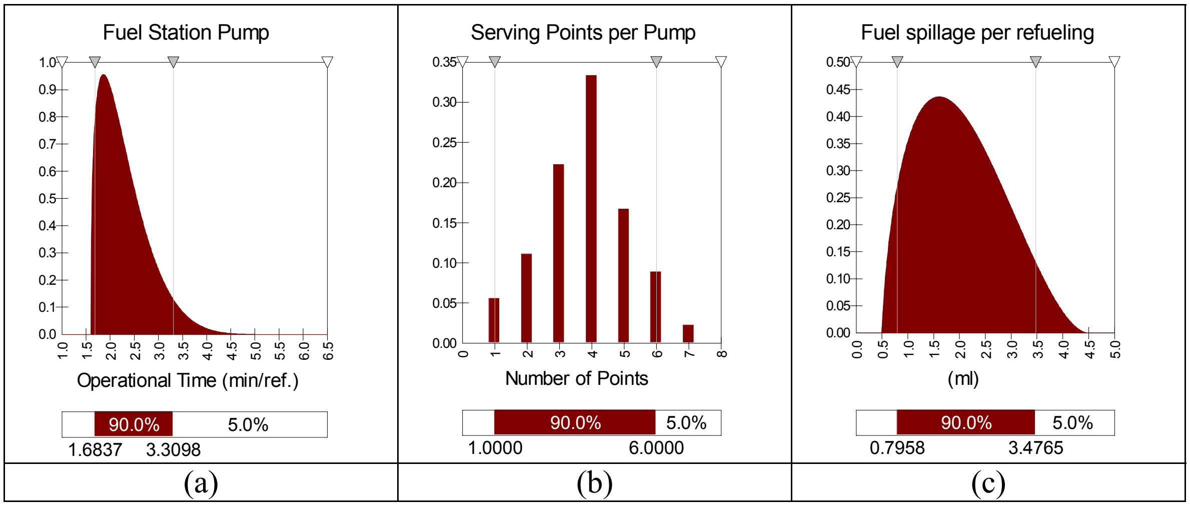
Equation 4-4:
$$FR = \frac{Fd}{OpT} \cdot Sp$$

where,

Fd is the fuel dispensed per refueling, according to the discussion above, *OpT* is the operational time of the pump (minutes) per refueling. The pump starts to work when the serving point is selected. The assumed probabilistic curve is a Beta General distribution with a minimum of 1.6 min. and maximum of 6 min. using α_1 equal to 1.4 and α_2 equal to 7.4. The probabilistic curve is presented in Figure 4-8a. A positive rank correlation factor between *Opt* and *Fd* is assumed (see section 4.7). And,

Sp is the serving points per pump, since each pump is used to delivered fuel for multiple points within the fuel station. A discrete function is assumed and presented in Figure 4-8b.

Primary emissions in the vehicle refueling activities are mainly fugitive NMOG associated with the fuel evaporation that can occur from eventual fuel spills, from the amount of fuel remaining at the nozzle (making it wet) and from the fuel vapor in the vehicle tank that is forced out when the new fuel is added.



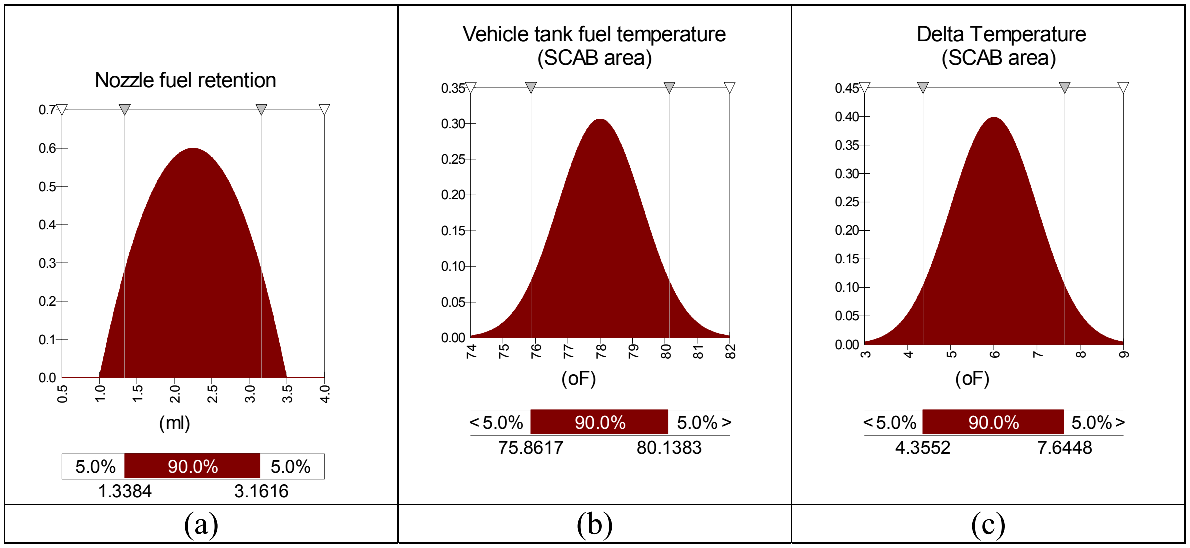
(a) (b) (c)

Figure 4-8: Second set of assumptions for the vehicle refueling calculation

For the emissions associated with spills, the Company A study assumed 3.20 ml of gasoline spilled per refueling, which translates into 2.30 grams per refueling and 60.8

mg per liter of gasoline refueled (or 0.51 lb/1000 gallon). The California Air Resource Board (CARB) and Unnasch *et al*. (1996) use 83.9 mg/L or 0.70 lb/1000 gal based on Asregadoo (1992). For the Unnasch study it translates into 2.86 grams per refueling or 3.97 ml of gasoline per refueling. This study also assumes for future scenarios 0.42 lb/1000 gal and 0.31 lb/1000 lb based on Morgester (1992) that measured 0.42 lb/1000 gal and probably on the API (1989) that measured the value of 0.2 lb/1000 gal. The value assumed by EPA in the AP-42 (1995) is 0.67 lb/1000 gal or 80.0 mg/L. Another EPA study (EIIP, 1997) uses the same values as the AP-42 (1995) and therefore is not going to be quoted here. The FUEEM assumption for the year 2010 is a Beta General curve with a mean of 2.0 ml/refueling. The curve showed in Figure 4-8c uses the minimum of 0.5 and the maximum of 4.5 with α_1 equal to 1.7 and α_2 equal to 2.83. The shape of the curve is based on the API (1989) study. Based on the fuel dispensed per refueling and on the fuel density assumed, the mean of the resulting is 48.8 mg/L or 0.41 lb/1000 gal for gasoline. For methanol it is 53.9 mg/L (0.45 lb/1000 gal) and for Fisher Tropsch Naphtha it is 46.8 mg/L (0.39 lb/1000 gal). For the assumed fuel density curves see section 4.5.4.

The nozzle fuel retention is a section that needs more investigation in the future. The Company A study assumes the retention of 3.5 ml of gasoline per refueling, translating into 66.49 mg/L or 0.55 lb/1000 gal of gasoline dispensed. The FUEEM expert network decided to assume a Beta General curve with the minimum of 1.0 and the maximum of 3.5 with α_1 equal to 2.0 and α_2 equal to 2.0. The curve is presented in Figure 4-9a and it has a mean of 2.25 ml/refueling. According to the fuel characteristics it translates into a curve with a mean of 54.8 mg/L (0.46 lb/1000 gal) for gasoline, 60.6 mg/L (0.51 lb/1000 gal) for methanol and 52.6 mg/L (0.44 lb/1000 gal) for FTN.



(a) (b) (c)

Figure 4-9: Third set of assumptions for the vehicle refueling calculation

For the vapors displaced from the vehicle tank by the fuel displaced without any control system, the CARB emission factor is 1198 mg per liter of gasoline or 10 lb/1000 gal (Asregadoo, 1992). The EPA-AP-42 (1995) average emission factor for uncontrolled refueling is 1320 mg/L or 11 lb/1000 gal. In fact, the EPA presents a formula that allows one to calculate the uncontrolled refueling emission (E_R) based on the fuel composition and temperature. FUEEM adopts the EPA method expressed in the Equation 4-5:

Equation 4-5: $$E_R = 264.2[(-5.909) - 0.0949(\Delta T) + 0.0884(T_D) + 0.485(RVP)]$$

where:

E_R = mg/L

T_D = temperature of dispensed fuel, ^{o}F

ΔT = difference between temperature of fuel in vehicle tank and temperature of dispensed fuel, ^{o}F

RVP = Reid Vapor Pressure, psia

The temperature is associated with the local characteristics and can differ greatly from region to region. The default value for calculation in the EPA-AP-42 (1995) is 80 ^{o}F (26.7 ^{o}C) for the fuel in the vehicle tank and a temperature of 75 ^{o}F (23.9 ^{o}C) for the fuel dispensed (ΔT = 5 ^{o}F or 2.8 ^{o}C). CARB assumes the same ΔT as the AP-42 but 76 ^{o}F (24.4 ^{o}C) for the fuel in the vehicle tank (Asregadoo, 1992); Unnasch *et al*. (1996) assume 80 ^{o}F (26.7 ^{o}C) for the fuel in the vehicle tank temperature and a ΔT of 10 ^{o}F (5.6 ^{o}C) for the Los Angeles area (SCAB) analyzed. For the same local area (SCAB) FUEEM assumes for the fuel temperature at the vehicle tank a normal distribution curve with a mean of 78 ^{o}F (25.6 ^{o}C) and standard deviation of 1.3 ^{o}F (0.7 ^{o}C). The curve is presented in Figure 4-9b. For the difference between temperature of fuel in vehicle tank and temperature of dispensed fuel (ΔT) FUEEM assumes a normal distribution curve with mean of 3.3 ^{o}F (25.6 ^{o}C) and standard deviation of 1.0 ^{o}F (0.6 ^{o}C). The ΔT curve is presented at the Figure 4-9c. It is important to point out that the environmental analysis tends to be conservative and, in this case, it always focuses on summer time when the evaporative emissions of hydrocarbons are greater and the secondary formation of ozone due to the sunlight exposure tends to be critical.

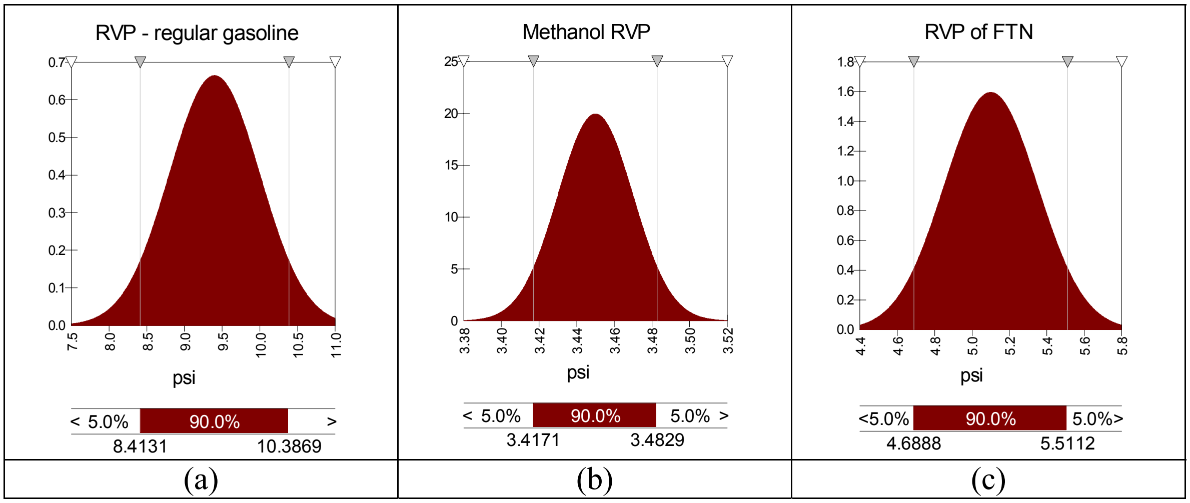
The Reid Vapor Pressure (RVP) is a special means to measure the fuel vapor pressure trying to represent how quickly fuel evaporates. The following definition (Reid Method) can be found in the D323-99a Standard Test Method for Vapor Pressure of Petroleum Products (ASTM - AMERICAN SOCIETY FOR TESTING AND MATERIALS, 2001): “Because the external atmospheric pressure is counteracted by the atmospheric pressure initially present in the vapor chamber, the Reid vapor pressure is an absolute pressure at 37.8°C (100°F) in kilopascals (pounds-force per square inch). The

Reid vapor pressure differs from the true vapor pressure of the sample due to some small sample vaporization and the presence of water vapor and air in the confined space."

According to the EPA-AP-42 (1995), the RVP of gasoline can range from 7.0 to 13.0 psi depending on the composition. In fact, in some states such as California there is a mandatory requirement to reduce the RVP of the "summer gasoline" to reduce evaporative emissions in the critical air quality period. This "controlled" gasoline is, in general, called reformulated gasoline. For regular gasoline AP-42 assumes the RVP of 10 psi for their default calculation and CARB assumes 9.2 psi (in Unnasch *et al.*, 1996). Unnasch *et al.* (1996) assume for reformulated gasoline in the Los Angeles area the RVP of 8.4 (Table 5-44). At this point FUEEM does not intent to analyze the gasoline pathway; however, it uses a regular gasoline calculation to serve as a reference and for checking parameters of the model. This calculation option remains in the model but for future analysis of gasoline it is suggested that one check the RVP data for the analyzed area under study and change the values in the model, especially for the controlled gasoline case not discussed here. Figure 4-10a shows the curve assumed for the regular gasoline case.

For the methanol RVP, Unnasch *et al*. (1996) assume incorrect values, probably based on the true vapor pressure. They use 4.63 psi in table 5-39 and 4.5 psi in table 5-44. This same value was used again in table 4-28 of Unnasch *et al*. (2000). A similar problem can be found in the World Bank (1996) report that uses 4.6 psi. Methanol RVP assumed in FUEEM is a normal distribution curve with a mean of 3.45 psi and standard deviation of 0.02 psi. With 90 % confidence the range goes from 3.42 to 3.48 psi (see Figure 4-10b). This assumption is consistent with the Methanex Responsible Care (1997) file where the value used is 3.4 psi and it is also consistent with the California Energy Commission value of 3.5 psi used in table VII.D.2 of their report (CEC, 1996).

The assumed RVP for the Fisher-Tropsch Naphtha (FTN) is presented in Figure 4-10c. It is based on the established FTN composition (see section 4.4.3) and the vapor pressure values presented in chapter 7 of the EPA-AP-42 (1996).



(a) (b) (c)

Figure 4-10: Fuel Reid Vapor Pressures used for the evaporative emission calculations.

To control the vehicle tank vapor displacement emission, special nozzles at the service station pump and special hoses at the vehicle tank pipe can be installed in such a way that the fuel vapor at the vehicle tank can be transferred back to the fuel station storage tank at the same time the fuel is displaced (Figure 4-11a).

The so-called EPA Stage II control can use an “in balance” system where the natural pressure differential is responsible for the vapor transfer, or a “vacuum assisted” system using a vacuum pump to force the vapor transfer.

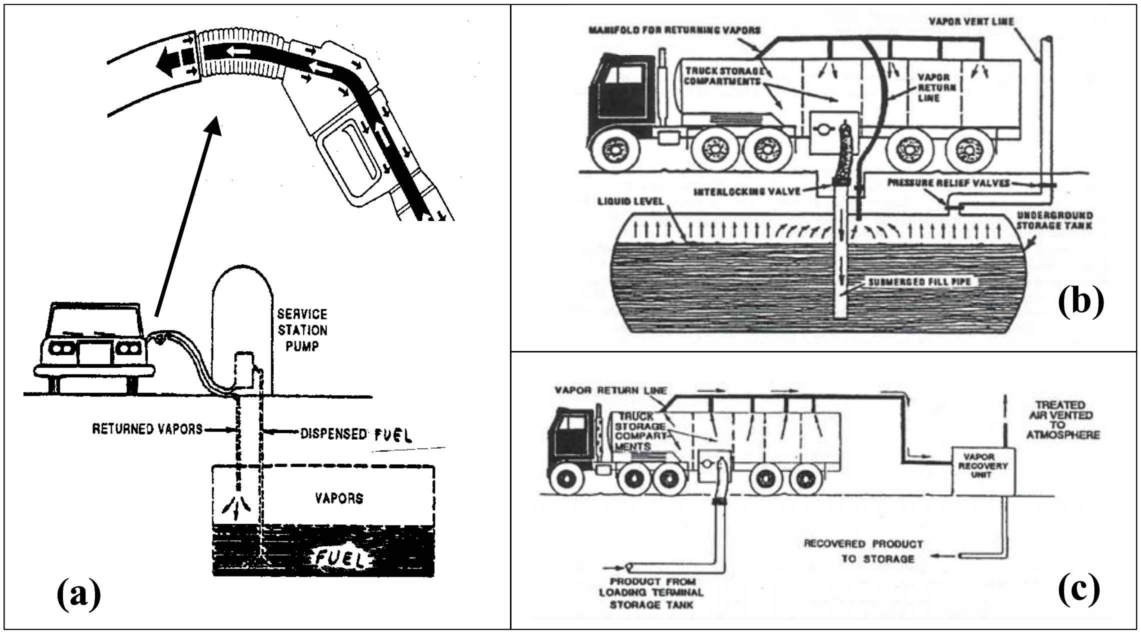


Figure 4-11: Evaporative control technologies for liquid fuel marketing (source: AP-42, 1995 and CEC, 1996).

FUEEM assumes that the balance system will be the one most frequently used by 2010 and so modeled it. According to EPA-AP-42 (1995) the overall system control efficiency is in the range of 88 to 92 %. CARB split the overall efficiency into the control efficiency and defect rate of the system. The control efficiency is related to fugitive emissions from the system especially when the vehicle tank is opened. It uses for the default calculation the control efficiency of 95 %. The same value is adopted by Unnasch *et al*. (1996). The defect rate is the percentage of systems that may not work properly over time and CARB uses 5 % as do Unnasch *et al*. (1996). FUEEM assumes for the control efficiency a Beta General curve with a mean of 95.1 % (see Figure 4-12a) and for defect rate in 2010 it assumes a normal distribution with a mean of 4 % according to Figure 4-12b.

4.3.1.2 Storage at the Fuel Station:

For safety reasons every fuel tank, in most cases an underground tank, has a vapor vent line with a pressure valve control. These vent emissions are called tank breathing losses and the EPA-AP-42 (1995) and CARB (Asregadoo, 1992) emission factor for the gasoline uncontrolled system is 120 mg/L (or 1.0 lb/1000 gal). Based on that, FUEEM assumes a normal distribution curve with a mean of 120 mg/L and standard deviation of 2 mg/L. The curve is presented in Figure 4-12c.

A vapor recovery device can control the tank breathing losses and according to CARB (Asregadoo, 1992) the efficiency of this type of control is 90 % if Stage II and I control are in effect. It translates into the emission factor of 12 mg/L (1.0 lb/1000 gal). Unnasch *et al*. (1996) uses this same value and the Company A study uses half of it (6 mg/L) which is equivalent to the control efficiency of 95 %. For the control efficiency in the 2010 time frame, FUEEM assumes a normal distribution curve with a mean of 92 % and standard deviation of 1.3. The curve is presented in Figure 4-13a.

For methanol and FTN the same control efficiencies are assumed and the emission factor curves for the uncontrolled cases are the same curve assumed for the gasoline case but corrected according to the RVP of each fuel. The correction is made following Equation 4-6:

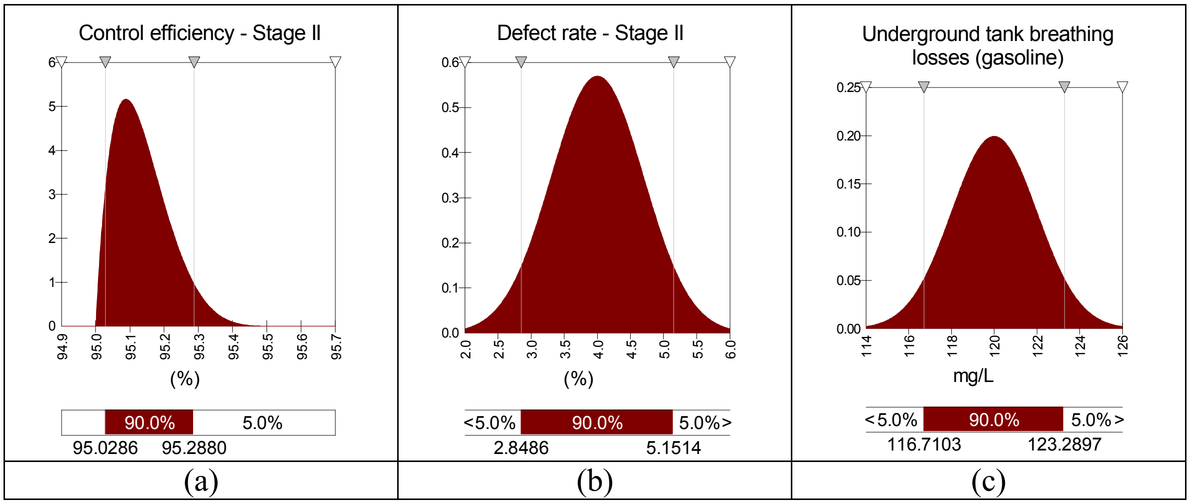
Equation 4-6: $$Tbl_{fuel} = Tbl_{gasoline} * RVP_{fuel} / RVP_{gasoline}$$

where,

Tbl_{fuel} is the tank breathing losses of the fuel analyzed, mg/L

$Tbl_{gasoline}$ is the assumed tank breathing losses for gasoline, mg/L and

RVP is the Reid Vapor Pressure of each fuel.

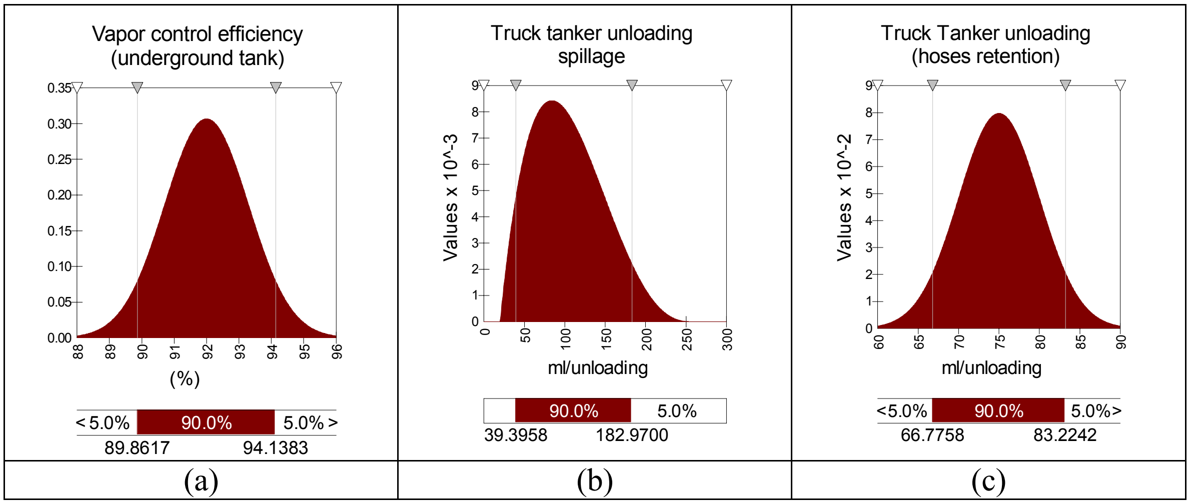


(a) (b) (c)

Figure 4-12: Input assumptions for emission control at the fuel station.

For comparison purposes, the calculation for methanol translates into a curve with a mean of 44.0 mg/L (0.37 lb/1000 gal) in the uncontrolled case and 3.5 mg/L (0.03 lb/1000 gal) in the controlled case. Unnasch *et al.*'s (1996) result for the controlled case is 1.80 mg/L. The calculation for the FTN translates into 65.1 mg/L (0.54 lb/1000 gal) for uncontrolled systems and 5.2 mg/L for the controlled one.

For the loading process of the fuel station underground tank (from a truck tanker) the same problem of spillage and hose retention applies. Unnasch *et al.* (1996) is the only life cycle study that explicitly included these emissions the calculation. It quoted Lyons' study with the emission factor of 0.07 lb/1000 gal for both problems associated. Unnasch' study split the factor assuming 0.05 lb/1000 gal for spillage and 0.02 lb/1000 gal for hose retention. For a 8,000 gal underground tank assumed in the study, the spillage figure is equivalent to 250 ml per refueling and the hose retention equivalent to 100 ml per refueling. With the agreement that this is an area that needs more measurement, the FUEEM experts believed that the Unnasch figures may overestimate the problems and the consensus curves assumed have lower values. A Beta General curve with a mean of 103.5 ml/refueling was assumed for the spillage part. The curve presented in Figure 4-13b uses the minimum of 20 ml and the maximum of 260 ml (α_1 equal to 2.0 and α_2 equal to 3.75). For a 8,000 gal (30,280 L) assume the average spillage is 2.7 mg/L for gasoline, 2.9 mg/L of methanol and 2.6 mg/L of FTN.



(a) (b) (c)

Figure 4-13: Input assumptions for the emission control of marketing activities.

For the hose retention case FUEEM assumes a normal distribution with a mean of 75 ml/unloading and standard deviation of 5 ml. The curve is presented in Figure 4-13c and translates into an emission factor curve with the average of 1.93 mg/L for gasoline, 2.14 for methanol and 1.85 for FTN.

The fuel vapor displacement at the fuel station underground tank occurs in the same way that the vehicle tank refueling does. For uncontrolled tanks EPA-AP-42 (1995) assumes an emission factor of 880 mg/L (7.3 lb/1000 gal) considering submerged filling. For the splash method (dropping the fuel from the top of the tank using an open hatch cover) the value is larger (1,380 mg/L or 11.5 lb/1000 gal). The CARB emission factor for uncontrolled activity is 1,338 mg/L (9.5 lb/1000 gal). To control the vapor displacement emissions a balance system associated with submerged filling can be put in place.

Figure 4-11b shows this idea where the displaced fuel vapor is transferred back to the truck. This control system is termed Stage I in the EPA rules. The control system has efficiency ranging from 93 % to 100 % according to EPA-AP-42 (1995), and the EPA average value used is 40 mg/L (0.33 lb/1000 gal) meaning 95.5 % efficiency. The CARB emission factor is 57 mg/L (0.48 lb/1000 gal) assuming 95 % control efficiency (Asregadoo, 1992). Unnasch *et al*. (1996) uses the CARB emission factor and the Company A study also assumes 95 % control efficiency translating into an emission factor of 50 mg/L (0.42 lb/1000 gal). For the control efficiency in the year 2010, FUEEM assumes a Beta General curve with values about 98 %. The curve is presented in Figure 4-14a. The decision to assume a more efficient system was based on the CARB enhanced vapor recovery (EVR) program initiated in July of 2001 that plans to reduce this kind of emission in the next seven years. It was also, based on a study done by Shearer and Gilson (1994) that discovered in their measurements that the use of pressure/vacuum valves in vent lines reduces by at least one order of magnitude the emission values published as emission factors for controlled systems.

To calculate the emission rate FUEEM uses the Equation 4-7 from EPA-AP-42 (1995) that allow adjustments for the fuel composition and temperature.

Equation 4-7
$$L_L = 12.46 \frac{SPM}{T} \left(1 - \frac{eff}{100} \right)$$

where,

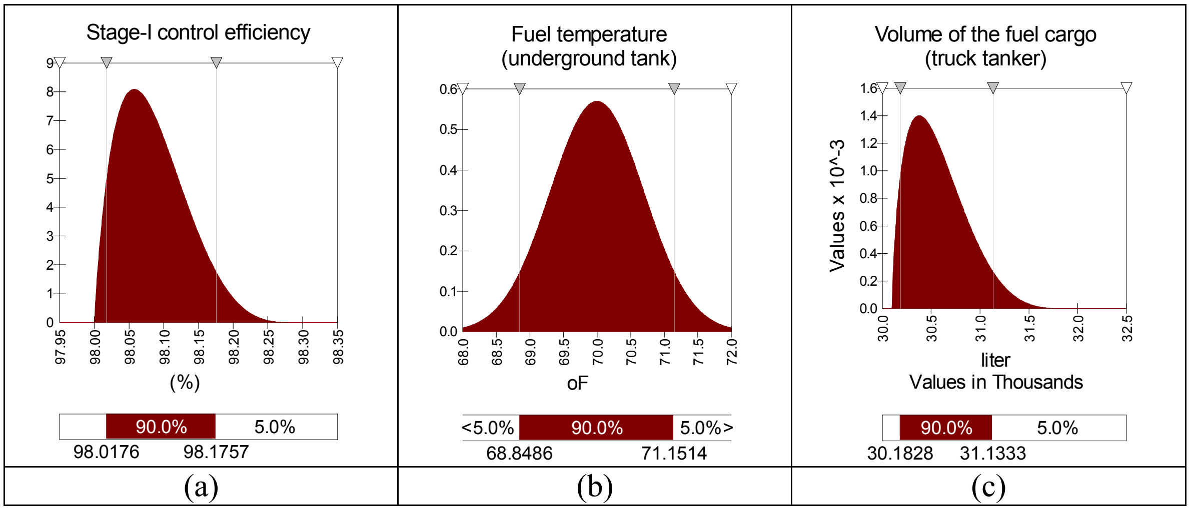
L_L is the tank loading losses (vapor displacement).

S is the saturation factor presented in table 5.2-1 of the EPA document. For the splash filling method the value is 1.45, for the submerged filling with dedicated vapor balance system the value is 1.0.

M is the molecular weight of the fuel vapors (see section 0).

T is the fuel temperature in ^{o}R (^{o}F + 459.67).

eff is the overall control reduction efficiency discussed earlier.



(a) (b) (c)

Figure 4-14: More input assumptions for the emission control of marketing activities.

For the particular situation of analyzing SCAB and assuming the fuel temperature of the underground tank as the curve presented in Figure 4-14b, the calculated emission rates are curves with the following means (for comparison purposes):

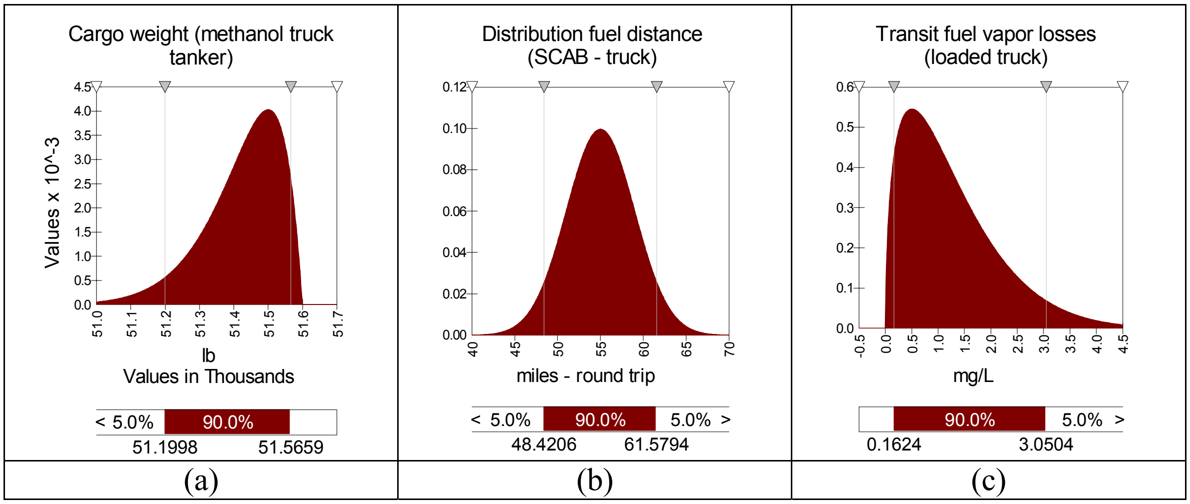
- Gasoline uncontrolled system (splash filling): 1660 mg/L or 13.85 lb/1000 gal
- Gasoline controlled system (submerged filling): 21.9 mg/L or 0.18 lb/1000 gal
- Methanol uncontrolled system: 259.7 mg/L or 2.17 lb/1000 gal
- Methanol controlled system: 3.43 mg/L or 0.03 lb/1000 gal
- FT Naphtha uncontrolled system: 1186.6 mg/L or 9.90 lb/1000 gal

- FT Naphtha controlled system: 15.67 mg/L or 0.13 lb/1000 gal

4.3.1.3 Fuel Distribution

In the fuel distribution activity this study considers only the transport of the fuel from the fuel terminal (bulk storage) to the fuel station. Fuel loading and unloading are considered at the fuel storage site. The environmental aspects associated with the fuel distribution are the NMOG fugitive emission from the tanker, the diesel consumed by the truck, and all the emissions associated with the combustion of diesel in the truck engine. The emissions associated with the production of the diesel consumed are calculated as secondary emissions (see section 4.5.6). Diesel trucks (class 8b - in the EPA classification) are considered in this activity and the tanker design is assumed to be similar to existing gasoline tankers.

Depending on the mass density of the fuel transported, the truck capacity is limited by the volume of the tanker or by the maximum axle weight requirements. Gasoline tanker volumes can go up to 8,500 gallons (32,173 L) but in the cases they are 8,000 gallons (30,280 L). The EPA-AP-42 uses the value of 8,000 gal, Unnasch *et al.* (1996) uses 8,500 gal and Delucchi (1993) assumes 8,800 gal. He and Wang (2000) used 7,800 gal (29,523 L) referring to Unnasch *et al.*'s (2000) assumption; however, the cited study does not analyze gasoline and 7,800 gal is the value used for methanol. FUEEM assumes for the volume cargo of gasoline and FT-naphtha a Beta General curve shown in Figure 4-14c which uses the minimum of 30,100 liters (7,952 gal) and the maximum of 32,000 L (8,454 gal) with α_1 equal to 1.7 and α_2 equal to 5.1. For the methanol case a maximum axle weight requirement of 52,000 lb (for this vehicle class) is a constraint that limits the amount of fuel that can be transported. Unnasch *et al*. (1996) assume the average weight transported of 51,500 lb translating into 7,803 gal. (29,534 L). FUEEM assumes a Beta General curve with a higher probability concentration around 50,000 lb. The curve is presented in Figure 4-15a and uses the minimum of 50,000 lb (22.68 tons) and the maximum of 51,600 lb (23.41 tons) with α_1 equal to 16.0 and α_2 equal to 2.0. This mean value of the assumed curve translates into the methanol volume cargo capacity of 7,756 gal (29,356 L).



(a) (b) (c)

Figure 4-15: Other set of input assumptions for the emission control of marketing activities.

Another variable to calculate the energy requirement and emissions associated with the fuels distribution is the distance between the fuel terminals and the fuel stations. Unnasch *et al*. (1996) assume in their study the value of 50 miles for the round trip in the Los Angeles area. He and Wang (2000) used 60 miles round trip for the USA national average value and Delucchi (1993) for the same national average uses 60 miles for gasoline but 100 miles for methanol. The FUEEM model assumes a normal distribution curve for the round trip and applies it for all fuels, assuming that the fuel terminal location will be the same for all. The curve assumed for the Los Angeles area is shown in Figure 4-15b; it has a mean of 55.0 miles (88. 5 km) and standard deviation of 4 miles (6.4 km).

For the fuel transit losses or, in other words, for the evaporative emissions associated with the truck tanker breathing there are two emission factors according to EPA-AP-42 (1995). One emission factor is for the trip loaded with liquid fuel that creates few spaces for vapor generation in the tank. The other is for the trip back when the tank is full of fuel vapor and practically no liquid fuel is present. In both cases the emissions are not directly proportional to the time spent in transit according to the report. For the gasoline loaded trip the typical emission factor values range from 0 to 1.0 mg/L. Extreme values can go up to 9.0 mg/L. Based on this information FUEEM assumes a Beta General curve presented in Figure 4-15c. For the unloaded trip the typical emission factor values range from 0 to 13.0 mg/L. Extreme values can go up to 44.0 mg/L. FUEEM assumes a Beta General curve presented in Figure 4-16a. For methanol and FT-naphtha FUEEM used the same gasoline emission factor curves and corrected them based on the vapor pressure associated with the fuel temperature.

The fuel temperature is also used to calculate the evaporative losses at the truck loading process in the fuel terminal. For the SCAB area the fuel temperature at the bulk storage tanks is assumed to be a normal distribution curve with a mean of 68°F and standard deviation of 1°F. The curve is presented in Figure 4-16b.

The calculus of the true vapor pressure (*P*) associated with the refined petroleum fuel temperature is based on the equation presented in Figure 7.1-14b of the EPA-AP-42 (1995):

Equation 4-8:

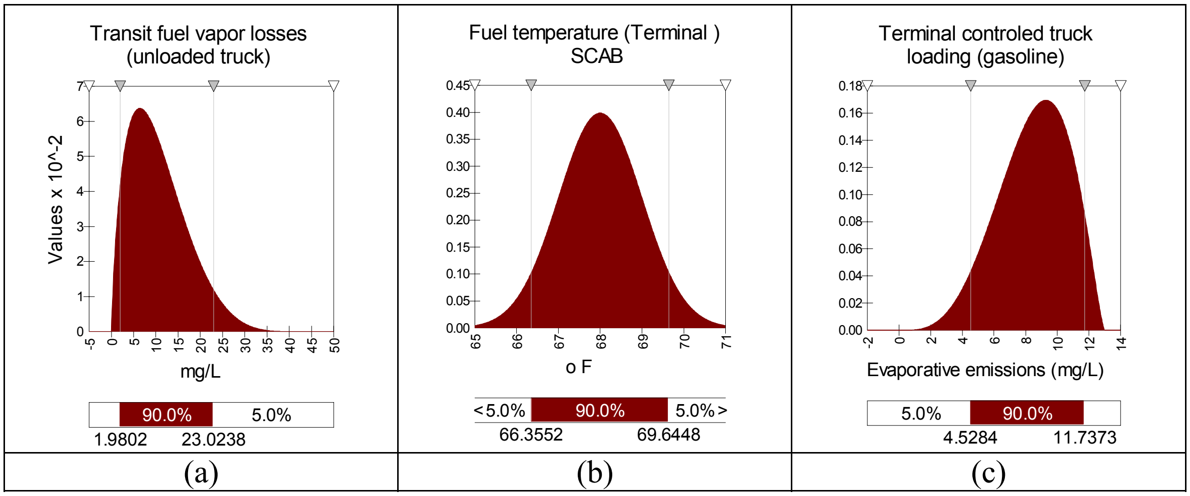
$$P = e^{\left\{\left[0.7553-\left(\frac{413.0}{T+459.6}\right)\right]S^{0.5}\log_{10}(RVP)-\left[1.854-\left(\frac{1042}{T+459.6}\right)\right]S^{0.5}+\left[\left(\frac{2416}{T+459.6}\right)-2.013\right]\log_{10}(RVP)-\left(\frac{8742}{T+459.6}\right)+15.64\right\}}$$

Where,

T is the fuel temperature (^{o}F) at the terminal storage, see discussion above,

RVP is the fuel Reid vapor pressure (psi), see Figure 4-10.

S is the slope of the ASTM distillation curve at 10 percent evaporated, in degrees Fahrenheit per percent. For regular gasoline a normal distribution curve with a mean of 3.0 and standard deviation of 0.03 is assumed. Reformulated gasoline assumes the mean of 3.1 and the same standard deviation. For FT-Naphtha the mean is assumed to be 3.5. The assumptions are based on Figure 7.1-14a of the EPA-AP-42 (1995).



(a) (b) (c)

Figure 4-16: Input assumptions for the emission control of the fuel terminal and truck.

Since methanol is a single component product, the true vapor pressure associated with the fuel temperature can be found in the literature. Based on the values presented by table 7.1-3 of the EPA-AP-42 (1995), a second order polynomial equation was derived using the regression method. The curve is presented in Figure 4-17.

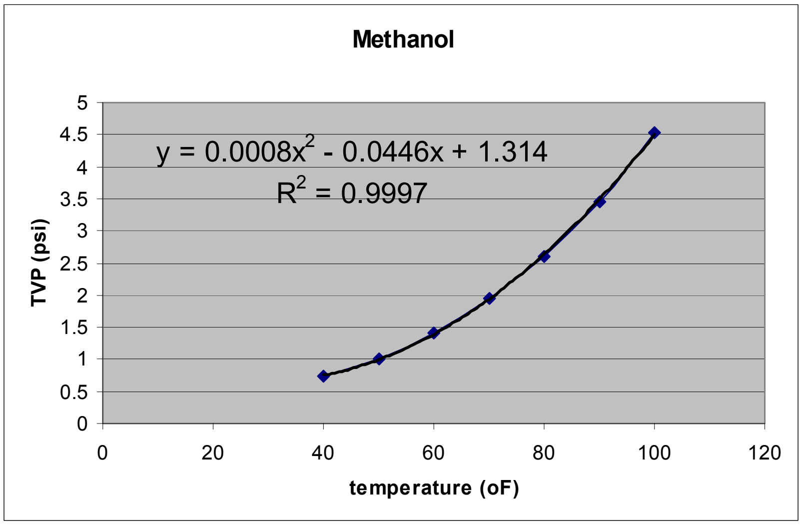


Figure 4-17: Methanol true vapor pressure (source: EPA-AP42, 1995).

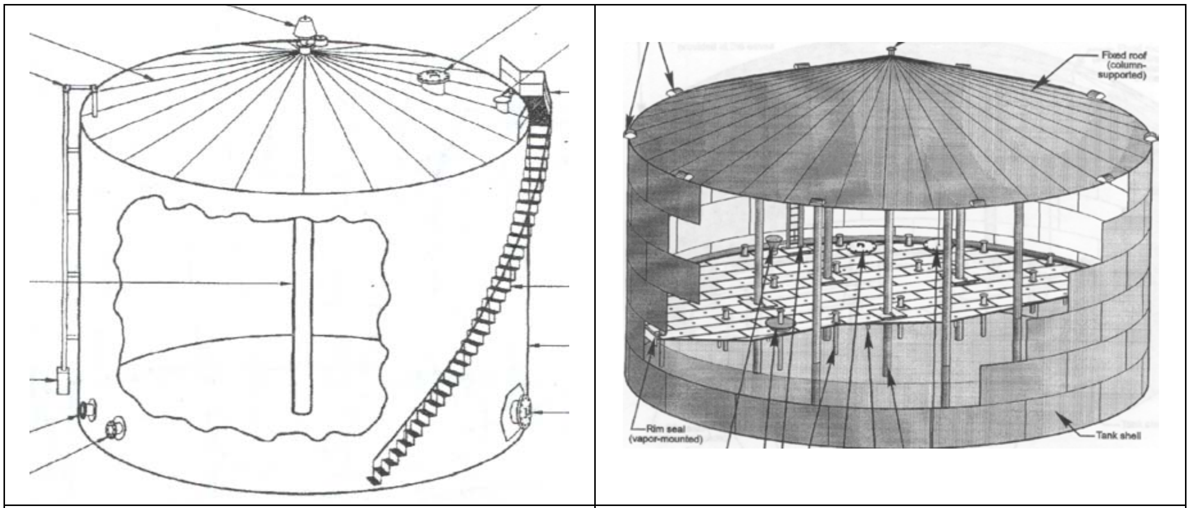
For the truck loading process at the terminal, the uncontrolled evaporative losses are calculated using Equation 4-7 and the terminal fuel temperature discussed above. To control the emissions a vapor return line in the truck can be used associated with a vapor recovery unit (see Figure 4-11c). According to the EPA-AP-42 (1995) the vapor collection efficiency is 90 % for vessels passing an annual leak test; otherwise 70 % should be assumed. According to the same document the terminal vapor recovery efficiency ranges from 90 % to 99 % (pp. 5.2-6). Using the EPA method assuming 98 % for the terminal vapor recovery and 90 % for the vapor collection efficiency, the result is 0.68 lb/1000 gal or 81.0 mg/L. However, the CARB certification requirement for the recovery unit is 10 mg/L and some local districts may require up to 2.5 mg/L. Less tight control in California is at most equal to 13 mg/L. Unnasch *et al*. (1996) assume the emission rate of 8.0 mg/L or 0.07 lb/1000 gal. FUEEM assumes a Beta General curve going from 4.5 to 11.7 mg/L with 90 % confidence. The curve is presented in Figure 4-16c. Methanol and FT-Naphtha uses the same assumption for gasoline but adjusted for true vapor pressure factor.

4.3.1.4 Fuel Terminal Activities:

The environmental aspects of bulk storage at the fuel terminal is related to the evaporative emissions of volatile organic compounds and related to the energy consumption to pump the fuel. To calculate the evaporative emissions EPA has a robust software called "TANK" that uses a meteorological database, fuel information, and detailed tank design information allowing the user to perform several analyses. The theory behind the model is presented in chapter 7 of the EPA-AP-42 (1995). FUEEM currently uses values based on the version "TANK 4.0" released in 2001.

Several "runnings" of the TANK 4.0 were performed to collect several single results and then based on those the expert network came up with a distribution curve. A variation in the tank diameter was performed around 100 feet (30.5 m) with the tank volume around 2,100,000 gallons (~ 8,000 m^3). The tank turnover was established at approximately 12 times given the net throughput of around 25,200,000 gallons per year. In this case the meteorological data used was for Los Angeles. Most of these basic values assumed were based on Unnasch *et al.* (1996). For the uncontrolled situation a vertical fixed roof tank (Figure 4-18a) was selected with a shell height around 40 ft (12.2 m). For the controlled situation an internal floating roof tank with vapor-mounted rim-seal system, typical welded deck and 6 columns (Figure 4-18b) was selected.

The TANK 4.0 software provides the results in terms of pounds of volatile organic compounds (VOC) emitted per year and using the net throughput assumed one can calculate the emission rate in terms of pounds per thousand gallons or milligrams per liter of fuel stored. For the gasoline uncontrolled system FUEEM assumed that all VOC is NMOG (Non-methane organic gases) and uses, as emission rate value, a normal distribution curve with a mean of 325,000 lb/year and standard deviation of 4,500 lb/year. The curve is presented in Figure 4-19a. The mean of the emission rate curve generated is 1546.6 mg/L or 12.9 lbs/1000 gal.

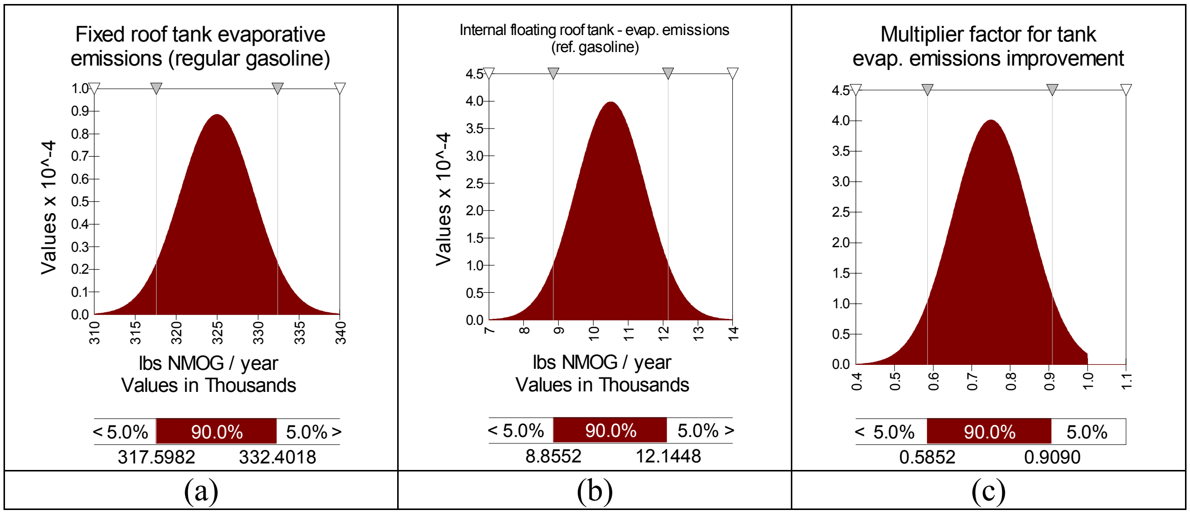


(a) Vertical fixed roof tank

(b) Internal floating roof tank

Figure 4-18: Liquid fuel bulk storage technologies (source: EPA-AP-42)

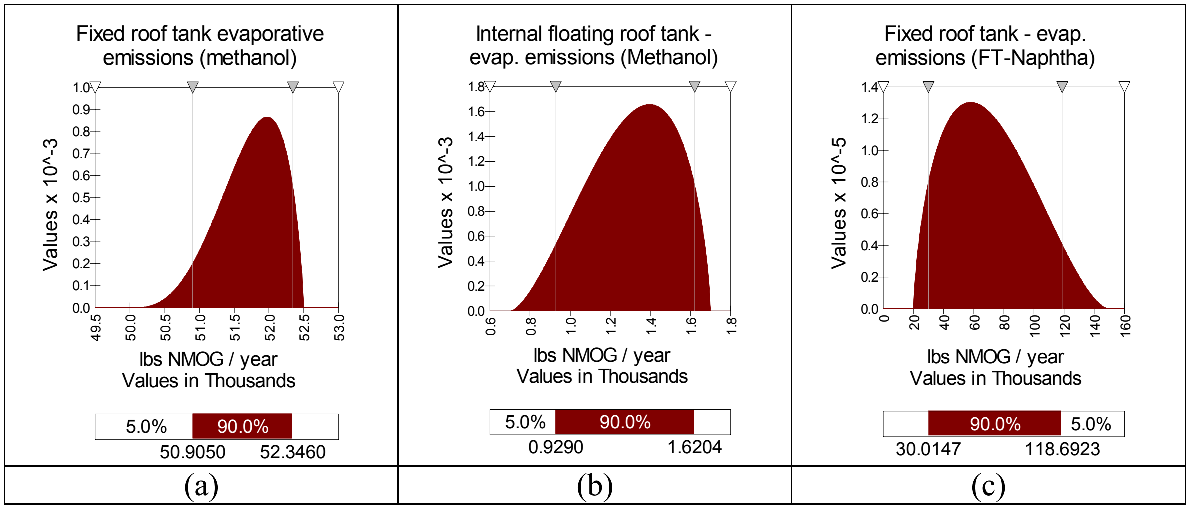
For the gasoline controlled system the current emission rate assumed is a normal distribution curve with a mean of 10,500 lbs/year and standard deviation of 1,000 lbs/year. The curve is presented in Figure 4-19b. To adjust for the year 2010 a multiplier factor was assumed. The factor is a normal distribution curve with a mean of 0.75 and standard deviation of 0.1 (see Figure 4-19c). A similar factor is used by Unnasch *et al.* (1996) for their future scenario analysis but the factor used is 0.1 which means an improvement of around 90 % in a little more than a decade. FUEEM experts decided to use a more conservative factor. The combination of the current emission rate curve and improvement factor generates a 2010 emission rate curve with a mean of 37.4 mg/L or 0.31 lbs/1000 gal. For comparison purposes the Unnasch *et al.* (1996) result is 1.01 mg/L, a much lower value since they assume a good improvement factor over an already excellent emission rate of 10.12 mg/L (2,123 lbs/year).



(a) (b) (c)

Figure 4-19: FUEEM assumptions for the liquid fuel terminal activities

Following the same criteria for the methanol uncontrolled system, FUEEM assumes a Beta General function with a minimum of 50,000 lbs/year and maximum of 52,500 lbs/year using α_1 equal to 4.0 and α_2 equal to 1.8. The curve is presented in Figure 4-20a. The result translates into a curve with a mean of 246.0 mg/L (2.1 lbs/1000 gal). For the methanol controlled system the assumed current emission rate is a Beta General function with a minimum of 700 lbs/year and maximum of 1,700 lbs/year using α_1 equal to 2.6 and α_2 equal to 1.7. The curve is presented in Figure 4-20b. Using the same adjustment factor for the year 2010 as the gasoline case, the calculated emission rate translated into a curve with a mean of 4.6 mg/L or 0.039 lbs/1000 gal. For comparison purpose the Unnasch *et al*. (1996) result is 0.166 mg/L or 0.001 lbs/1000 gal.


Fixed roof tank evaporative emissions (methanol)

Internal floating roof tank - evap. emissions (Methanol)

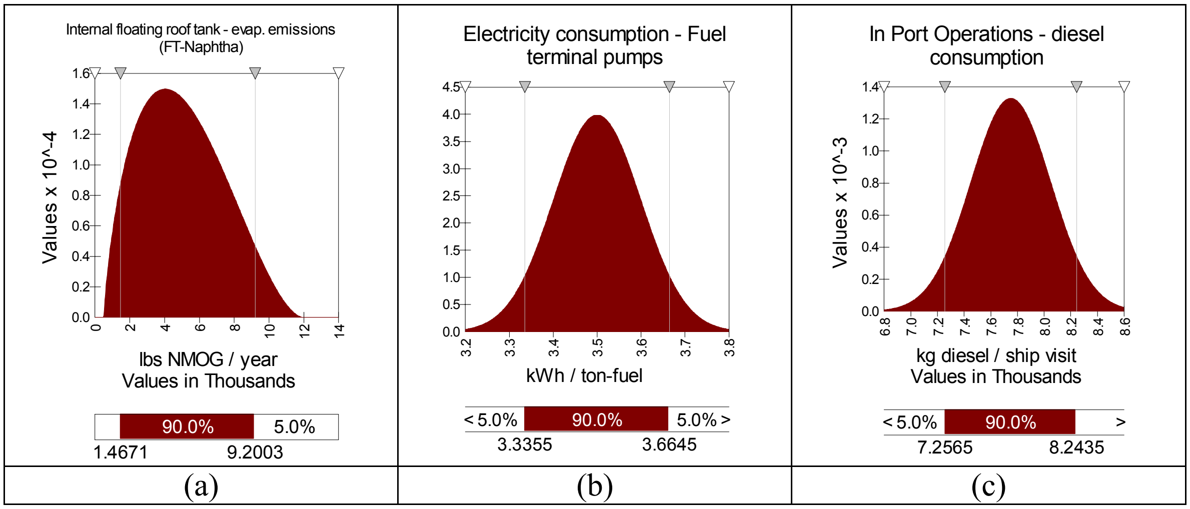
Fixed roof tank - evap. emissions (FT-Naphtha)

(a) (b) (c)

Figure 4-20: FUEEM assumptions for the liquid fuel terminal activities

For the Fisher-Tropsch Naphtha (FTN) several runs on TANK 4.0 were made with different components and several results was determined with the variation of the percentages of the considered components (n-octane, iso-octane, n-heptane, n-hexane and n-pentane). For the FTN uncontrolled situation the expert network decision was to use a Beta General function with a minimum of 20,000 lbs/year and maximum of 150,000 lbs / year using α_1 equal to 1.7 and α_2 equal to 2.7. The curve is presented in Figure 4-20c. For the FTN controlled situation the emission rate assumed is a Beta General function with a minimum of 500 lbs/year and maximum of 12,000 lbs / year using α_1 equal to 1.8 and α_2 equal to 2.8. The curve is presented in Figure 4-21a.

The energy consumption at the fuel terminal was calculated based on the information existent in Gover *et al.* (1996). This study establishes the amount of electricity consumed to pump fuels into the terminal reservoirs as 3.51 kWh per ton of fuel pumped. FUEEM adopted a normal distribution curve with a mean of 3.5 kWh/ton-fuel and standard deviation of 0.1. The curve is presented in Figure 4-21b.



(a) (b) (c)

Figure 4-21: FUEEM assumptions

4.3.2 Marine activities

4.3.2.1 In Port Operations

The emissions and energy requirement associated with tanker ships approaching the port area are calculated by Unnasch *et al*. (1996) based on a CARB workshop on marine emissions. Diesel auxiliary engines producing electricity for the ship and diesel tugboats to help the ship maneuvering into the port are the main activities. For crude oil transportation they assumed 2 hours for port transit time plus 30 hours of hotel load and 8 hours of tugboat operation. They came up with the value of 7, 716 kg of diesel consumed per ship visit. Similar values were assumed in FUEEM with a normal distribution curve of 7750 kg of diesel per visit and a standard deviation of 300 kg. The curve is presented in Figure 4-21c.

The Unnasch study also calculates some emissions generated in this operation. Based on those and on the emission factors for diesel engines (from EPA-AP-42, 1995) FUEEM assumed the emission rate curves presented in Table 4-13.

Table 4-13: Emission rate curves for in port activities

g-pollutant/kg-diesel	NOx	NMOG	CO	PM10	SOx	CH4	N2O	CO2
Unnasch, 1996	37	6.9	13.9	-	-	-	-	3200
FUEEM-unct[a] (mean)	36	12	40	1.7	0.86	0.1	0.19	3215
FUEEM-unct[a] (st. dev.)	2	2	4	0.15	c	0.03	0.01	c
FUEEM-ct[b] (mean)	11	3	12.5	0.6	0.06	0.1	0.13	3215
FUEEM-ct[b] (st. dev.)	1	0.8	1.3	0.05	c	0.03	0.01	c

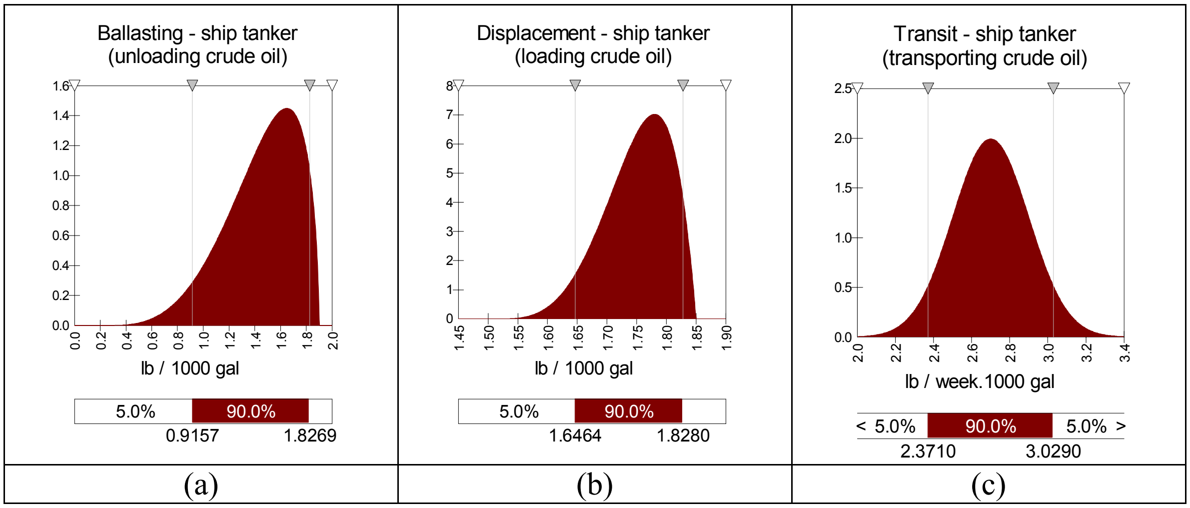
a: uncontrolled situation b: controlled situation
c: calculated based on the fuel composition. See section 4.5.5.

4.3.2.2 Fuel Transportation

The environmental aspects of marine fuel transportation are related to the evaporative emissions during the tanker ship transit, loading, and unloading activities. It is also related to the combustion of the residual oil (bunker fuel) in the ship engines that is presented in section 4.6.1.

All the evaporative emissions are non-methane organic gases (NMOG). For the tanker ship unloading activity, at the same time that the fuel is unloaded from the ship, the empty tanks are partially filled with water to keep the ship balanced. This activity is called ballast and generates emissions by pushing out the existing fuel vapor in the tank. According to the EPA/AP-42 (1995) report, in general, 15 % to 40 % of the tanker capacity is ballast.

The CARB (1997a) emission factor for ballasting crude oil shipment is 1.8 lb/1000 gal of fuel delivered. The EPA/AP-42 (1995) emission factor is 0.32 lb/1000 gal of oil (or 0.8 lb/gal of ballast water). FUEEM assumes a Beta General curve with a mean of 1.45 lb/1000 gal of oil. Figure 4-22a presents the variable. Adjusting the oil values by using the vapor pressure of the fuels, the ballasting of FT-naphtha delivered translates into a curve around 0.75 lb/1000 gal of naphtha and the ballasting of methanol delivered is around 0.50 lb/1000 gal of methanol.



(a) (b) (c)

Figure 4-22: Emission rates assumed for the marine transportation activities.

A similar situation occurs when the tanker is loading the fuel. The tanks are filled to from 80 % to 100 % of their capacity and the emissions occur due to the fuel vapor displacement. The CARB (1997b) emission factor value for crude oil is 1.8 lb/1000 gal of oil and the EPA/AP-42 (1995) value is 1.7 lb/1000 gal of oil. FUEEM assumes a Beta General curve with mean of 1.75 lb/1000 gal of oil. The curve is presented in Figure 4-22b. Adjusting to load FT-naphtha, the value translates into a curve around 0.9 lb/1000 gal of naphtha. To load methanol, the curve translates into 0.6 lb/1000 gal.

Finally, the evaporative emissions value during the tanker transit with crude oil is provided by the EPA/AP-42 (1995) as 2.7 lb per week per 1000 gal of oil. The same value was assumed in FUEEM with a standard deviation of 0.2 lb/week per 1000 gal (see

Figure 4-22c). The value for FT-naphtha is a curve about 1.39 lb/week/1000 gal and 0.93 lb/week/1000 gal for methanol. Using the speed of the ship the values can be calculated in terms of lb per mile per 1000 gal.

4.4 Gas-to-Liquids production

Gas-to-Liquid plants can be roughly divided in four main activities:

- Gas preparation
- Syngas production
- Fuel synthesis
- Fuel separation or conversion

The gas preparation phase is similar to the gas preparation phase explained for hydrogen production. Basically, the sulfur content in marketable natural gas is reduced to levels lower than 0.5 ppm to protect the reformer catalysts (DOE, 1989). This is most often done by hydrodesulfurization process that utilizes a hydrogenation vessel followed by a sulfur (H_2S) removal process with zinc-oxide beds. Heat exchangers and gas compression brings the gas to a temperature and pressure optimized for syngas production, the next activity in the cycle.

4.4.1 Syngas production

Syngas is the name used for a synthetic gas containing a mixture of H_2, CO, some CO_2, and traces of hydrocarbons. It can be produced from different feedstocks (NG, coal, biomass, etc.) and different processes (SMR, POX, ATR, etc.) as explained earlier in section 4.2.

An important section for gas-to-liquid (GTL) production based on syngas feedstock is that each different process/feedstock produces a different syngas composition and so is an important parameter in the GTL plant design. The syngas composition is frequently expressed in terms of the H_2/CO ratio. In the case of GTL production, CO_2 appears in the stoichiometric number calculation, since its presence consumes hydrogen during the fuel synthesis (Lange, 2001). The molar ratio (R) or stoichiometric number of the synthesis reaction is calculated as:

$$R = \frac{(H_2 - CO_2)}{(CO - CO_2)} \qquad \text{Equation 4-9}$$

The important difference is that the “balanced gas” or, in other words, the best molar ratio for methanol production, is around 2.0 to 2.1, due to the methanol synthesis reactions presented next. In the case of Fisher-Tropsch fuel production, the ratio varies from 1.6 to 2.1 for low-temperature processes and from 2.6 to 2.8 for high-temperature processes.

A table from Tindall *et al.* (1995) shows the R-value for syngas produced by different reformation technologies and designs (Table 4-14). Steam methane reformation is the preferred process for hydrogen production since its molar ratio is 3.0 and theoretically it can increase to almost pure hydrogen by adding shift converters in the plant design. In fact, at some point the economy will favor a CO cleanup process as opposed to several shift converters to obtain a high level of hydrogen purity. Some details of the SMR process (Figure 4-23a) are described in section 4.2. It is important for the discussion here to remember that the steam methane reaction ($CH_4 + H_2O \leftrightarrow CO + 3H_2$) is highly endothermic ($\Delta H_{298K} = + 206$ KJ/mol), the syngas outlet temperature is around 840 to 870 ^oC (1550 to 1600 ^oF), and it is a well-known technology.

To balance (i.e., reduce the R value) the SMR syngas for the methanol or Fisher-Tropsch synthesis, the following alternatives exist:

- To extract the extra-hydrogen from the syngas and sell it, or burn it as reformer fuel. Selling the hydrogen can be a good option if a hydrogen market exists. On the other hand, since H_2 is more expensive (more processed) than the NG, to burn it in the reformer (as opposed to NG) is not the optimum option, but it is the most common approach used today (Allard, 2000).
- To inject some extra CO_2 in the syngas. This idea is similar to the Tindall *et al*. (1995) alternative of recycling CO_2 back in the SMR process as a means of reducing the syngas molar ratio. The reverse water-gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) will take place, consuming some H_2 and generating some CO. The difference with gas-to-liquid fuels is that GTL synthesis will consume carbon molecules (CO and CO_2) and therefore there is no extra CO_2 flow to recycle back. Importing CO_2 can be an interesting solution for GTL production if CO_2 is available. However, in general, it will hardly be the case for large volumes of GTL production.
- To combine the steam methane reformation (SMR) process that has a higher molar ratio (R) with the partial oxidation (POX) process that has lower "R." The combination can occur by sequencing primary and secondary reformers or integrating them in single vessels called auto-thermal reformers (ATR), which also improves the heat management of the system. These options are explained below.

The production of syngas by means of partial oxidation (POX) occurs via radical reactions in the gas phase within controlled flame and without catalysts (Figure 4-23b). According to Lange (2001), the desired operational POX temperature is about 1000 to

1200 ^oC (1830 to 2190 ^oF). Tindall *et al*. (1995) suggest higher temperatures – in the range of 1370 ^oC (2500 ^oF). The partial oxidation is an exothermic reaction (ΔH_{298K} = –35 KJ/mol, for the methane case) and the produced energy facilitates a thermal integration with SMR.

Table 4-14: H_2/CO ratio summary for natural gas feed reforming (source: Tindall *et al*., 1995)

H_2/CO ratio	**Import CO_2**	**Total CO_2 recycle**	**No CO_2 recycle**	**Increase steam**	**Add shift converter**
SMR	< 3.0	3.0	5.0	> 5.0	~ ∞
Combined	< 2.5	2.5	4.0	> 4.0	> 5.0
ATR	< 1.6	1.6	2.65	> 2.65	> 3.0
POX	< 1.6	1.6	1.8	> 1.8	> 2.0

Another benefit of using POX is the low cost (capital investment) to install it; however, the necessity of pure oxygen in the process requires an expensive air separation unit with high compression and heat exchange requirements (Figure 4-23g). The alternative of using air or $O_{2\text{-enriched}}$ air (Figure 4-23h) instead of pure oxygen (O_2) may work for Fisher-Tropsch (FT) production but not for methanol production that has a high recycling system requirement. The presence of high amounts of nitrogen (N_2) in the airflow requires higher compression and heat exchange duties. On the other hand, the diluted syngas will reduce the synthesis conversion efficiency per pass in the reactor, especially in the methanol case where the efficiency per pass with pure O_2 is already low. A new concept in methanol production considers mega-size plants, reducing the costs of oxygen production by economy of scale. This approach does not apply to FT production because the level of current technology development is still at a level that huge scale up was not demonstrated yet.

A combined SMR/POX reformation process or "two-step" reforming process works well to balance the syngas for GTL production. According to Lange (2001), a simple combination of the SMR syngas with POX syngas provides the molar ratio of 2 – ideal for GTL production. The development of catalytic POX (cat POX), a POX reactor with a noble metal catalytic bed (e.g., Rh), motivated the combined reformation development towards mass integration and heat integration. The catalyst reduces the activation energy of the POX reaction and by doing so increases the rate of the reaction. A relative smaller reactor is possible (Figure 4-23c) and the output syngas temperature drops to around 1040 °C (1900 °F) according to Tindall *et al.* (1995).

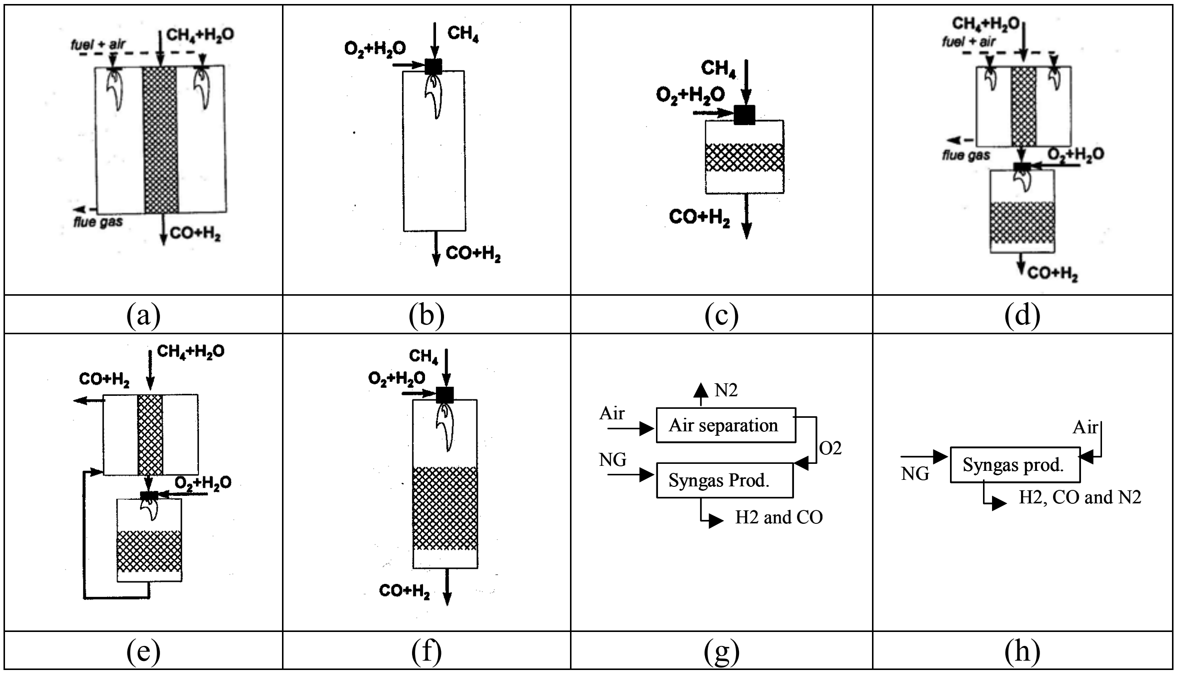


Figure 4-23: Syngas production technologies (source: Lange, 2001)

The mass integration (Figure 4-23d) occurs when the syngas of the primary reformer (SMR) is fed into the secondary reformer (cat. POX) and the heat integration

(Figure 4-23e) occurs when the heat content in the secondary reactor outlet drives (or partially drives) the endothermic reaction in the primary reactor.

The autothermal reactor (ATR) is in fact a sophisticated mass and heat integration within a single vessel (Figure 4-23f). More commercial application will be necessary to increase a knowledge base for these reactors.

4.4.2 Methanol production

According to Lee (1990) and Cheng *et al*. (1994), methanol was first isolated by Sir Robert Boyle in 1661, and was first commercialized in 1830, produced by from destructive distillation of wood. Dumas and Peligot established its chemical formula in 1831. Paul Sabatier suggested the synthetic methanol route in 1905 and by 1913 a German patent was issued to the Badische Anilin-und-Soda-Fabrik (BASF). In 1923 BASF built the first synthetic methanol plant using a zinc oxide/chromium oxide catalyst operating at 300 ^oC and 200 atm (~ 570 ^oF and ~ 2,900 psi). Similar production processes dominated until the 1960's, known today as high-pressure methanol synthesis. According to DOE (1989), in general, these high-pressure processes operated in the pressure range of 250 to 350 atm (3,700 to 5,000 psi) and in the temperature range of 320 to 400 ^oC (600 to 750 ^oF). The biggest problem of high-pressure synthesis was the small selectivity of catalysts to methanol formation allowing several other by-products to be formed.

In the 1960's, with the development of a more efficient purification process for syngas production, mainly removing sulfur and metal carbonyls, the use of other catalysts became possible. In 1966, the Imperial Chemical Industries (ICI) announced their low-pressure methanol synthesis process (40 to 150 atm) using a Cu/ZnO catalyst. After this, all new methanol plants built use low-pressure synthesis differing in details of how to improve the technology targeting mainly the reactor cooling system, pressure drop, economy of scale, and catalyst (material and preparation process).

4.4.2.1 Methanol synthesis

The following equations represent the basic methanol synthesis reactions.

$CO + 2 H_2 \leftrightarrow CH_3OH$ (- 21.66 Kcal/g-mol) Equation 4-10

$CO_2 + 3 H_2 \leftrightarrow CH_3OH + H_2O$ (- 11.83 Kcal/g-mol) Equation 4-11

$CO + H_2O \leftrightarrow CO_2 + H_2$ (+ 9.84 Kcal/g-mol) Equation 4-12

There are several scientific controversies regarding the role of each reaction, in the Cu-based methanol synthesis, referring to the by-products formation, water formation, and active ingredients in the catalyst. In spite of this, the new technologies are much more efficient and selective towards methanol production than the old ones. Lee (1990) suggested that the selectivity of existing processes is on the order of 99 %. However, hydrocarbon formation through the Fisher-Tropsch reaction, reactions after the methanol formation (producing superior alcohols such as ethanol, propanol and butanol; producing dimethyl ether, acetone, aldehydes, etc.) and carbon deposition from the Boudouard reaction ($2 CO \leftrightarrow CO_2 + C$), are still concerns, providing a motive for continuing investigation.

According to Cheng *et al*. (1994) the selectivity of the catalysts increases with lower pressures. Lower pressures also favor a system compression requirement that is significantly high. Selectivity also increases at high space velocity (residence time), at high H_2/CO ratio and at lower temperature. The development of new catalysts (inter-metallic Cu/Th, Cu/Lanthanides, Pt group on silica, etc.) also target higher conversion-per-pass, which reduces the recycling cost as well as the overall heat transfer necessity. The conversion of CO per pass is normally 40 to 60% in the ICI process according DOC (1985) and 6 to 8 % in the Lürgi process (LeBlanc *et al*., 1994).

As shown earlier, the methanol synthesis reactions are mild exothermic, making the reactor a "heating machine" according to DOC (1985). High temperature or local hot spots deactivate the catalyst permanently, making the dissipation of the reaction heat one of the most important factor to control and understand, in order to maintain or improve reactor stability and efficiency (Lee, 1990).

According to LeBlanc *et al*. (1994), the variations in the reactor design can be classified as:

- Quench: ICI and Mitsubish Gas Chemical (MGC).
- Inter-cooled: Haldor-Topsøe and Kellog (spherical).
- Isothermal and pseudo-isothermal: ICI (tube-cooled), Lürgi (tubular), Linde (spiral-wound) and MGC (double-tube).
- Other: MGC (fluidized bed) and Air Products (slurry-pilot unit).

Different reactor designs (catalyst contact rates, pressure and temperature), and catalyst system (reactivity and selectivity), as well as the initial gas composition, will define the equilibrium concentration, the rate of this equilibrium and ultimately the rate of the methanol and other by-products production. It also imposes more or less duty in the next phase – the distillation. Table 4-15 shows some operational parameters of the existing methanol synthesis.

Table 4-15: Heterogeneous processes for methanol production (source: Lee, 1990)

Process	Catalyst	Temperature (^oC)	Pressure (atm)
BASF	$CuO-ZnO-Al_2O_3$	200 - 350	50 - 250
ICI	$CuO-ZnO-Al_2O_3$	220 - 280	50 - 100
Nissui-Topsoe	$CuO-ZnO-Cr_2O_3$	230 - 260	100 - 150
Lurgi	CuO-ZnO	230 - 250	40 - 50
Chem. Systems	$CuO-ZnO-Al_2O_3$	250 - 275	50 - 120

4.4.2.2 Methanol distillation

The product of the methanol synthesis reactor is called crude methanol, usually stored in fixed roof tanks during the methanol production. Internal floating roof tanks can be a tank alternative if evaporative hydrocarbon emissions are a concern. For fuel cell vehicles a chemical grade product is assumed by FUEEM to avoid problems in the on-board steam reformer. This requires a plant design with a filtering process to remove traces of waxes and with double distillation columns (topping and refining) to remove water and the liquid organic impurities described earlier (superior alcohols, hydrocarbons, and others). It is important to point out that currently all methanol produced in the world is chemical grade.

The water removed from the bottom of the refining column is recycled back to the saturator. Sometimes the fusel oil (liquid organic impurities) is dumped in the saturator as well, or it can be burned in the primary reformer furnace in the absence of air quality enforcement. In the USA fusel oil is considered a hazardous material and it cannot be burned in regular furnaces. Generally, fusel oil in the USA undergoes a biological treatment plant for a further liquid discard (LeBlanc *et al*., 1994).

The purged gas from the distillation, separation and synthesis process is recycled back to the reformers to be used as fuel too. In general, the purge gas flow runs turbines to help with the compression requirements of the system. According to Coogee Chemicals (2001), the power demand of rotating equipments is about 2.2 MW for a plant capacity of 164 tons of MeOH per day. A high-pressure (HP) steam system and a low-pressure (LP) steam system are designed to provide the power requirement. Eventual extra steam for exportation may occur in the LP system. Some plants may also require small amounts of external electricity. Figure 4-24 summarizes the possible configurations adopted in FUEEM.

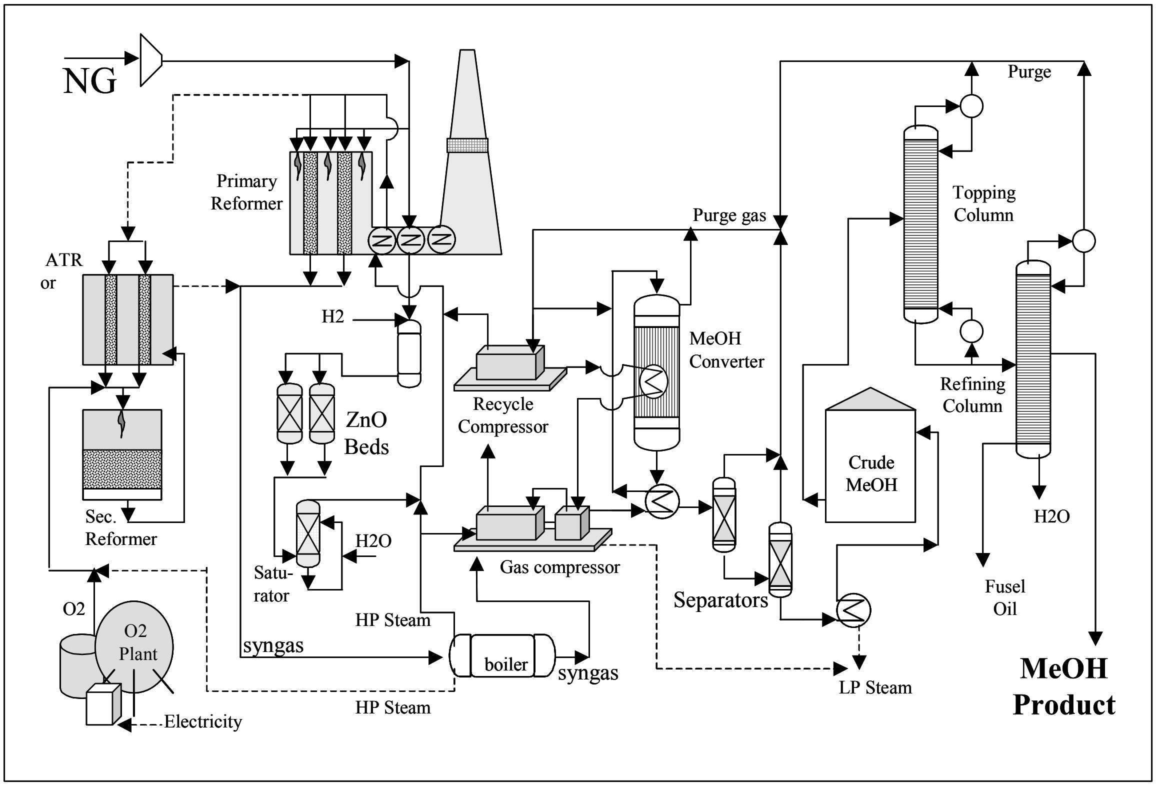
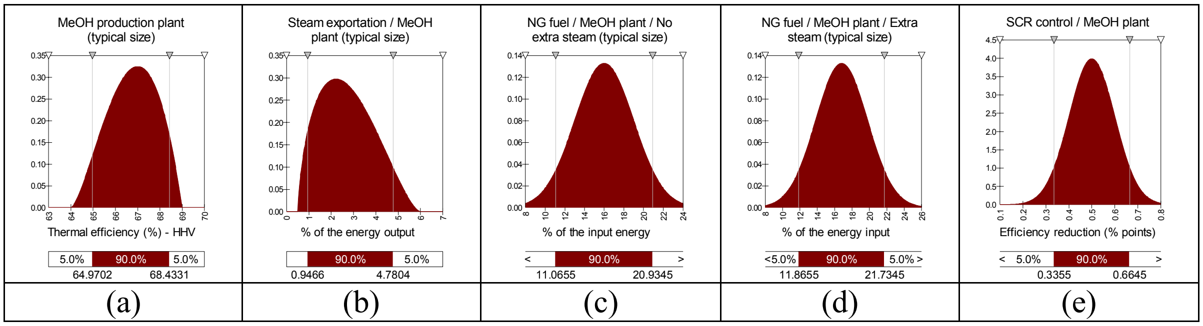


Figure 4-24: Simplified scheme of a new methanol plant.

4.4.2.3 FUEEM assumptions

The FUEEM component model for methanol production calculates the values for two plant sizes: a typical-size plant of about 2,500 metric tons per day (MTPD) using steam reformation syngas that burns the extra hydrogen as fuel, and a mega-size plant of about 10,000 MTPD using a combined reformation (SR/POX) syngas and pure oxygen.

The data available in the literature on the thermal efficiency of a typical-size methanol plant is presented in Table 2-2. For an uncontrolled air emission situation and without the consideration of extra steam exportation, the assumed efficiency in FUEEM is around the most probable value of 67 %. The assumed curve is presented in Figure 4-25a, and it is important to point out that the assumption considers some improvements until 2010 (better catalyst system and heat integration). When steam exportation is considered, co-product credit is given based on the energy content. The steam exported represents, on average, about 2.7 % of the total energy output. The assumed curve is presented in Figure 4-25b.



(a) (b) (c) (d) (e)

Figure 4-25: Energy requirement assumptions for a typical size methanol plant (HHV).

For emission calculation it is important to define the percentage of NG that is used as fuel. It is good to remember that the fusel oil approach and the amount of purge gas recycled back will play a role in the reformer emissions as well. The percentage of natural gas used as fuel is shown in Figure 4-25c for plants without steam exportation and in Figure 4-25d for plants with extra steam. For plants located in areas with high enforcement air emissions control, utilization of a selective catalytic reduction (SCR) system is considered. Some losses in efficiency occur when a SCR is used; therefore, a reduction in the plant efficiency is assumed. The assumed curve has a mean of around 0.5 % in terms of efficiency point reduction and is presented in a Figure 4-25e.

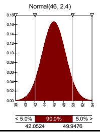
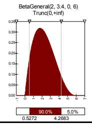
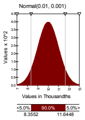
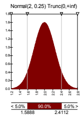
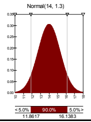
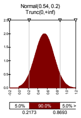
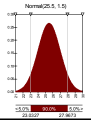
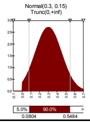
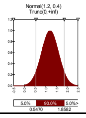
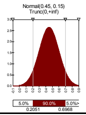
The purge gas flow assumes a Beta General curve with a minimum of 17 scf/MBtu of methanol produced, a maximum of 22 scf/MBtu, with α_1 equal to 2.0 and α_2 equal to 2.6. The purge gas composition in terms of percentage by mol is presented in Table 4-16, with the difference to 100 % being hydrogen. The energy content of the purge gas is calculated based on Van der Lugt's (1986) method that considers non-ideal gas relations.

Table 4-16: Purge gas composition of a typical-size methanol plant with SMR.

Gas (% mol)	CH_4	CO	CO_2	N_2 / Air
mean	13.0	1.3	1.7	1.5
standard deviation	1.0	0.5	0.2	0.2

The emission rates for syngas reformer and for fugitive emissions in typical-size methanol plants, from existing studies, are presented in Table 4-19. Most are extrapolations of emission factors of natural gas furnaces, since EPA (AP-42) and CARB do not provide methanol plant values. FUEEM assumes uncontrolled emission rates for the syngas reformer furnace in terms of grams of pollutants per energy (MBtu) of reformer fuel consumed (natural gas plus purge gas). The fugitive emissions are assumed in terms of grams of pollutants per energy (GJ) content in the methanol output. The curves are presented in Table 4-17.

Table 4-17: FUEEM emission rates for a typical-size methanol plant (HHV).

Pollutants	Reformer emissions (g/MBtu-burned)				Fugitive emissions (g/GJ-MeOH)			
	Min / Max[a]	Mode	Mean	Shape	Min / Max[a]	Mode	Mean	Shape
NO_x	42.1/50.0	46.0	46.0		-	-	-	-
CO	0.5/4.3	1.7	2.2		8.4/11.6 x 10^{-3}	0.01	0.01	
NMOG	1.6/2.4	2.0	2.0		11.9/16.1	14	14	
CH_4	0.22/0.87	0.54	0.54		23.0/28.0	25.5	25.5	
SO_x	0.08/0.548	0.31	0.30		-	-	-	-
PM_{10}	0.55/1.86	1.20	1.20		-	-	-	-
N_2O	0.21/0.70	0.45	0.45		-	-	-	-

a: At 90 % of confidence.

* To transform to lb/MBtu multiply by 2.326 x 10^{-3}

Table 4-18: Air emission control efficiency for a typical-size methanol plant with SMR.

Pollutant	NO_x	CO	NMOG	CH_4	PM_{10}	N_2O
mean (%)	90.0	2.0	35.0	1.0	8.0	50.0
standard deviation	1.0	1.0	3	1.0	1.0	3.0

Table 4-19: Emission rates for a typical-size methanol plant from current studies.

(grams/MBtu-NGfuel)	NOx	NOx	CO	CO	NMOG	NMOG	CH4	CH4	SOx	SOx	PM10	PM10	N2O	N2O
Typical Size - SR syngas	Ref.	Fug.	Ref.	Fug.	Ref.	Fug.	Ref.	Fug.	Ref.	Fug.	Ref.	Fug.	Ref.	Fug.
Acurex (1996)	14.34	0	4.85	0	0.42	1.69	0.42	3.06	-	-	-	-	-	-
Greet 1.4 (1998)	23.34	0	17.61	0	0.6	0	0.13	0	0.28	0.14	1.32	0	0.19	0
Greet 1.5a (2000)	35.3	15.89	37.1	26.46	2.43	1.35	0.99	0	0.28	0	3.34	0	0.99	0
Delucchi (1997 and 93)	31.2	-	4.2	-	0.3	-	6	-	0.11	-	0.1	-	0.5	-
Darrow/GRI (1994)	3.1	-	3.6	-	-	-	-	-	-	-	0.1	-	-	-

Table 4-20: Energy requirement rates for a mega-size methanol plant from current studies.

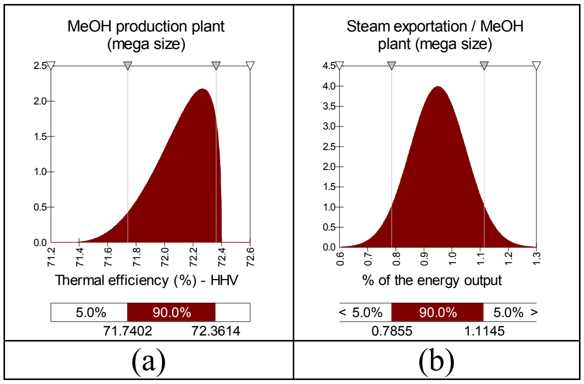
Mega Size: 10,000 metric tons of MeOH per day – Combined SR and POX syngas							
HHV	Efficiency (%)		Electric. used (%)		NG used as fuel (%)		C effic
Extra Steam/Electricity	Without	With	Without	With	Without	With	(%)
Acurex (1996)	72.3	-	0.8	-	21.5	-	-
DeLucchi (97, 93)	71.4	-	0.6-0.7	-	-	-	-
Korchnak (in MAD)	66.5	-	-	-	-	-	-
Hyd. Proc (in MAD)	68.5	-	-	-	-	-	-
DOE (89)	70-75	-	-	-	-	-	-
Allard (2000)	72	-	0	-	-	-	88
Levelton (2000)	75.3	-	-	-	-	-	-
MIT (2000)	69.8	-	-	-	-	-	83

Table 4-21: Emission rates for a mega-size methanol plant from current studies.

(grams/MBtu-NGfuel)	NOx	NOx	CO	CO	NMOG	NMOG	CH4	CH4
Mega-Plant - SR/POX comb.	Ref.	Fug.	Ref.	Fug.	Ref.	Fug.	Ref.	Fug.
Acurex (1996)	3.13	0	1	11.16	0.11	1.79	0.11	3.24

For typical-size plants with air emission controls, such as low-NO_x burners, CEMS, SCR and internal floating roof tanks, FUEEM assumes a control efficiency factor per pollutants. The factors are established in terms of percentage of emission reduction over the uncontrolled situation and their curves are presented in Table 4-18.

The data found in the literature on the thermal efficiency of a mega-size methanol plant is presented in Table 4-20. For an uncontrolled air emission situation and without extra steam exportation consideration, the assumed efficiency in FUEEM is around the most probable value of 72.3 %. The assumed curve is presented in Figure 4-35a. When steam exportation is considered, a co-product credit is given based on the energy content. The steam exported represents, on average, around 0.95 % of the total energy output. The assumed curve is presented in Figure 4-35b.



(a) (b)

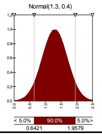
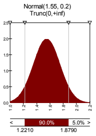
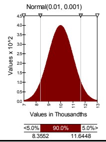
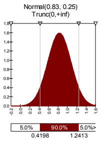
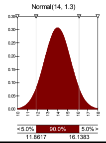
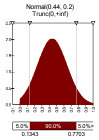
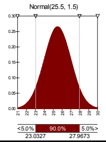
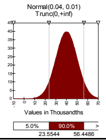
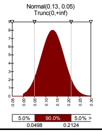
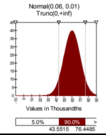
Figure 4-26: Energy requirement assumptions for a mega-size methanol plant (HHV).

For emission calculation in mega-size plants using combined syngas production, FUEEM assumes emission rates directly in terms of grams of pollutant per Giga Joule (GJ) of methanol produced. The emission rates account for some mass and heat integration between the SMR and the POX. The values are presented in Table 4-23. The air emission control factors for the mega-size plants are presented in Table 4-22.

Table 4-22: Air emission control efficiency for a typical-size methanol plant with SMR.

Pollutant	NO_x	CO	NMOG	CH_4	PM_{10}	N_2O
mean (%)	85.0	50.0	65.0	65.0	8.0	50.0
standard deviation	2.0	3.0	4	4.0	1.0	3.0

Table 4-23: FUEEM emission rates for a mega-size methanol plant (HHV).

Pollutants	Reformer emissions (g/GJ-MeOH)				Fugitive emissions (g/GJ-MeOH)			
	Min / Max[a]	Mode	Mean	Shape	Min / Max[a]	Mode	Mean	Shape
NO_x	0.64/1.96	1.3	1.3		-	-	-	-
CO	1.22/1.88	1.55	1.55		8.4/11.6 x 10^{-3}	0.01	0.01	
NMOG	0.42/1.24	0.83	0.83		11.9/16.1	14	14	
CH_4	0.13/0.77	0.44	0.45		23.0/28.0	25.5	25.5	
SO_x	0.024/0.056	0.04	0.04		-	-	-	-
PM_{10}	0.05/0.21	0.13	0.13		-	-	-	-
N_2O	0.044/0.076	0.06	0.06		-	-	-	-

a: At 90 % of confidence.

4.4.3 Fisher-Tropsch Naphtha production

At the beginning, the hydrocarbon conversion from synthesis gas is closely related to the history of methanol synthesis. In 1902, Sabatier and Senderens discovered that CO could be hydrogenated to methane over nickel (Ni) catalysts. In 1910, the development of a promoted iron (Fe) catalyst for the synthesis of NH_3 was carried on by Mittasch, Bosch and Haber (Anderson, 1984). Scientists at BASF, in 1913, received patents for the hydrogenation of CO for the formation of oxygenated compounds and higher hydrocarbons at higher pressure. However, synthetic hydrocarbon production from synthesis gas is today called the Fisher-Tropsch (FT) process due to the work of Franz Fischer and Hans Tropsch at the Kaiser Wilhelm Institute in Mühlheim-Ruhr (Germany). In 1923 they produced Synthol (mostly oxygenates) using alkalized Fe and other catalysts at high pressure (10 to 15 MPa), according to Anderson and Boudart (1981).

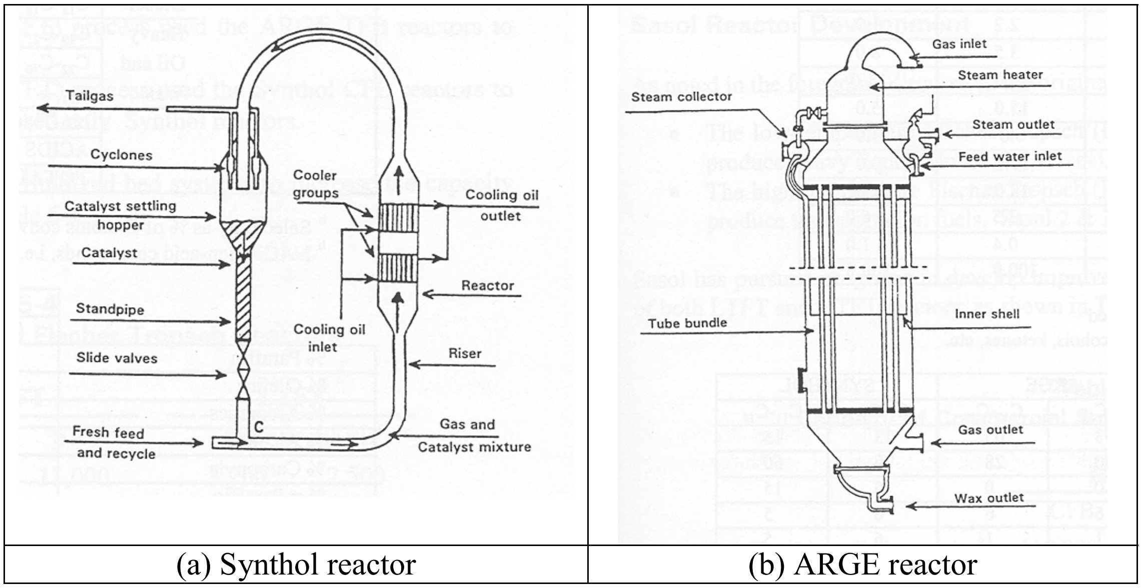
Since BASF held the patents covering high-pressure synthesis, Fischer and Tropsch started to work with hydrocarbon synthesis at normal pressure (1 atm). In 1925, they announced positive results over cobalt (Co) and nickel (Ni) catalysts, hypothesizing the idea that hydrocarbon was produced at low pressure and oxygenates at higher pressure. According to Anderson (1984) this hypothesis may have delayed the development of useful Fe catalysts for a decade as Fe catalysts deactivated rapidly at lower pressures. In spite of the concern about cobalt supply at that time, the nickel catalyst was discarded later because of its high tendency to produce methane and because of the formation of nickel carbonyl in the reactor.

After that, several German companies developed and commercialized the FT process with cobalt as the catalyst. Four Fischer-Tropsch production plants started operation in 1936. In 1944, during World War II, German production of synthetic hydrocarbon (mainly motor fuel) peaked around 700,000 tons/year. According to Anderson and Boudart (1981), nine plants were in operation by that time, and the "standard" catalyst was Co:ThO_2:MgO:diatomite (100:5:8:200). The synthesis gases were produced from coal by mean of gasification.

In 1937, Fischer and Pichler discovered that the life of the iron catalyst and the FT synthesis perform much better operating around 15 to 20 atm. From 1943 to 1944, at Schwarzheide, five companies participated in an effort to replace the cobalt-based catalyst with an iron-based catalyst. The effort was apparently successful, but no replacement occurred during the war. After World War II ended, the FT production in Germany stopped. Two firms, Lurgi and Ruhchemie, formed ARGE working on fixed bed reactor and precipitated iron catalysts.

In the USA, in 1948, Standard Oil and Hydrocarbon Research Inc. developed a fluidized bed reactor, as opposed to the traditional tubular reactor, for a new FT plant (Carthage Hydrocol, Inc.) commissioned in Brownsville, Texas. By 1950, the Kellogg Co. was investigating a circulating entrained catalyst version of the fluidized bed reactor, today known as the Synthol reactor. The Hydrocol plant had a capacity of 365,000 tons/year and it mainly produced gasoline from cheap natural gas (Tijm *et al*., 1995). The plant had several operational problems, such as achieving uniform fluidization, which required the construction of a new reactor. It was installed in 1953, apparently solving the problems; however, in 1957, the natural gas price more than doubled and the plant was shut down (Anderson, 1984). In the mid 1950's the discovery of large oil deposits in the Middle East reduced the price of petroleum and interest in the Fischer-Tropsch synthesis.

For political reasons, Fisher-Tropsch processes survived only in South Africa, producing fuels and chemicals from coal. Built and operated with government support, SASOL-I was designed having ARGE and Synthol reactors with an iron-based catalyst. The ARGE process produces a high yield of wax as opposed to the Synthol process producing a high yield of a liquid gasoline type fuel. SASOL-I began operation in 1955 with a capacity of about 5,000 barrels per day (bbl/day); however, the Synthol process took more than one year of mechanical and process modification to become operational. Figure 4-27 shows the actual version of these reactors at Sasol.



(a) Synthol reactor | (b) ARGE reactor

Figure 4-27: Sasol Fisher-Tropsch reactors (sources: Steynberg *et al.*, 1999 and Espinoza *et al.*, 1999)

The oil embargo in 1973 renewed the interest for R&D in Fischer-Tropsch. In 1975, South Africa decided to build SASOL-II, commissioned in 1980, and in 1979, they decided to build SASOL-III, commissioned in 1982. The new plants have the capacity of 50,000 bbl/day each and their configuration is pretty much the same as SASOL-I but only

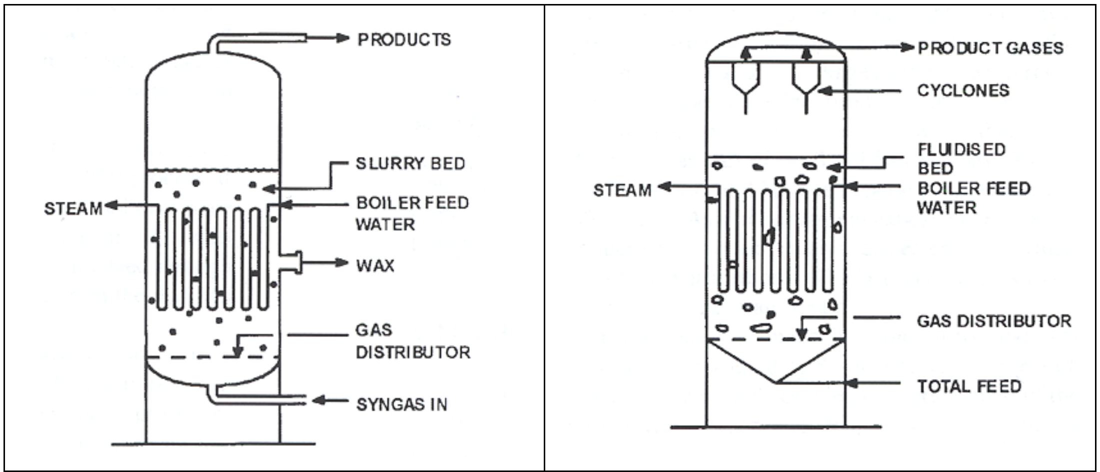
Synthol reactors are used, with some modifications made to them (heat exchangers, reactor diameter and pressure).

The worldwide recession in the 1980's and the low price of petroleum at that time slowed down the interest in coal again. In the 1990's interest shifted to natural gas due to the discovery of several large reserves, and also due to environmental concerns about vented and flared gas. Huge investments on Fisher-Tropsch research and development have occurred since then, mainly targeting the development of new catalyst systems and reactor design for better efficiency and cost reduction. Today, the key players are: Sasol, Shell, Exxon, Statoil, IFP, Syntroleum/ARCO, Rentech, BP/Kvaener, Energy International and Conoco/DuPont.

The ARGE type of reaction, which produces more heavy paraffin, is classified today as the low-temperature Fisher Tropsch process, operating between 220 and 270 ^{o}C (Farrauto, 1997). One of its evolutions led to the development of a slurry phase reactor within Sasol called SSPD (Sasol Slurry Phase Distillate). According to Espinoza *et al*. (1999), the SSPD process uses a new proprietary catalyst, which is mainly promoted cobalt supported on either silica, alumina or titania. Since 1993, Sasol has operated a slurry phase distillate (SSPD) reactor of 2,500 bbl/day capacity. A slurry type of reactor for low-temperature FT synthesis is also under development by Exxon. According to Eisenberg *et al*. (1998) it is called AGC-21 and also uses a cobalt-based catalyst. A sketch design for this kind of reactor is presented in Figure 4-28a.

According to Tijm *et al*. (1995), between 1973 and 1990 Shell Research Amsterdam developed the SMDS (Shell Middle Distillate Synthesis) and applied it in a 12,500 bbl/day plant commissioned in 1993 at Bintulu, Malaysia. The plant uses natural gas as feedstock and uses a new proprietary catalyst (silica or alumina-supported cobalt promoted with Zr, Ti or Cr). The low-temperature SMDS is still using a multi-tubular fixed-bed reactor because, according to Geerlings *et al*. (1999), the optimized reactor/catalyst combination favors the tubular configuration due to absence of catalyst attrition and of necessity for separation units between the catalyst and the liquid product.

On the other hand, Sasol is still developing the Synthol process, classified today as high-temperature FT-synthesis (300 to 350 ^{o}C). According to Steynberg *et al* (1999) the product of this process is mainly a gasoline type of fuel containing olefins (60 % to 70 %), some aromatics (5 % to 15 %) and some oxygenates (10 % to 12 %). The reactor evolution is an 11,000 bbl/day fluidized bed reactor called SAS (Sasol Advanced Synthol). Syngas is bubbled through a fluidized bed between 20 and 40 bars (290 to 580 psi) of pressure, containing a reduced fused iron oxide catalyst. The new design targeted the reduction of the temperature differences and the complexity of circulating catalyst loads (Jager, 1998). Figure 4-28b presents a sketch of the SAS reactor.



(a) Slurry bed reactor - SSPD

(b) Fluidized bed reactor - SAS

Figure 4-28: Sasol new generation of FT reactors (source: Jager, 1998)

4.4.3.1 Fisher-Tropsch synthesis

Several chemical reactions occur in the Fisher-Tropsch synthesis depending on the catalyst system used and the operation parameters utilized. Through a catalytic conversion the process converts synthesis gases into hydrocarbons, alcohol, ketones, and organic acid products. According to Lee (1997), if the syngas hydrogen/carbon monoxide ratio is 2.0, then the main reaction will be:

$$n\,CO + 2n\,H_2 \leftrightarrow (\text{-}CH_2\text{-})_n + n\,H_2O \qquad \text{Equation 4-13}$$

And for the hydrogen/carbon monoxide ratio of 0.5 it will be:

$$2n\,CO + n\,H_2 \leftrightarrow (\text{-}CH_2\text{-})_n + n\,CO_2 \qquad \text{Equation 4-14}$$

Both equations are linked to the water shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$), and the carbon deposition over the catalyst, by means of the Boudouard reaction ($2\,CO \leftrightarrow CO_2 + C$), is always an operational concern. The bonds established between the reactants and the catalyst are more important than the general equations 4-13 and 4-14. These bonds define the hydrocarbon chain growth and branching, as well as the termination and selectivity towards a certain type of product. Even after a long period of Fisher-Tropsch practice, its theory is still generating a lot of scientific investigation. The problem is to find a general FT model/theory that simulates the product and by-product selectivity under certain conditions. The actual selectivity found in practice, for example, is very different from that expected from thermodynamic calculation. It is not the objective of this dissertation to present details of this scientific discussion, but a good overview of it can be seen in Dry (1981) and Schulz (1999). A general FT reaction scheme is presented in Figure 4-29.

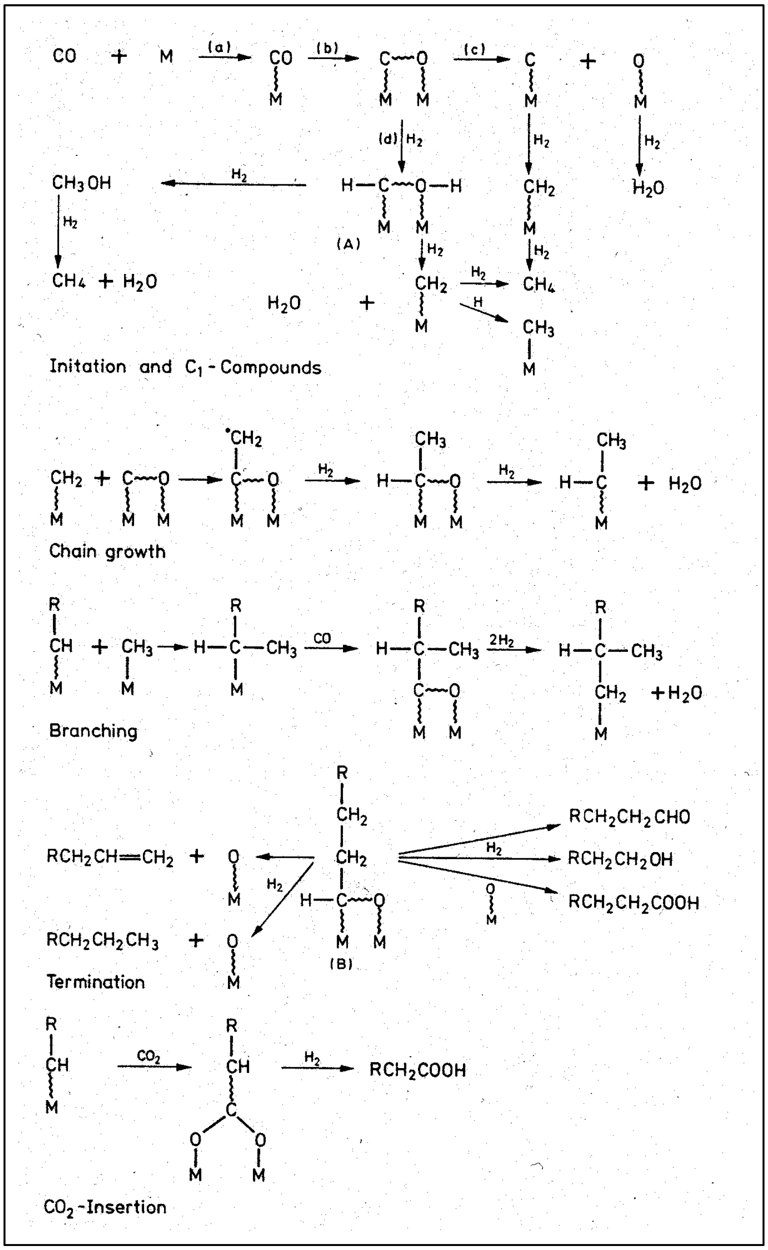


Figure 4-29: General Fisher-Tropsch synthesis reaction scheme (source: Dry, 1981)

Some issues related to the FT synthesis are important to understand, however. One issue is understanding that the product from the synthesis reactor will be a mix of components that will require a downstream separation/processing treatment. Part of the selectivity limitation is inherent to the chain growth mechanism that is governed by ASF

(Anderson-Schulz-Flory) kinetics according to Farrauto *et al*. (1997). In other words, it shows that the degree of polymerization can be altered only partially by choosing process conditions and/or catalyst. Figure 4-30 shows the percentage of different hydrocarbon FT product cuts related to the probability of chain growth (α).

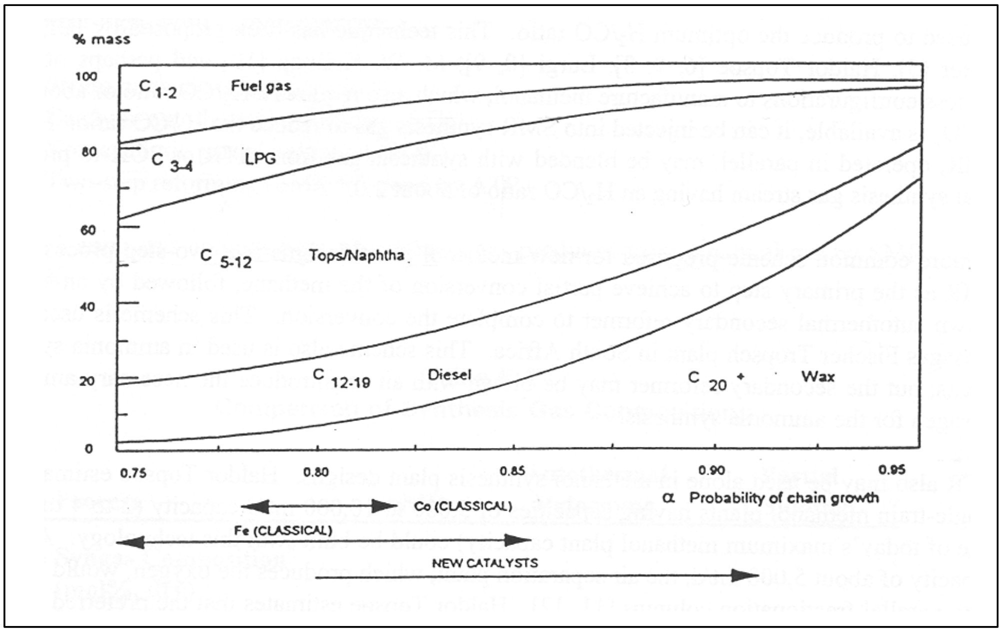


Figure 4-30: Generic Fisher-Tropsch yields associated with the catalyst used (source: Tijm *et al*, 1995)

A second issue is related to the development of the “wax/crack” technology. The high temperature FT synthesis, which is based on a iron catalyst, produces a high percentage of gas out of gas (up to C_4) decreasing the efficiency of the system. On the other hand, most of the new catalysts developed to improve “α” are, in general, cobalt based catalysts working on low temperature synthesis that produces a high percentage of wax.

It is important to say that the high temperature FT synthesis is a very good process when the syngas has a low H_2/CO ratio, such as the syngas from coal gasification, and when the product octane number is of interest, such as gasoline for internal combustion engines. The olefins and aromatic compounds coming from the iron catalyst reactions are responsible for increasing the octane number of the liquid fuel produced. This high octane number is not achieved in the liquid fuels produced from the low temperature FT synthesis due to its high paraffin content.

However, the high paraffin content produces high cetane numbers, good for a diesel type of fuel, and the low octane number for hydrogen carrier fuels (fuel for fuel cell vehicles) is not applicable. By increasing "α" and the carbon efficiency of the FT reaction, the new low temperature process produces a high quantity of wax that can be hydrocracked later into diesel, kerosene and naphtha fuels. In addition, no FT fuels have sulfur in them, which makes the FT-diesel very valuable as a blend fuel to respond to the worldwide pressure for low-sulfur and low-aromatic diesel. The sulfur-free naphtha portion of it is also an interesting fuel for reformation. This market combination of the clean FT-diesel and the special fuel for fuel cell vehicles (FT-naphtha) can make the FT process much more attractive in economic terms. According to Schulz (1999), many authors regard low temperature FT synthesis as the most efficient process for clean FT-diesel production.

The wax cracking process can also be controlled to make the FT plant more flexible for several cuts. Tijm *et al*. (1995) suggested that the Shell process (SMDS) can operate in two different modes: Gas-oil and kerosene. Figure 4-31, from Sie *et al* (1988), presents the FT composition after the Shell hydrocracking process.

4.4.3.2 FUEEM assumptions

As explained above, FUEEM assumes the low temperature Fisher-Tropsch synthesis as the most probable technology to produce zero-sulfur naphtha fuel, to be used as a hydrocarbon carrier for reformation on-board a fuel cell vehicle. By doing that, some parameters in the FT plant design can be discussed and established.

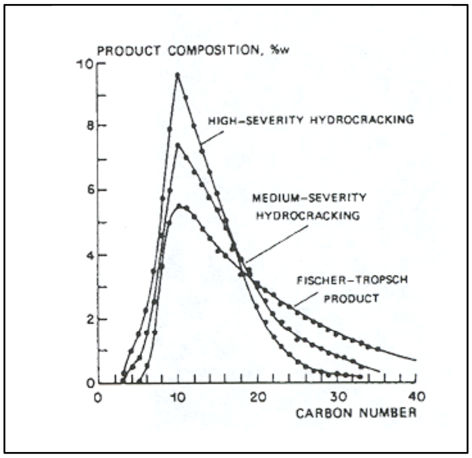


Figure 4-31: Selective hydrocracking process performance with FT product (source: Sie *et al*, 1988).

One parameter assumed is the plant capacity of 5,000 mtpd. It is a conservative size for some experts who believe the reactors can be scaled up without problems, especially by the slurry configuration. However, for other experts it is not so simple and needs to be demonstrated first. The ideal H_2/CO ratio for low temperature synthesis is around 2.0, perfect for combined steam methane reformation with partial oxidation syngas production with the chosen plant capacity. Future bigger plants may use autothermal reformation.

Another parameter is the system pressure, in the range of 18 to 26 atm (260 to 380 psi) much lower than the methanol synthesis. It allows the Fisher-Tropsch plant design to consider an alternative approach of using air for the reformation instead of pure oxygen. The extra energy required to compress inert gases (mainly N_2) through the system may economically compensate for the elimination of the O_2 production plant. Both designs are considered in FUEEM.

The major low-temperature Fisher-Tropsch reaction is highly exothermic (for example, - 167.4 KJ/mol-CO for the equation 4-13 with $n = 1$). It makes the FT reactor design more of a challenge but it motivates heat integration for extra-steam production. The thermal efficiency for a FT plant using a slurry reactor, pure oxygen and no extra-steam generation is in the range of 58.5 % to 66 % (90 % of confidence). The curve is presented in Figure 4-32a. For a similar plant but with extra-steam produced for exportation, the efficiency is in the range of 65 % to 71 % after incorporating the steam credits in an energy basis. The curve is presented in Figure 4-32b. To calculate the carbon mass balance for CO_2 emissions, the carbon efficiency of this same plant is assumed between 77.8 % and 78.8 %. The carbon efficiency is defined as the total carbon out (in the fuels) per the total carbon in the natural gas consumed. The carbon efficiency curve is presented in Figure 4-32c.

The thermal efficiency for a FT plant using a multi-tubular reactor, pure oxygen and no extra-steam generation is in the range of 52 % to 55 %. The curve is presented in Figure 4-33a. For a similar plant but with extra-steam produced for exportation, the efficiency is in the range of 58.5 % to 64.3 % after incorporating the steam credits in an energy basis. The curve is presented in Figure 4-33b. To calculate the carbon mass balance for CO_2 emissions, the carbon efficiency of this same plant is assumed between 72 % and 73 %. The carbon efficiency curve is presented in Figure 4-33c. In all cases, the efficiency reduction applied when an air control emission design is assumed (i.e., SCR) is the same assumed for methanol production.

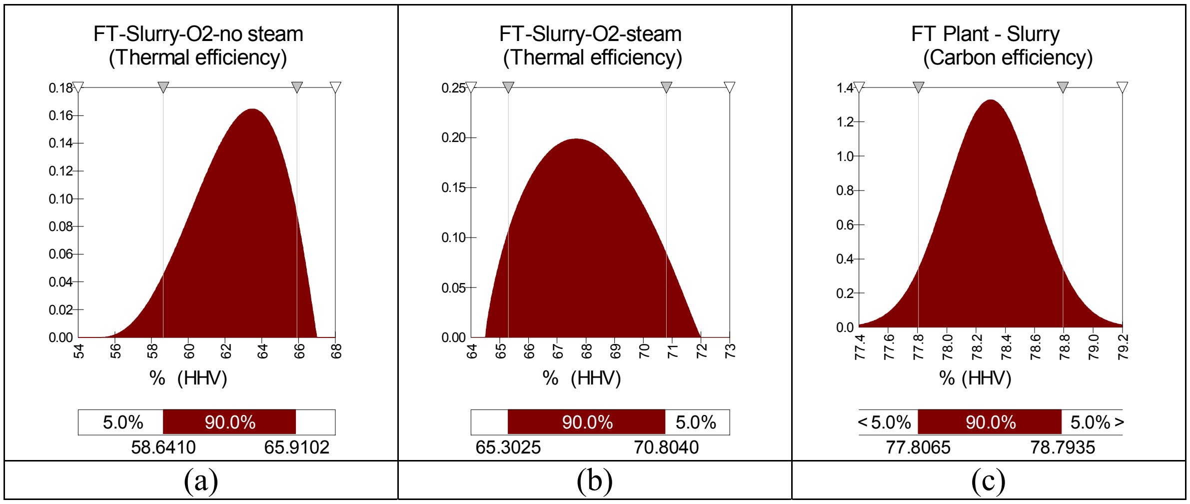


Figure 4-32: FUEEM assumptions for a FT plant with a slurry reactor and no SCR.

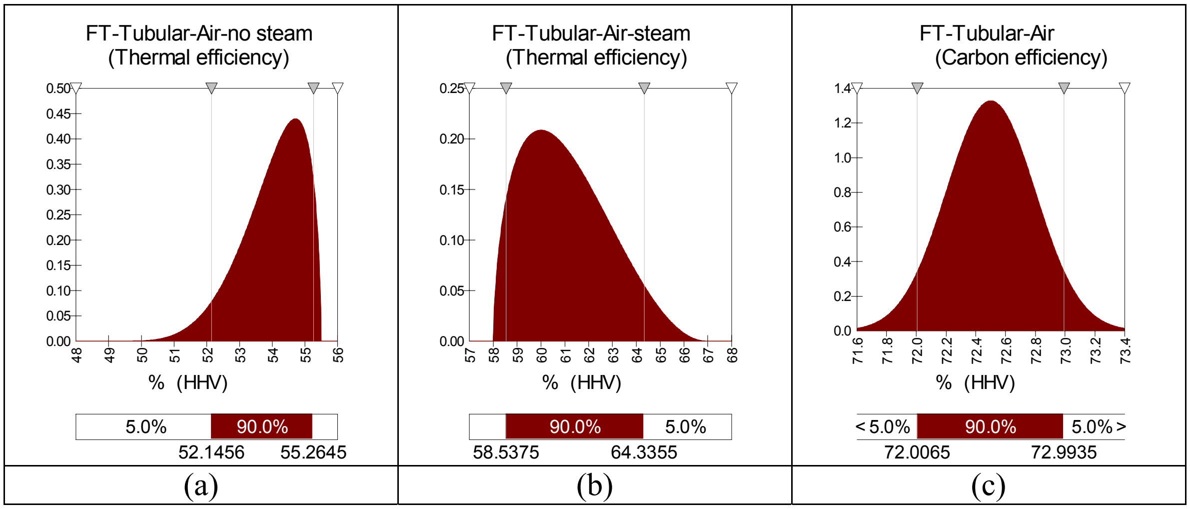
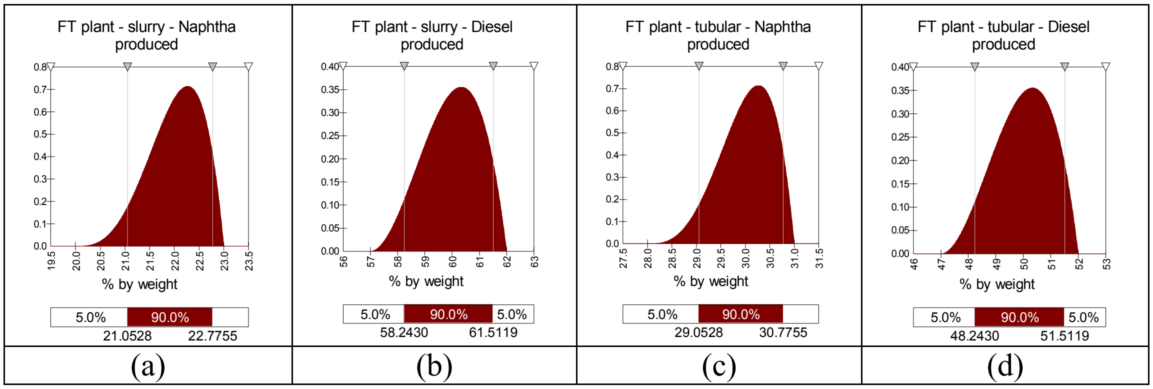


Figure 4-33: FUEEM assumptions for a FT plant with a tubular reactor and no SCR.

The final product cuts (after hydrotreating, hydrocracking and distillation) are classified in terms of Naphtha having a carbon number between 5 and 8 (C_5 to C_8), Kerosene (C_9 to C_{11}) and Diesel (C_{12} to C_{18}). For the slurry plant configuration, the percentage by weight of naphtha produced is assumed between 21 % and 22.8 % (90 % confidence) and diesel between 58 % and 61.5 %. The curves are presented in Figure 4-34 a and b. The difference to 100 % is kerosene cut. For the tubular plant configuration, the percentage by weight of naphtha produced is assumed between 29 % and 30.8 % and diesel between 48.2 % and 51.5 %. The curves are presented in Figure 4-34 c and d.

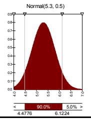
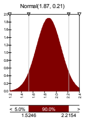
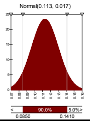
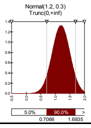
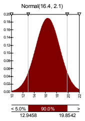
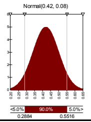
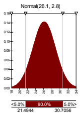
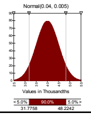
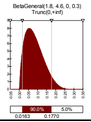
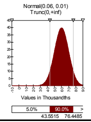


(a) (b) (c) (d)

Figure 4-34: FT production cuts for the slurry plant configuration (a and b) and for the tubular plant configuration (c and d).

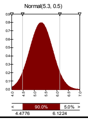
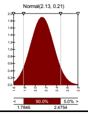
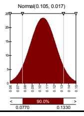
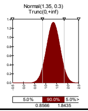
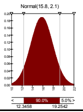
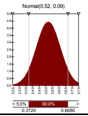
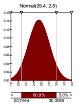
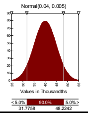
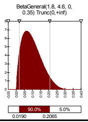
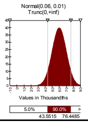
The emissions released by the plants are calculated based on the emission rates assumed for the uncontrolled situation. Table 4-24 presents the emission rates for the slurry plant design using pure oxygen for syngas production and no extra-steam production. Table 4-25 presents the emission rates for the tubular plant design using air for syngas production and no extra-steam production.

Table 4-24: FUEEM emission rates for a uncontrolled FT plant using slurry reactor, O_2 syngas plant and no steam exportation (HHV).

Pollutants	Reformer emissions (g/GJ-FTmix)				Fugitive emissions (g/GJ-FTmix)			
	Min / Max[a]	Mode	Mean	Shape	Min / Max[a]	Mode	Mean	Shape
NO_x	4.48/6.12	5.30	5.30		-	-	-	-
CO	1.52/2.22	1.89	1.89		0.08/0.14	0.11	0.11	
NMOG	0.71/1.70	1.20	1.20		12.9/19.9	16.4	16.4	
CH_4	0.29/0.55	0.42	0.42		21.5/30.7	26.1	26.1	
SO_x	0.03/0.05	0.04	0.04		-	-	-	-
PM_{10}	0.02/0.18	0.05	0.08		-	-	-	-
N_2O	0.21/0.70	0.45	0.45		-	-	-	-

a: At 90 % of confidence.

Table 4-25: FUEEM emission rates for a uncontrolled FT plant using tubular reactor, air syngas plant and no steam exportation (HHV).

Pollutants	Reformer emissions (g/GJ-FTmix)				Fugitive emissions (g/GJ-FTmix)			
	Min / Max[a]	Mode	Mean	Shape	Min / Max[a]	Mode	Mean	Shape
NO_x	6.00/7.62	6.80	6.80		-	-	-	-
CO	1.78/2.48	2.13	2.13		0.08/0.13	0.11	0.11	
NMOG	0.86/1.84	1.35	1.35		12.3/19.3	15.8	15.8	
CH_4	0.37/0.67	0.52	0.52		20.8/30.0	25.4	25.4	
SO_x	0.03/0.05	0.04	0.04		-	-	-	-
PM_{10}	0.02/0.21	0.06	0.10		-	-	-	-
N_2O	0.21/0.70	0.45	0.45		-	-	-	-

a: At 90 % of confidence.

4.5 Fuel Characteristics

The objective of this section is to present some of the details and assumptions related to fuel composition, energy content, fuel density, etc. It also presents the assumptions for the life cycle values of some secondary fuels.

4.5.1 Natural Gas

The FUEEM database for raw natural gas composition (at the wells) has data for the average U. S. gas composition, and for the average composition of gas withdrawn in the state of Texas and California. It also has data for Medanos and Ventura – both local regions within California. For other countries it has data from Canada, Venezuela, Algeria, Malaysia and the North Sea. Based on these data, FUEEM assumed a "typical" raw natural gas composition for associated gas coming from oil wells, and a "typical" composition for non-associated gas. The assumed composition curves are basically normal distribution and their means and standard deviations are presented in Table 4-26.

Table 4-26: FUEEM natural gas composition assumed.

Composition	**NG Raw**				**Processed NG**			
	Oil Wells		**Gas Wells**		**typical**		**High N_2/air**	
	mole %		**mole %**		**mole %**		**mole %**	
	(mean)	(std dev.)	(mean)	(std dev.)	(mean)	(std dev.)	(mean)	(std dev.)
Metane (CH_4)	83.27	calculated	89.88	calculated	92.53	calculated	86.50	calculated
Ethane (C_2H_6)	5.61	1.4	4.17	0.3	4.50	0.9	3.00	0.31
Propane (C_3H_8)	3.85	1	2.59	0.19	0.70	0.19	0.80	0.2
Higher Hydroc.	3.10	0.9	1.97	0.04	0.35	0.1	0.40	0.12
CO_2	0.59	0.2	0.42	0.15	0.50	0.15	0.30	0.1
N_2/air	1.80	0.6	0.90	0.3	1.42	0.6	9.00	0.8
H_2S (Hyd. Sulfide)	0.07	0.021	0.07	0.021	0.0003	0.0001	0.0003	0.0001
H_2O	1.70	0.4	0	0	0	0	0	0
Total	100.00		100.00		100		100	

For the gas processed (marketable piped gas) the database has data for the average U.S. gas, and for Texas, California, Los Angeles, and San Francisco area. In terms of other countries, the FUEEM database contains Canada, the United Kingdom, Chile, and Australia. Based on these data, FUEEM assumed a “typical” natural gas composition and a natural composition rich in nitrogen. The assumed composition curves are basically normal distribution and their means and standard deviations are presented in Table 4-26 as well.

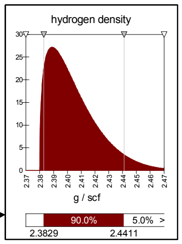
If a change in the gas composition is necessary, the model automatically calculates the energy content of the gas and its density, based on Van der Lugt’s (1986) method that considers non-ideal gas relations.

4.5.2 Hydrogen

Hydrogen is a pure substance and the variation in its physical properties is very small. The values encountered in the literature are presented in Table 2-3. Table 4-27 presents the mean and the standard deviation for each of the FUEEM assumed curves. All of them but the hydrogen density are normal distribution curves. The fuel density, in terms of gram per standard cubic feet, assumes a Beta General curve. The shape of it is indicated parallel to Table 4-27.

Table 4-27: FUEEM assumptions for hydrogen fuel.

Analized Fuel	**Hydrogen - H2**	
	mean	std dev.
Energy content (Btu/scf - HHV)	324	0.7
Energy content (Btu/scf - LHV)	274	0.3
Molecular Weight (g/mol)	2.016	0.0005
Fuel density (g/scf)	2.40	0.018



4.5.3 Methanol

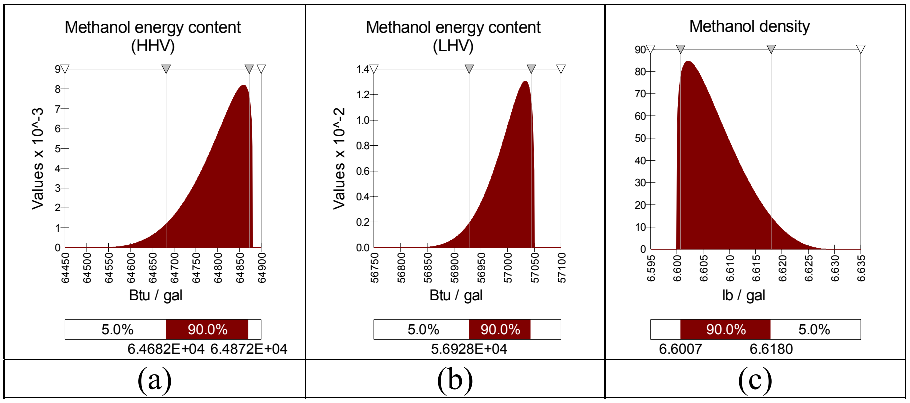
Methanol is also a pure substance and its physical properties do not change with the fuel composition. The physical properties used by existing studies are presented in Table 4-28. Under the AP-42 column there is a mix of values from different studies other than the EPA-AP/42 (1995). The energy content is from DTI (1998) and the Reid Vapor Pressure (RVP) is from CEC (1996). The True Vapor Pressure (TVP) is dependent on the temperature and the value of 2.61 psi refers to 80 ^{o}F. A 3.5 psi assumed by Acurex (1996) refers to a temperature over 90 ^{o}F according to Table 7.1-3 of the EPA-AP/42 (1995). FUEEM considers the temperatures assumed in the marketing liquids calculation (see section 4.3) to calculate the TVP, following the EPA-AP/42 (1995) method.

The biggest disagreement in the literature data is related to the RVP. The RVP of 3.5 psi is used by the California Energy Commission (1996), and the Methanex Responsible Care (1997) uses 3.4 psi. Unnasch *et al*. (1996 and 2000) use 4.5 psi, which is similar to the value used by the World Bank (1996) report (4.6 psi). Since the RVP is measured at 100 ^{o}F, it is possible that these studies extrapolate the TVP for that temperature, and this is not the correct procedure. FUEEM assumes a normal distribution curve with a mean equal to 3.45 psi and standard deviation of 0.02 psi.

The other assumptions using Beta General curves are presented in Figure 4-35.

4.5.4 Fisher-Tropsch Naphtha

Fisher-Tropsch (FT) fuel is similar to crude oil in the sense that it contains several components and may have different compositions under the same name. At least, for a low-temperature FT reaction, olefins and aromatics are not present in the FT synthesis product, which, usually are only paraffin carbon chains.



(a) (b) (c)

Figure 4-35: FUEEM assumptions for the methanol characteristics

Similar to the crude oil industry, the literature divided the FT fuel products according to their number of carbon. From five carbons (C5) to eight carbons (C8) it is called naphtha, from C9 to C11 it is kerosene, from C12 to C19 it is diesel and over twenty carbons (> C20) in the molecular chain it is wax that is solid at room temperature. This classification is not a standard and may vary in different studies or companies. The molecular characteristics within the same number of chain carbon can also be different, changing the characteristics of the fuel (for example, iso-Heptane versus n-Heptane)

The literature data, in terms of density of the fuel (g/ml), high heating energy content (Btu/gal) and carbon ratio (% by weight), are presented in Table 4-29. FUEEM assumed curves for the FT product characteristics are presented in Table 4-30. The curves assumed are for each liquid fuel classified in the product (naphtha, kerosene and diesel) and all have normal distribution. The FT mix-product characteristics are calculated based on the composition assumed (see section 4.4.3).

Table 4-28: Methanol physical parameters used by existing studies.

Analized Fuels	**METHANOL - MeOH**									
Sources	AP-42 (95)	Heywood (88)	Acurex (96)	ADL (2000)	DeLucchi (93)	Greet 1.5a	MIT (00)	Methanex(00	Ogden (99)	ITS (2001)
Energy content (Btu/gal - HHV)	64600	64501	64800	64800	64500	64800			65000	64800
Energy content (Btu/gal - LHV)	56600	56829	57000	57000	57000	57000	57000	57000	57000	57011
Fuel density (lb/gal)	6.63	6.61	6.60	6.60	6.61	6.61	6.60			6.63
Molecular Weight (g/mol)	32.04	32.04								32.04
Carbon Content (% wt)			37.5		37.5	37.5	37.5			
RVP - Reid Vapor Pressure (psi)	3.5		4.5	4.5						
TVP - True Vapor Pressure (psi)	2.61		3.5	3.5						

Table 4-29: Fisher-Tropsch characteristics from the literature.

FT Product Characteristics											
	Density g/ml				HHV Btu/gal				Carbon ratio % by wt		
Naphtha	0.69	0.69				116500				84.1	
Kerosene	0.74	0.74				125000				84.5	
Diesel	0.80	0.78		0.77	128500	133000	128500	128726	86	85.0	86
FT-mix (for high temp. reactors)							103575				
FT-mix (for low temp. reactors)	0.769	0.755	0.786			127930				84.7	
Source	Company A	Shell	Sasol	Unnasch	Greet 1.5a	Company A	Unnasch	Louis (01)	Greet 1.5a	Company A	Unnasch

Table 4-30: FUEEM assumed curves for low-temperature Fisher-Tropsch fuels.

Characteristics	**Density (g/ml)**		**HHV (Btu/gal)**		**C ratio (% wt)**	
Fuels	mean	std. dev.	mean	std. dev.	mean	std. dev.
Naphtha	0.69	0.005	116500	400	84.1	0.25
Kerosene	0.74	0.006	125000	420	84.5	0.25
Diesel	0.79	0.008	129300	500	85.5	0.25

For the specific case of light naphtha considered for fuel cell vehicle fuel, FUEEM assumes the molecular weight of 98 g/mol (normal distribution with standard deviation of 2 g/mol) and the Reid Vapor Pressure (RVP) of 5.1 psi (standard deviation of 0.25). For the calculus of the True Vapor Pressure (TVP) FUEEM uses the EPA/AP-42 (1995) method (Figure 7.1-14b in the EPA report) assuming a fuel saturation factor equal to 3.5.

4.5.5 Secondary fuels

FUEEM assumes several characteristics of other fuels to use in the secondary calculations. Only the conventional gasoline data is used to extrapolate the liquid fuel evaporative data and also to compare the vehicle fuel economy in terms of gallon of gasoline equivalent. It is important to point out again that all the petroleum-based fuel is a mix of several components and changes for different situations. The database of FUEEM contains the information assumed for several of the existing studies but it is not presented here since the secondary calculation is not a significant contributor to the final result (see section 5.4.1.3).

FUEEM assumes that the energy content (HHV) of conventional gasoline is a probabilistic curve with a mean of 124,800 Btu/gal and standard deviation of 200 Btu/gal. The gasoline density assumed is 6.0 lb/gal (standard deviation equal to 0.1 lb/gal) with molecular weight of 70.5 g/mol (Beta General curve with minimum of 66 g/mol and maximum of 73 g/mol – α_1 equal to 3.7 and α_2 equal to 2). The RVP assumed is 9.4 psi (standard deviation of 0.6 psi) and for the calculus of the TVP a fuel saturation factor of 3.0 is assumed.

For diesel, the energy content (HHV) assumed is 139,000 Btu/gal (standard deviation equal to 500 Btu/gal) with density of 7.17 lb/gal (standard deviation equal to 0.1 lb/gal) and carbon content of 86.8 % by weight (standard deviation equal to 0.3 %). The assumed sulfur content is 430 ppm by weight for conventional diesel (standard deviation equal to 19 ppm) and 30 ppm by weight for reformulated diesel (standard deviation equal to 1 ppm).

For residual oil (bunker fuel), the energy content (HHV) assumed is 149,300 Btu/gal (standard deviation equal to 200 Btu/gal) with a density of 8.0 lb/gal (standard deviation equal to 0.1 lb/gal) and carbon content of 88.5 % by weight (standard deviation equal to 0.5 %). The assumed sulfur content is 1 % by weight (standard deviation equal to 0.2 %).

For crude oil (petroleum), the energy content (HHV) assumed is 19,500 Btu/lb (standard deviation equal to 50 Btu/lb) with a density of 7.1 lb/gal (standard deviation equal to 0.1 lb/gal) and carbon content of 85.0 % by weight (standard deviation equal to 0.7 %). The assumed sulfur content is 1.5 % by weight (standard deviation equal to 0.3 %).

4.5.6 Life cycle values for secondary fuels

For the life cycle values necessary for the secondary calculation, the total energy requirement of 104,000 Btu required per MBtu of fuel consumed (HHV) with a standard deviation of 2,600 Btu/MBtu is assumed for the residual oil. About 98 % of this energy comes from fossil fuel energy and about 65 % comes from petroleum. The assumed life cycle emissions for the residual oil are presented in Table 4-31.

Table 4-31: FUEEM assumptions for the life cycle emissions of residual oil.

Emissions (g/GJ)	Residual oil life cycle	
	mean	std. deviat.
NOx	45.29	8.2
NMOG	8.04	1.0
CO	32.06	6.5
PM10	4.5	1.2
SOx	19.79	5
CH4	88.13	2.1
N2O	0.45	0.2
CO2	9607	466

A life cycle total energy requirement of 122,000 Btu required per MBtu of fuel consumed (HHV) with a standard deviation of 5,000 Btu/MBtu is assumed for the reformulated diesel. About 99 % of this energy comes from fossil fuel energy and around 85 % comes from petroleum. The values for conventional diesel are around 97 % of the reformulated diesel values. The assumed life cycle emissions for both diesels are presented in Table 4-32.

Table 4-32: FUEEM assumptions for life cycle emissions of diesel.

Emissions (g/GJ)	Diesel life cycle		
	reformulated	conventional	std. deviat.
NOx	27.5	28.3	2.8
NMOG	11.5	11.7	2.0
CO	17.7	18.5	5.0
PM10	3.0	5.0	0.5
SOx	16.0	29.6	3.0
CH4	83.0	87.2	11.0
N2O	0.4	0.4	0.1
CO2	12500	13125	850

4.6 <u>Equipment characteristics</u>

The objective of this section is to present some of the details and assumptions related to marine tankers, trucks and general equipment such as boilers and engines. The assumed probabilistic curve values were used in the calculation and, wherever possible, they are referenced in each section.

4.6.1 Marine tankers

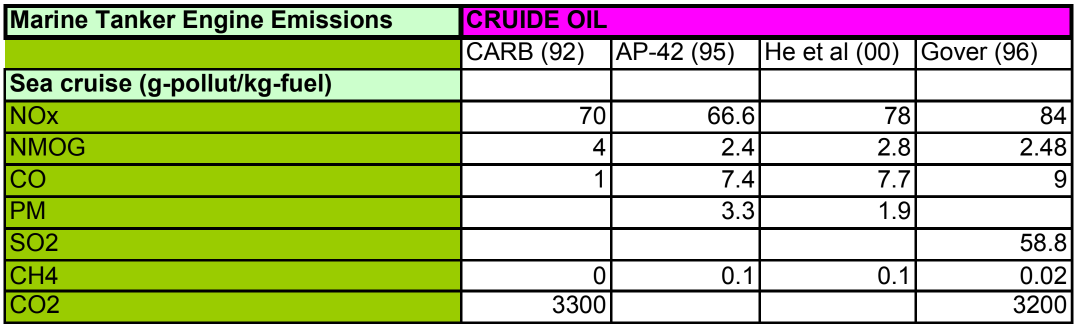
Most of the information about marine tankers relates to crude oil tankers. An exception is Giacomazzi's (1981) study presenting values for methanol, liquid hydrogen and liquid natural gas tankers. The tanker capacity is, in general, expressed in terms of dead weight tons (dwt). The range of the tanker capacity presented by Giacomazzi (1981) goes from 60,000 to 340,000 dwt for crude oil and methanol transport. According to him, the speed range of these tankers is from 14 to 17 knots[7]. He *et al*. (2000) report a speed of 16 knots and FUEEM assumes a normal distribution curve with a mean of 16 knots and standard deviation of 1 knot.

CARB uses in its calculation a 150,000 dwt with the energy intensity of 1.8 kg_{oil}/1000 tons-mile. These values are based on a 1990 report (in Unnasch, 1996). Values of 100,000 dwt are used by Specht *et al*. (1998) and by He *et al*. (2000). Gover *et al*. (1996) use a 250,000 dwt in their calculation. FUEEM uses a 150,000 dwt crude oil ship size in its calculation. Adjusting for the volumetric capacity, the methanol tanker carries on average 139,600 dwt and the Fisher-Tropsch naphtha tanker carries on average 121,650 dwt. A second scenario using the ship capacity of 250,000 dwt is recommended for future studies.

The fuel efficiencies of the ship engines, using bunker fuel (residual oil number 6 in the EPA classification) are reported by Pearson (1988) as 120 g of fuel per break horse power hour (bhp-hr). Cullinane *et al*. (1999) report the value of 125 g_{fuel}/bhp-hr. Based on them, FUEEM assumes for the fuel efficiency a normal distribution curve with a mean of 122.5 g_{fuel}/bhp-hr and a standard deviation of 1.8 g_{fuel}/bhp-hr.

The EPA (2000) reports the power capacity of 19,170 horsepower (hp) for a 100,000 dwt size ship. This value is consistent with the range of values presented by Giacomazzi (1981) for the same ship size. For a 150,000 dwt ship the range presented by Giacomazzi goes from 21,000 to 28,000 hp. FUEEM assumes for the 150,000 ship power capacity a normal distribution curve with a mean of 22,500 hp and standard deviation of 1,000 hp. This curve is adjusted for the methanol and FT-naphtha weight as well. Based on EPA (2000), the calculation also assumes an engine load factor of around 80 % (normal distribution with a mean of 80 % and standard deviation of 2 %).

Table 4-33: Emissions from the engines of a marine tanker using residual oil.



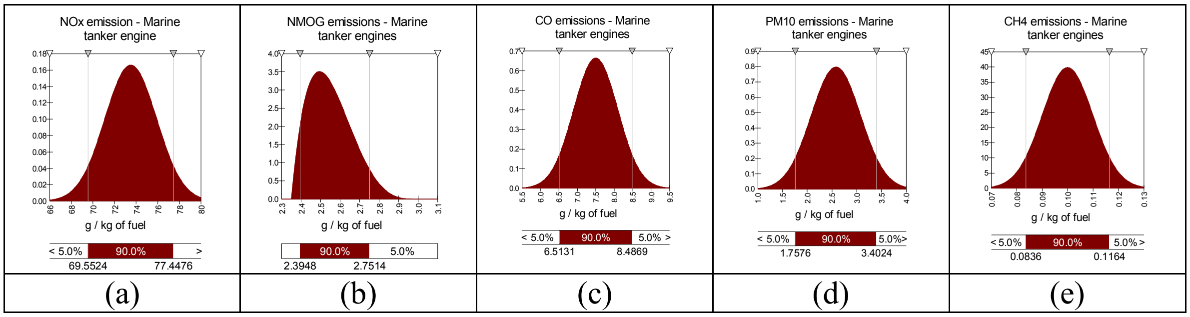
Marine Tanker Engine Emissions	**CRUIDE OIL**			
	CARB (92)	AP-42 (95)	He et al (00)	Gover (96)
Sea cruise (g-pollut/kg-fuel)				
NOx	70	66.6	78	84
NMOG	4	2.4	2.8	2.48
CO	1	7.4	7.7	9
PM		3.3	1.9	
SO2				58.8
CH4	0	0.1	0.1	0.02
CO2	3300			3200

The information about the emissions released by the engines of the ship tanker is presented in Table 4-33. According to He *et al*. (2000) the EPA (1998) uses test results from Lloyd's Register Inventory. The SO_2 emission data presented by Gover *et al.* (1996)

---

[7] knots is equal to 1 nautical miles (2000 yards) / hour or 1.137 miles/hour

are based on 2.8 wt % of sulfur content in the bunker fuel. SO_x and CO_2 emission rates in FUEEM are calculated by mass balance, considering the fuel composition. The emission rate curves of other pollutants are presented in Figure 4-36.



(a) (b) (c) (d) (e)

Figure 4-36: Emission rates for the marine tanker engines using bunker fuel.

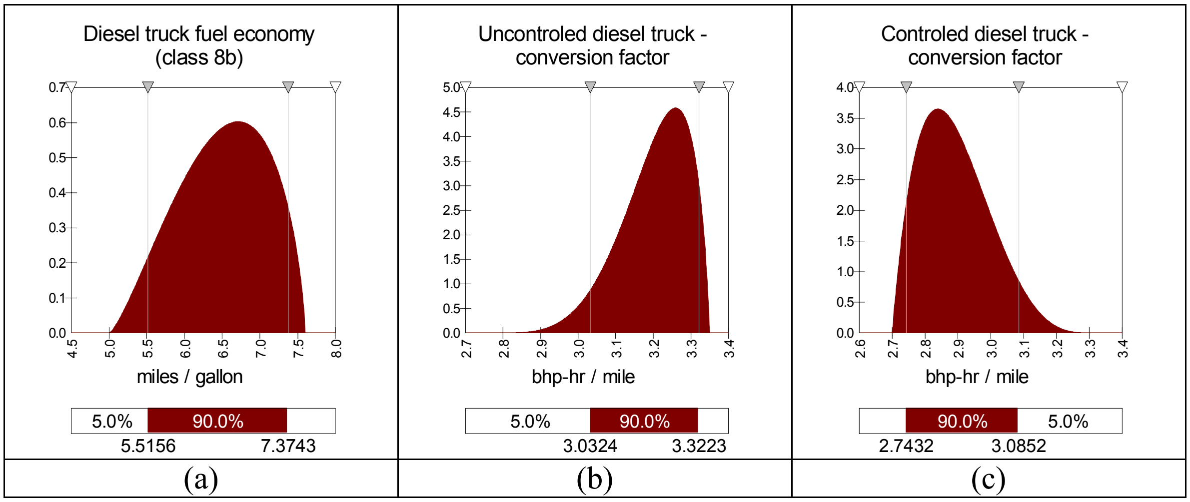
4.6.2 Trucks

Diesel trucks class “8b”(in EPA classification) are the most common size used in fuel marketing activities. The truck fuel economy values from some existing life cycle studies are presented in Table 4-34. In complement of that, Davis (2000) reports the truck fuel economy range from 5.9 to 6.2 miles per gallon (mpg). From table-5 of the EPA (1998) report, a class 8b truck in the year 2010 may have the fuel economy of 7.6 mpg. Considering that truck fuel economy and emissions measurement suffers from the same problems discussed for passenger vehicle measurement in section 5.2, FUEEM assumes for the diesel truck fuel efficiency a Beta General curve with a mean of 6.51 mpg (2.77 km/L). The curve is presented in Figure 4-37a.

In terms of emissions, the emission rates encountered in the literature are presented in Table 4-35, in terms of pounds per mile (lb/mile). In complement of that, the EPA-MOBILE 6 (1999) software forecast the emissions for heavy-duty trucks to be assembled after 2004. The MOBILE 6 calculates two types of emissions: one for brand new vehicles and another one for used vehicles, assuming some level of deterioration in the vehicle system. The emission factors are presented in terms of grams of pollutant per break horsepower hour (g / bhp-hr). Similar emission factor units are used by CARB in their EMFAC2000 software used in California emission inventory studies.

Table 4-34: Fuel economy of diesel trucks assumed by existing studies.

Diesel tanker truck (Class 8b)						
Studies/Models	ETSU (96)	DeLuchi (93)	Greet 1.5a	Darrow (94)	Acurex (96)	He et al (00)
Truck fuel economy (km/l)	3.05	2.55	2.13	2.13	2.13	2.13
Truck fuel economy (mi/gal)	7.17	6	5.0	5.0	5.0	5.0



(a) (b) (c)

Figure 4-37: FUEEM assumptions for diesel trucks (class 8b)

To convert the emission factor of g/bhp-hr into an emission rate in terms of pounds per mile or grams per kilometer, a conversion factor is necessary. Gaines *et al.* (1999) assume the conversion factor of 2.79 bhp-hr/mile, considering a reduction in the aerodynamic drag and rolling resistance in the future. Without the design optimization, the original value was 3.3 bhp-hr/mile. FUEEM assumes a Beta General curve for the conversion factor. For an uncontrolled truck, the curve has a mean of 3.2 bhp-hr/mile and is presented in Figure 4-37b. For a controlled truck, the conversion factor curve has a mean of 2.89 bhp-hr/mile and is presented in Figure 4-37c.

Table 4-35: Diesel truck emission rates assumed by existing studies.

Diesel tanker truck (Class 8b)						
Studies/Models	ETSU (96)	DeLuchi (93)	Greet 1.5a	Darrow (94)	Acurex (96)	He et al (00)
Truck emissions (lb/100mi)	controled	controled	controled	uncontroled	controled	controled
NOx	4.63	4.75	1.69	9.18	2.07	3.03
NMOG	0.16	1.16	5.08	2.92	0.37	0.15
CO	1.39	6.15	2.82	4.12	2.43	0.72
PM10	0.38	-	0.25	0.21	-	0.05
PM2.5	-	-	-	-	-	-
SOx	-	-	0.07	-	-	-
CH4	-	0.06	0.02	-	0	0.01
N2O	-	0.03	0.01	-	-	-
CO2	302.57	-	453.83	-	440.92	-

Since the final emission rate in terms of grams per kilometer (or lb/mile) is a composition of the conversion factor with the emission rates in terms of g/bhp-hr, and based on the fact that the conversion factor assumed in FUEEM has already incorporated the uncertainties in it, the decision was made to use fixed (deterministic) values for the assumptions in terms of g/bhp-hr.

The MOBILE-6 assumes the emission factor of 2.5 g/bhp-hr for a combination of NO_x and NMOG emissions. Based on Farshchi *et al*. (2001) FUEEM assumes the NO_x emission rate of 8.0 g/bhp-hr for uncontrolled trucks and 2.2 g/bhp-hr for controlled trucks. FUEEM also add the MOBILE-6 calculation for the system deterioration, considering the future VMT of 60,000 miles per year, according to Gaines *et al*. (1998). It is important to point out that the current vehicle miles traveled (VMT) is 46,513 miles per truck per year according to Davis (2000). The deterioration value calculated is 0.06 g of NO_x/km. The mean of the FUEEM total emission curve for controlled trucks is 4.02 g of NO_x/km, which is also consistent with the EMFAC-2000 result of 4.19 g of NO_x/km.

For NMOG the FUEEM assumption is 4 g/bhp-hr for uncontrolled trucks and 0.3 g/bhp-hr for controlled ones. The deterioration emission rate is 0.02 g/km. It is important to point out that the MOBILE-6 emission factor includes the crankcase emissions and five other sources of evaporative emissions (hot soak, diurnal, running loss, resting loss, and refueling).

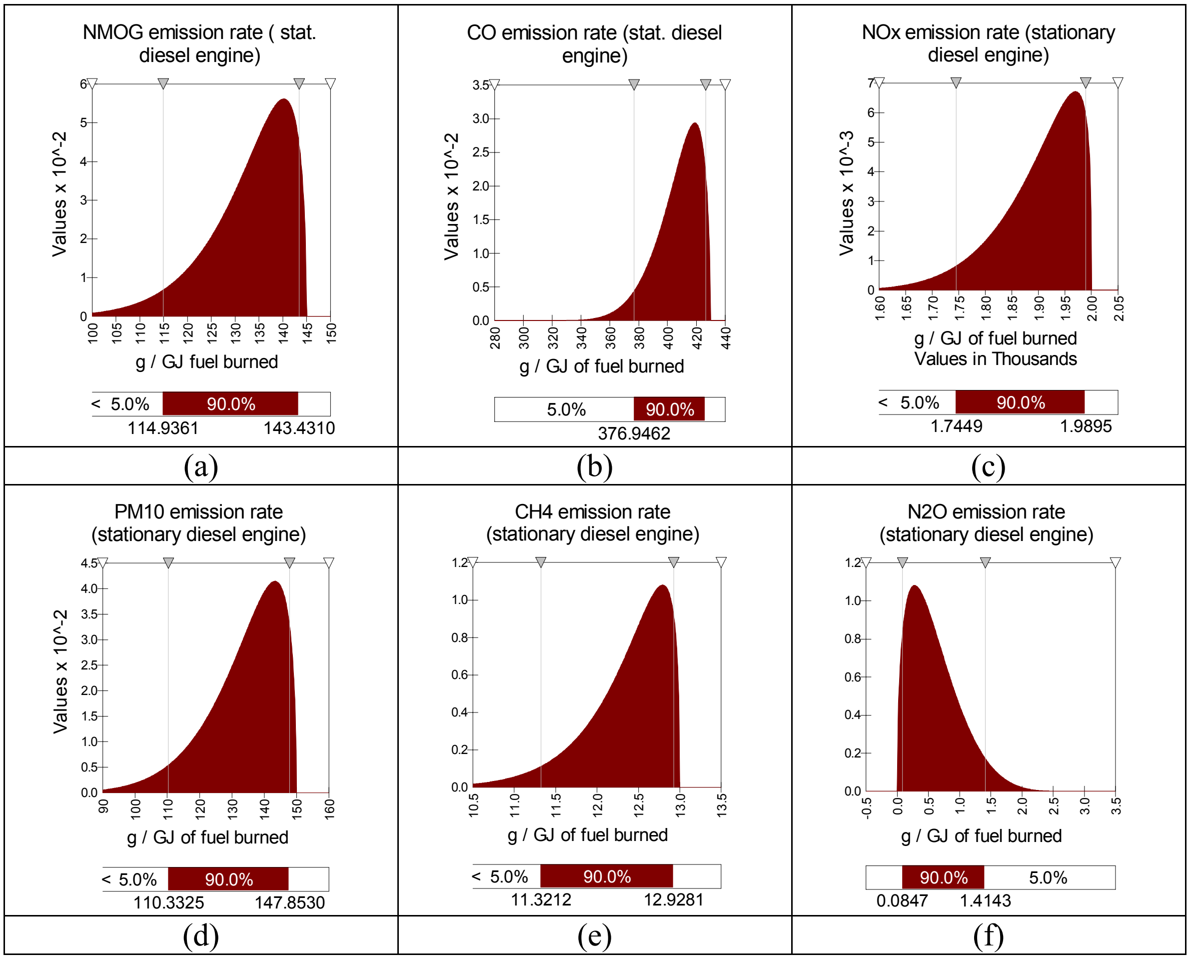
The MOBILE-6 emission factor for CO emissions is 15.5 g/bhp-hr. A similar emission rate was assumed for the FUEEM uncontrolled truck and an emission rate of 6.5 g/bhp-hr was assumed for the controlled truck. The PM_{10} emission rate assumed in FUEEM is 3.0 g/bhp-hr for the uncontrolled truck and 1.0 g/bhp-hr for the controlled one. These values are similar to the EMFAC-2000 emission factors.

4.6.3 Stationary diesel engines

The emission rates available in the literature for stationary diesel engines are presented in Table 4-36. The Greet 1.5 (2000) values are for the future technologies. EAP/AP-42 (1995) presents the value for total organic compounds (TOC) but it also states that 9 % of this emission is methane. The assumed FUEEM emission rate curves are presented in Figure 4-38.

4.6.4 Residual Oil Boiler

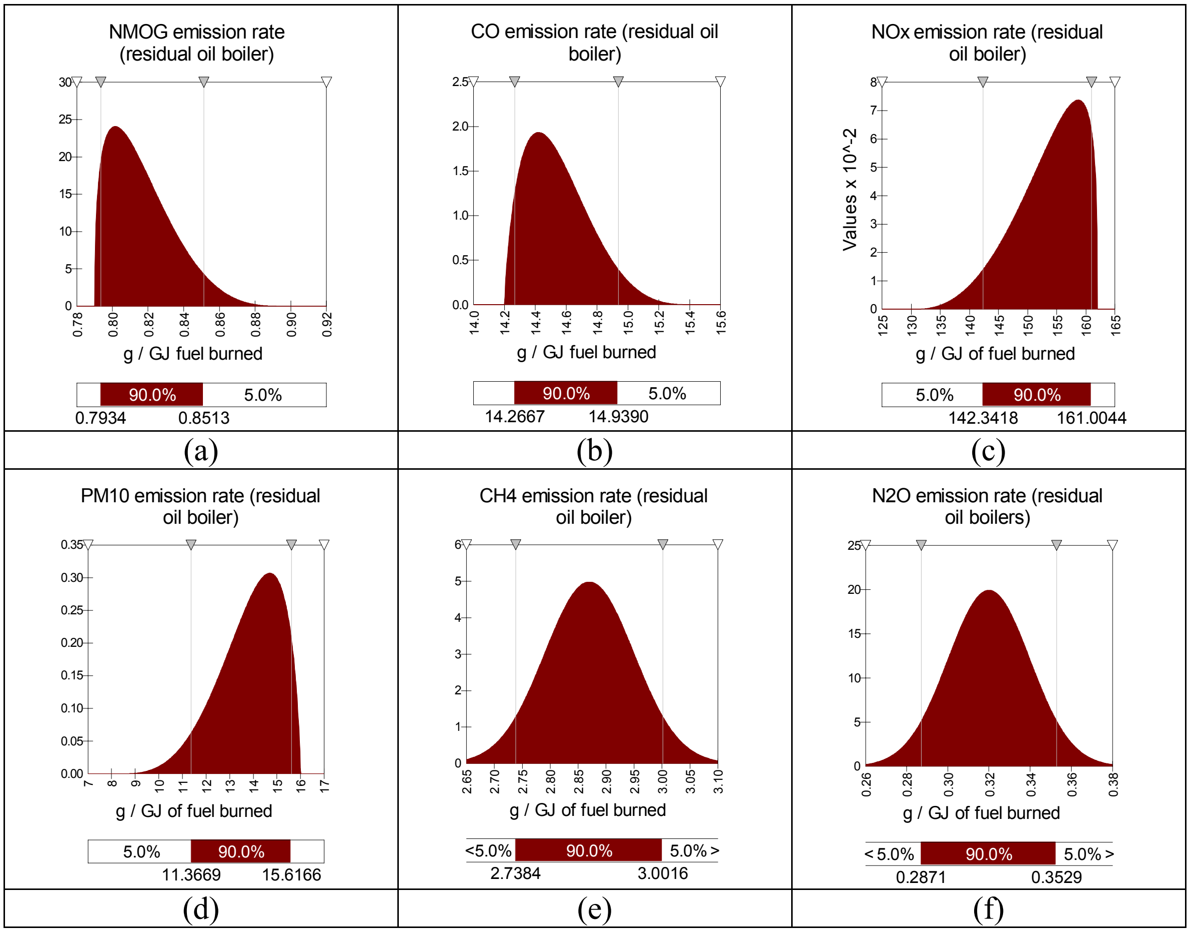
The emission rates available in the literature for industrial boilers operating with residual oil are presented in Table 4-37. The assumed FUEEM emission rate curves are presented in Figure 4-39.



(a) (b) (c)

(d) (e) (f)

Figure 4-38: FUEEM emission rates for uncontrolled stationary diesel engines (HHV).



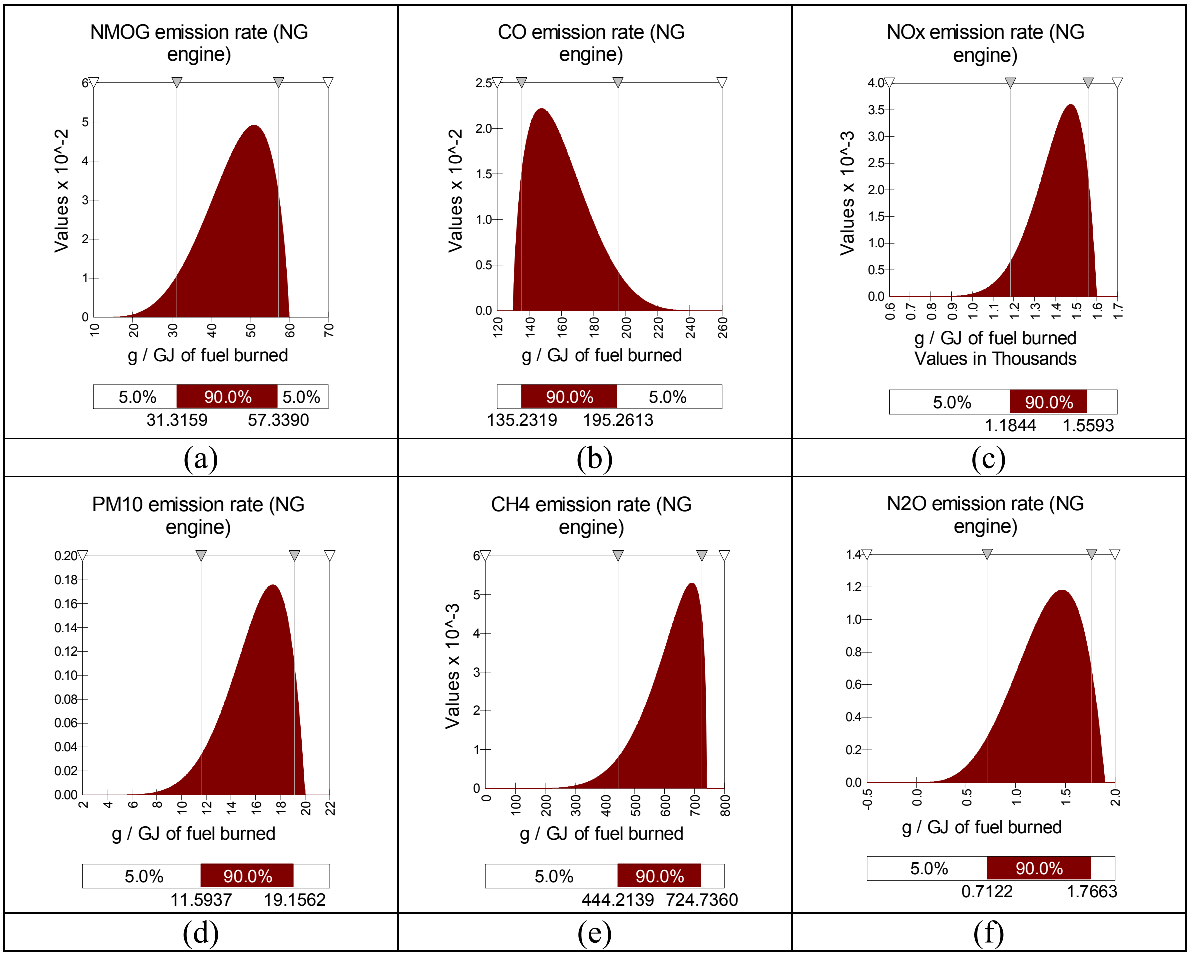
(a) (b) (c)

(d) (e) (f)

Figure 4-39: FUEEM emission rates for uncontrolled residual oil boilers (HHV).

4.6.5 Natural gas engines

The emission rates available in the literature for large engines operating with natural gas (NG) are presented in Table 4-38. The assumed FUEEM emission rate curves are presented in Figure 4-40.



(a) (b) (c)

(d) (e) (f)

Figure 4-40: FUEEM emission rates for uncontrolled natural gas engines (HHV).

4.6.6 Natural gas turbines

The emission rates available in the literature for large turbines operating with natural gas (NG) are presented in Table 4-39. The assumed FUEEM emission rate curves are presented in Figure 4-41.

4.6.7 Natural gas boilers

The emission rates available in the literature for industrial boilers operating with natural gas (NG) are presented in Table 4-40. The assumed FUEEM emission rate curves are presented in Figure 4-42.

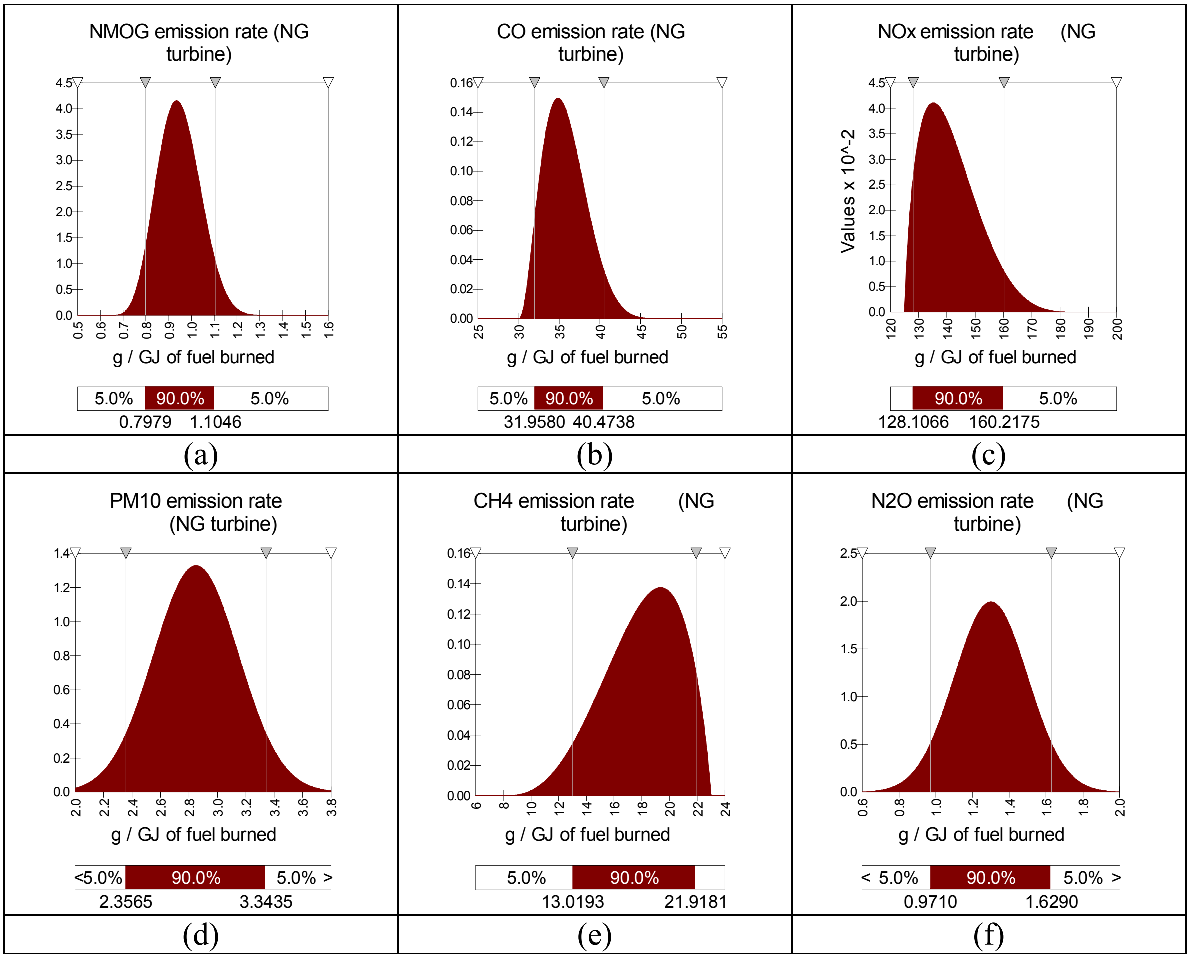
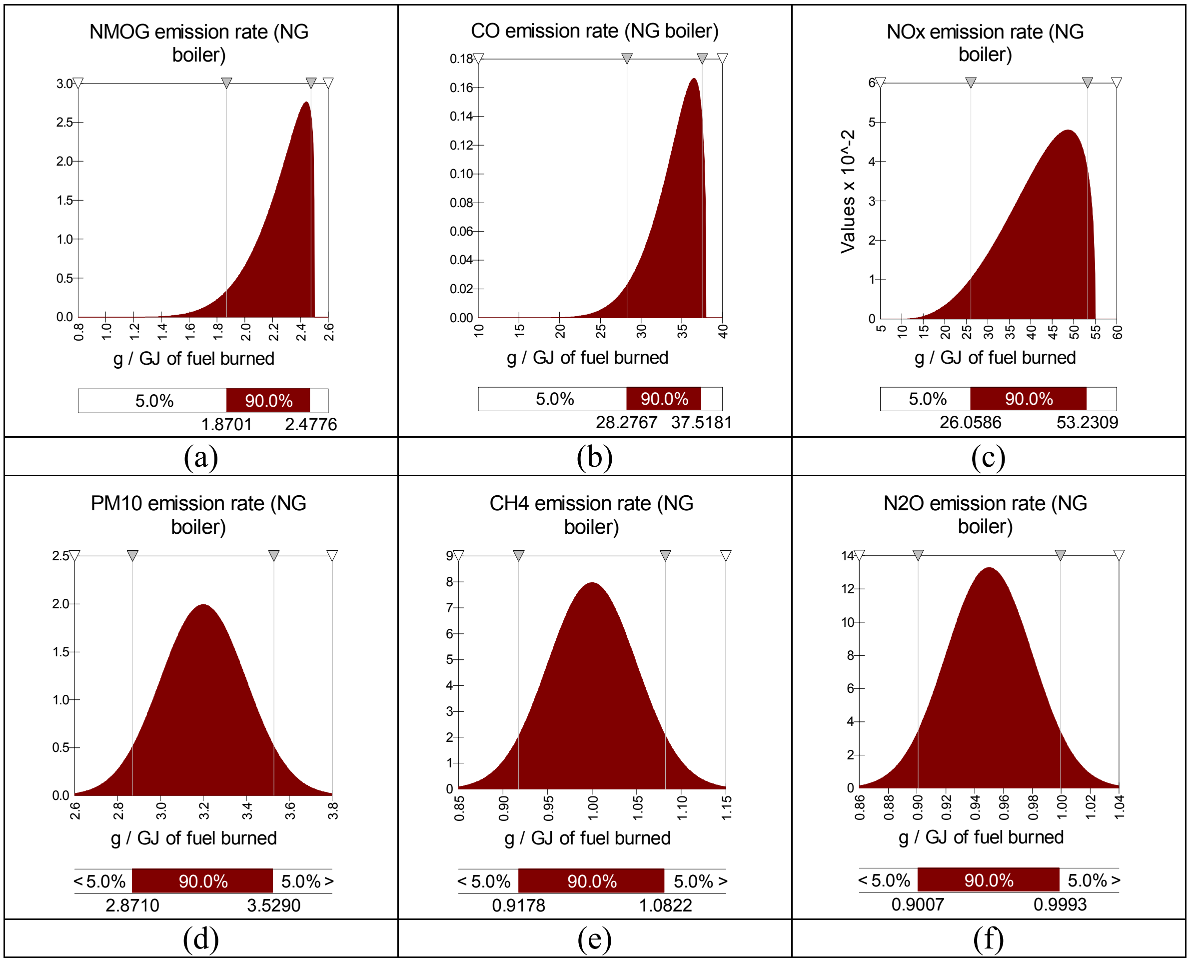


Figure 4-41: FUEEM emission rates for uncontrolled natural gas turbines (HHV).



(a) (b) (c)

(d) (e) (f)

Figure 4-42: FUEEM emission rates for uncontrolled natural gas boilers (HHV).

Table 4-36: Emission rates for stationary diesel engines from the literature.

Emission rates	DeLucchi97	ADL(96)	ADL(96)	Greet 1.5		AP-42	
(g/GJ of fuel burned)	HHV	HHV	HHV	LHV		HHV	
Pollutant/control system	uncontrol	control	uncontrol	uncontroled		uncontroled	
NMOG	133.5	45.0	45.0	40.86	38.73	0.32	137.58
CO	333.9	90.0	349.0	459.60	0.00	0.95	408.45
NOx	1535.3	132.2	1322.0	2133.60	0.00	4.41	1896.1
PM10	-	32.8	32.8	150.00	0.00	0.31	133.29
SOx	-	43.6	43.6	12.61	0.00	0.29	124.69
CH4	12.3	4.0	4.0	4.54	0.00	0.03	12.90
N2O				2.00	0.00		
CO2	71428.0	69360.0	69360.0	79570.62	0.00	164.0	70512.2
				(g/MBtu)	(g/GJ)	(lb/MBtu)	(g/GJ)

Table 4-37: Emission rates for residual oil boilers from the literature.

Emission rates	DeLucchi97	ADL(96)	ADL(96)	Greet 1.5		AP-42	
(g/GJ of fuel burned)	HHV	HHV	HHV	LHV		HHV	
Pollutant/control system	uncontrol	control	uncontrol	uncontroled		uncontrol	control
NMOG	0.8	0.8	0.8	0.9	0.9	0.80	
CO	15.2	14.4	14.4	16.2	15.4	14.33	5.45
NOx	152.4	15.8	158.2	144.7	137.1	157.65	23.65
PM10	-	0.1	9.1	6.2	5.8	14.51	3.20
SOx	-	45.3	452.8	51.9	49.2	139.91	13.99
CH4	3.0	2.9	2.9	3.2	3.1	2.87	
N2O				0.4	0.3	0.32	
CO2	75100	75229	75229	82674.9	78364.9	71659	
PM2.5				(g/MBtu)	(g/GJ)	9.45	0.67

Table 4-38: Emission rates for natural gas engines from the literature.

Emission rates (g/GJ of fuel burned) Pollutant/control system	DeLucchi97 HHV uncontrol	ADL(96) HHV control	ADL(96) HHV uncontrol	Greet 1.5 LHV uncontroled		AP-42 uncontroled					
						2 cycles lean-burn		**4 cycle lean-burn**		**4 cycle rich-burn**	
NMOG	38.3	65.0	47.3	61.3	58.1	0.1	51.6	0.1	50.7	0.03	12.7
CO	187.5	130.0	165.0	331.4	314.1	0.4	166.0	0.3	136.3	3.7	1599.4
NOx	1451.5	36.0	1165.0	871.7	826.2	3.2	1362.9	4.1	1754.2	2.2	950.2
PM10	-	20.0	20.0	11.6	11.0	0.0	16.5	0.0	0.0	0.0	4.1
SOx	-	0.3	0.3	0.3	0.3	0.0	0.3	0.0	0.3	0.0	0.3
CH4	723.5	260.0	615.0	289.0	274.0	1.5	623.4	1.3	537.4	0.2	98.9
N2O				2.0	1.9						
CO2	51223.0	50500.0	50500.0	58432.2	55386.0	110.0	47294.8	110.0	47294.8	110.0	47294.8
				(g/MBtu)	**(g/GJ)**	**(lb/MBtu)**	**(g/GJ)**	**(lb/MBtu)**	**(g/GJ)**	**(lb/MBtu)**	**(g/GJ)**

Table 4-39: Emission rates for large natural gas turbines from the literature.

Emission rates (g/GJ of fuel burned) Pollutant/control system	DeLucchi97 HHV uncontrol	ADL(96) HHV control	ADL(96) HHV uncontrol	Greet 1.5 LHV uncontroled		AP-42 HHV uncontroled	
NMOG	0.6	1.4	1.5	1.4	1.3	0.0	0.9
CO	49.9	3.6	46.0	2.5	2.4	0.1	35.3
NOx	131.5	3.8	190.0	39.6	37.5	0.3	146.2
PM10	-	8.3	8.3	3.6	38.7	0.0	2.8
SOx	-	0.3	0.3	0.3	435.6	0.003	1.5
CH4	11.2	4.6	8.8	2.5	2022.4	0.1	21.9
N2O				1.1	142.2	0.0	1.3
CO2	53509.0	50500.0	50500.0	59923.8	11.9	110.0	47294.8
				(g/MBtu)	**(g/GJ)**	**(lb/MBtu)**	**(g/GJ)**

Table 4-40: Emission rate for natural gas boilers from the literature.

Emission rates	DeLucchi97	ADL(96)	ADL(96)	Greet 1.5		AP-42		
(g/GJ of fuel burned)	HHV	HHV	HHV	LHV		HHV		
Pollutant/control system	uncontrol	control	uncontrol	uncontroled		uncontrol	part-control	control
NMOG	1.2	1.2	1.2	2.7	2.6	2.32		
CO	15.4	15.7	15.7	41.1	39.0	35.41	35.41	35.41
NOx	54.0	13.4	62.7	15.6	14.8	42.15	21.08	13.49
PM10	-	0.4	0.4	3.7	3.5	3.20		
SOx	-	0.3	0.3	0.3	0.3	0.25		
CH4	1.3	1.3	1.3	1.1	1.0	0.97		
N2O				1.1	1.0	0.93	0.27	
CO2	53588.0	50500.0	50500.0	59862.9	56742.1	50583		
				(g/MBtu)	**(g/GJ)**			

4.7 Correlations among variables

Variables correlations can be inserted in the model in different ways. When the model calculation departs from the bookkeeping process and starts to use a deeper level of details where physical parameters may appear, the mathematical expressions correlating the physical parameters are the most important way to input correlations in the model and should be encouraged. Some examples of these physical expressions used in FUEEM are:

1. The calculus of the natural gas (NG) energy content based on the NG input composition and some laws of non-ideal gas.
2. The use of dynamic flow equations to calculate first the pressure drop in the pipeline gas transportation and then the energy required to compress the gas.
3. The equations used in the EPA-Tank-4.0 software associating the fuel temperatures with the evaporative emissions.

The second level of correlations exist when the model details or available data are not so deep as to use physical expressions but there is an intuitive knowledge that some correlations are present. A good example is the increment of the fugitive emissions in gaseous systems when the pressure of the gas is increased. To input this kind of correlations two alternatives were studied in the hydrogen case – the envelope method and the rank correlation. Based on the results of that study (see section 4.2.3) and based on the discussion presented in section 3.2.1.6, FUEEM uses only the rank order correlation method.

An initial investigation to identify possible intuitive variable correlations was made, and based on the results, the coefficients of rank correlations were established. For the hydrogen production plant the share of the natural gas used as fuel was correlated with the electricity input share. The idea is that by using more input electricity (to run compressors, for example) less natural gas will be necessary since part of the compressors will not be run by NG engines or steam (produced by NG burning). The negative rank coefficient assumed was "- 0.427."

For the hydrogen plants with the alternatives to produce extra steam for exportation a positive correlation was established between the plant efficiency and the energy share of the steam exported. The idea is that a plant with better thermal integration may produce more extra steam. The assumed rank coefficient was "+ 0.427."

The hydrogen plant efficiency was correlated with the reformer emission factors as well. The idea is that a more efficient plant may burn less natural gas in the reformer furnace and therefore emit less pollutant. A negative rank correlation coefficient of "-0.35" was assumed for each pollutant. Other variables that may influence this parameter are the efficiency of the air quality control device (e.g., SCR) and the amount of hydrogen circulated back to the reformer furnace (tail gas).

In the marketing activities of the hydrogen fuel the fugitive losses of the gaseous systems were correlated with some variables that indicate the pressure of the system. These variables are the refueling over pressure that means the fuel station storage pressure is higher than the nominal pressure of the vehicle on board the storage tank. The positive rank coefficient assumed was "+ 0.7."

Similar to the rationale explained earlier for the hydrogen plants, the methanol production plant efficiency positively correlates with the share of extra steam produced (rank coefficient of "+ 0.257"). The methanol plant efficiency also negatively correlates with the share of natural gas used as fuel (rank coefficient of "- 0.257") and negatively correlates with the emission factors of the reformer furnace (rank coefficient of "- 0.257").

The reformer emissions of the Fisher-Tropsch (FT) fuel production plant also negatively correlate with the efficiency of the plant (rank coefficient of "- 0.308") because of the same idea that a less efficient plant will burn more fuel per energy produced and therefore emit more. Since several liquid compounds are produced in the FT process, a variable for carbon efficiency (representing the amount of carbon from the natural gas incorporated in the liquid output) was introduced in the model. The carbon efficiency variable has a positive correlation with the plant efficiency (rank coefficient of "+ 0.410") representing the idea that more liquid produced out of gas also means a more efficient process (as opposed to producing gas out of gas).

In the liquid fuel marketing activities, the fuel temperature was associated with evaporative emissions in some activities. The idea is that a higher temperature will evaporate more fuel and may facilitate more fugitive emissions (positively correlated). Based on that, the temperature of the fuel in the vehicle tank is correlated with the tank breathing losses (rank coefficient of "+ 0.8"), and the emission factors for the bulk storage tanks are correlated with the regional temperature as well (rank coefficient of "+ 0.408").

Finally, the liquid fuel dispensed per refueling was positively correlated with the pump operation time representing the idea that more fuel delivered will require more time. The rank coefficient assumed was "+ 0.95").

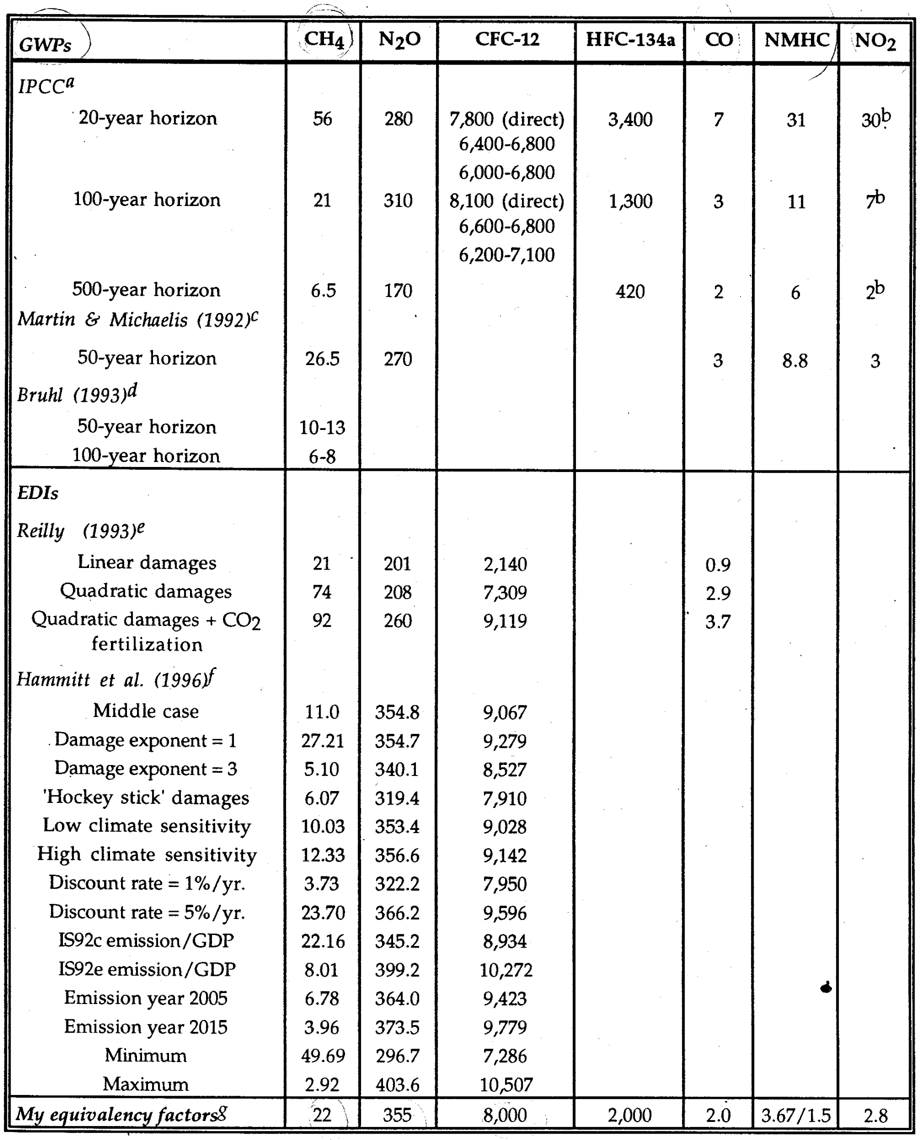
All these explained rank coefficients are located in several correlation matrices created in the correlation spreadsheet part of FUEEM. A problem for further investigation is the fact that the software @Risk functions performs an automatic check for inconsistency in the rank correlation coefficients and when an inconsistency is found in a matrix, the software presents its suggestion for change. In most case, the suggestions were accepted, but, since it may change the original input provided by the experts, some alternatives should be investigated to create the matrix (or the variable input) in a different way to avoid inconsistencies.

4.8 Greenhouse gases assessment

The assessment of the greenhouse gases, in terms of $CO_{2\text{-equivalent}}$, is performed in two different ways. The first option is to use the Global Warming Potential (GWP) developed by the International Panel of Climate Change (IPCC, 1996). The deterministic hundred-year horizon time values were assumed according to the IPCC recommendation as well as the newest update of the factor (IPCC, 2001). Table 4-41 presents the GWP factors assumed.

Table 4-41: Deterministic Global Warming Potential values assumed (based on the International Panel of Climate Change - 100 year horizon)

Gas	IPCC, 1996	IPCC, 2001	Assumed
CO2	1	1	1
CH4	21	23	23
N2O	310	296	296



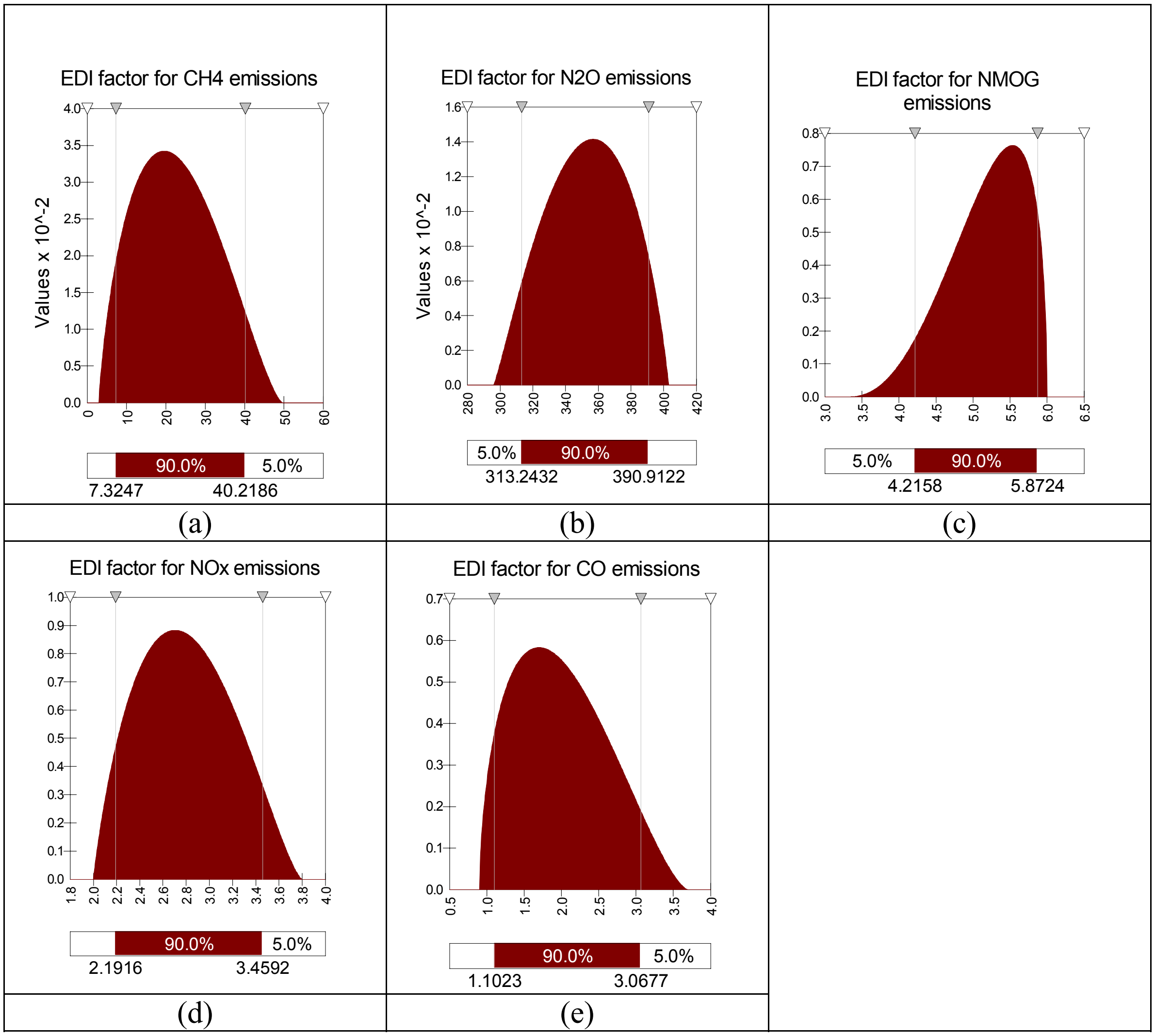
GWPs	CH_4	N_2O	CFC-12	HFC-134a	CO	NMHC	NO_2
IPCC[a]							
20-year horizon	56	280	7,800 (direct) 6,400-6,800 6,000-6,800	3,400	7	31	30[b]
100-year horizon	21	310	8,100 (direct) 6,600-6,800 6,200-7,100	1,300	3	11	7[b]
500-year horizon	6.5	170		420	2	6	2[b]
Martin & Michaelis (1992)[c]							
50-year horizon	26.5	270			3	8.8	3
Bruhl (1993)[d]							
50-year horizon	10-13						
100-year horizon	6-8						
EDIs							
Reilly (1993)[e]							
Linear damages	21	201	2,140		0.9		
Quadratic damages	74	208	7,309		2.9		
Quadratic damages + CO_2 fertilization	92	260	9,119		3.7		
Hammitt et al. (1996)[f]							
Middle case	11.0	354.8	9,067				
Damage exponent = 1	27.21	354.7	9,279				
Damage exponent = 3	5.10	340.1	8,527				
'Hockey stick' damages	6.07	319.4	7,910				
Low climate sensitivity	10.03	353.4	9,028				
High climate sensitivity	12.33	356.6	9,142				
Discount rate = 1%/yr.	3.73	322.2	7,950				
Discount rate = 5%/yr.	23.70	366.2	9,596				
IS92c emission/GDP	22.16	345.2	8,934				
IS92e emission/GDP	8.01	399.2	10,272				
Emission year 2005	6.78	364.0	9,423				
Emission year 2015	3.96	373.5	9,779				
Minimum	49.69	296.7	7,286				
Maximum	2.92	403.6	10,507				
My equivalency factors[g]	22	355	8,000	2,000	2.0	3.67/1.5	2.8

Figure 4-43: Delucchi's Economic Damage Index search values (source: Delucchi, 1997).

The second option is to use probabilistic curves created based on the Economic Damage Index (EDI) discussed by Delucchi (1997) and developed by several authors. Figure 4-43 presents Delucchi's research results and assumptions.

The probabilistic curves assumed in FUEEM are presented in Figure 4-44. They represent the EDI factor in terms of grams of $CO_{2\text{-equivalent}}$ per grams of pollutant. The

CO_2 economic damage index is used as a reference and therefore it assumes the value of one (1).



(a) (b) (c) (d) (e)

Figure 4-44: FUEEM probabilistic curves assumed for EDI factors (grams of $CO_{2\text{-equivalent}}$ / grams of pollutant).

5 FUEEM DEMONSTRATION EXAMPLE

5.1 Analysis details

To demonstrate the FUEEM process, a life cycle inventory and assessment (for greenhouse gases) is conducted for three Fuel Cell Vehicle technologies concepts, hypothetically operating in the South Coast California Air Basin (SCAB) in the year 2010 and beyond. The analyzed vehicle concepts are Direct Hydrogen Fuel Cell Vehicles (DHFCV), Indirect Methanol Fuel Cell Vehicles (IMFCV), and Indirect Hydrocarbon Fuel Cell Vehicles (IHFCV). SCAB was chosen because of its well-known air quality problems, its high probability of leading fuel cell vehicle introduction, and its being a location with several data available. The vehicle technologies represent mid-size passenger cars with platforms and performance similar to existing passenger car of the same class, running in "real world" driving cycles.

The requested fuels for the vehicles (hydrogen, methanol and hydrocarbon) are all based on the natural gas pathway. Natural gas (NG) is the "most feasible" near-term feedstock to produce hydrogen in areas where electricity is expensive, such as California, the US and Europe. A similar conclusion was reached with respect to methanol production when methanol is produced from inexpensive, large and remote NG reserves, such as Chile, Trinidad-Tobago, Malaysia, etc. For indirect-hydrocarbon fuel cell vehicles, Fischer Tropsch Naphtha (FTN) is chosen as the hydrocarbon fuel, due to the potential need for a clean (sulfur free) and easier-to-reform (saturated hydrocarbon) fuel for FCVs. There is also a sense that future oil prices and social pressure for the cleanest diesel fuel should make viable the use of the high-quality Fischer Tropsch (FT) diesel as a blending stock. Based on that, the establishment of a market for the light fraction (naphtha) of the FT process appears to be very attractive. Of course, this is not to say that a “gasoline-type” fuel from the crude oil pathway should not be considered and analyzed in future studies.

FUEEM provides the values for the energy consumption disaggregated into fossil fuel and petroleum consumption as well as the total consumption. It also assesses the major urban air criteria emissions and greenhouse gases (NO_x, NMOG, CO, PM_{10}, SO_x, CH_4, N_2O, CO_2 and $CO_{2\text{-equivalent}}$) disaggregated into three different areas selected by the analyst. The three chosen areas are South Coast Air Basin - SCAB (analyzed area), the state of California (without SCAB), and the total emissions including the emissions generated in the rest of the world.

The operational unit of the analysis is kilometers driven over the vehicle’s life. The energy requirement comparison is done in terms of mega Joule of energy required over the entire life cycle per kilometer driven (MJ / km). High heating values are used through the entire calculation. The air emissions comparison is done in terms of milligrams of pollutants released over the entire life cycle per kilometer driven (mg / km). For the CO_2 inventory and for the assessment of the greenhouse gases in terms of $CO_{2\text{-equivalent}}$ the comparison is done in terms of grams of pollutant per kilometer driven (g / km).

The boundaries for the fuel upstream calculation include all the operational stages of the activities, from feedstock extraction to the final vehicle refueling stage. In particular, the activities or stages include the feedstock extraction, processing, storage, and transportation, as well as the fuel production, storage, transportation, and distribution.

The secondary fuels and electricity consumed in each activity are also considered from the feedstock extraction to the final use. More details of the boundaries are presented in the fuel upstream scenarios definition (section 1.1).

5.2 Fuel cell vehicles assumptions

Vehicles are complex systems in themselves. Even when a single class is specified, such as mid-size passenger car, as is the case in this demonstration analysis, several variables may bring uncertainties into the calculation.

Similar to conventional vehicles, the design is one important variable. The vehicle design can target fuel economy, vehicle performance, or both, in a continuum that may involve variations in the vehicle frontal area and body shape, changing the aerial drag coefficient, tire specifications related with the tire friction values, and vehicle body weight that can be correlated with safety specifications and also with the vehicle decommissioning recycle share.

The propulsion system characteristic is another important variable. Transmission, engines, fuel storage, and auxiliaries can also be specified for both targets – fuel economy or performance. More recently, hybridization has been brought into market making the vehicle system analysis even more complex. In summary, hybrid systems use an energy storage package (battery or ultra-capacitors) connected with electrical motors that regenerate some energy when the vehicle is breaking. They also use some power generators (internal combustion engines or fuel cells) to recharge the batteries and sometimes to provide wheel traction, in the case of the internal combustion engine, or electricity directly to the motors to run the vehicle. The idea is to increase the range and/or the fuel economy of the vehicle by allowing these "engines" [8] to operate most of the time at their highest efficiency, by providing the peak energy consumed in hard accelerations from the energy storage package. The hybridization configuration can vary from an almost pure battery electric vehicle to an almost pure load following vehicle. In the fuel cell vehicle case, hybridization can also be considered to help the start up time and, in the case of indirect systems, to help with the dynamic response of the fuel processors.

The control system of the hybrid configurations, which determines when the used energy is coming from the energy storage package or from the "engines," can also be another important variable.

Over-time deterioration of all these systems, engines and eventual air quality control devices may also change the fuel efficiency and emission values for the real fleet on the road compared with the values for new vehicles.

Finally, the drive cycle used to simulate the way the vehicle is going to be operated in the real world, by different drivers, is very important as well. Some studies use the U.S. EPA federal highway cycle (HIWAY) and federal urban driving schedule (FUDs) to simulate the drive conditions. In general, they combine the cycles following the equation:

$$mpg_{combined} = \frac{1}{\frac{0.55}{mpg_{FUDs}} + \frac{0.45}{mpg_{HIWAY}}} \qquad \text{Equation 5-1}$$

---

[8] I use the word engines but, in fact, fuel cells are electrochemical devices.

These cycles are based on data collected in the Los Angeles area in the 1970's but they are still being used to certify new vehicles in the U.S. (Kruse *et al*., 1973 and Kuhler *et al*. 1978). However, several studies and authors (DTI, 1998; Effa *et al*. 1993 and Carlson *et al*., 1997) believe these drive cycles are far from representing actual drive conditions, and even the EPA has created a new cycle, the US06, trying to minimize this problem. Several studies use the combined cycle and in addition apply a factor of 1.25 or 1.05 as presented in Table 5-1. The fuel efficiency values available in the literature try to capture all of the explained variables in a single number representing the average of a national or regional fleet.

The fuel efficiency assumptions used in this FUEEM demonstration analysis are presented in Figure 5-1. They represent a mid-size passenger fleet of fuel cell vehicles running in the SCAB area about 2010 and they try to capture the real world operation, as opposed to the certification drive cycle. As explained earlier, these vehicle assumptions are my personal educated guesses and need be revisited following FUEEM methodology. These educated guesses are partially based on the results of running the FCVSim model developed by the Fuel Cell Vehicle Modeling Program (FCVMP) at the Institute of Transportation Studies at the University of California – Davis (Hauer, 2001). The FCVSim is a robust and dynamic model that works very well for load following configurations (the option for hybrid configuration is under development).

To represent the real world drive conditions a mixed result of simulations, considering the US06 drive cycle and a faster (1.25 factor) combined EPA cycle, was used. It is assumed that, by 2010, the fuel cell vehicle fleet will still be using regular a steel body, but it is also assumed that the fuel cell stack and the fuel cell system efficiency will be better than the existing technologies.

The only vehicle technology selected by the FUEEM expert network is the hydrogen onboard storage. Several hydrogen onboard storage technologies are in development to provide pure hydrogen for the vehicle fuel cell stack. For the purposes of this analysis, a high-pressure tank at 3.45×10^4 kPa (5000 psi) was chosen as the storage technology due to its actual stage of development, relative low cost, and better energy efficiency compared to the cryogenic liquid option.

The data about the emissions of fuel cell systems using reformers are very scarce. Table 5-2 and Table 5-3 present the literature data searched for this section. In general, the data are from modeled emission studies or are from measurements of stationary devices running in steady-state conditions, or both, as is the case for the CARB (1999) study and for the Epix (2000) study.

The assumptions used in the FUEEM demonstration analysis are presented in Figure 5-2 and Figure 5-3. The reformer technologies selected are steam reformation (SR) for the methanol case (Ramaswamy *et al*., 2000) and autothermal reformer for the hydrocarbon case (Ramaswamy *et al*., 2001). In both cases, the emissions try to replicate the real world operations including the cold start up. Vehicles with pressurized fuel systems are analyzed to comply with the zero evaporative emissions rule to be adopted in California.

Table 5-1: Fuel economy of fuel cell passenger cars – data from the literature

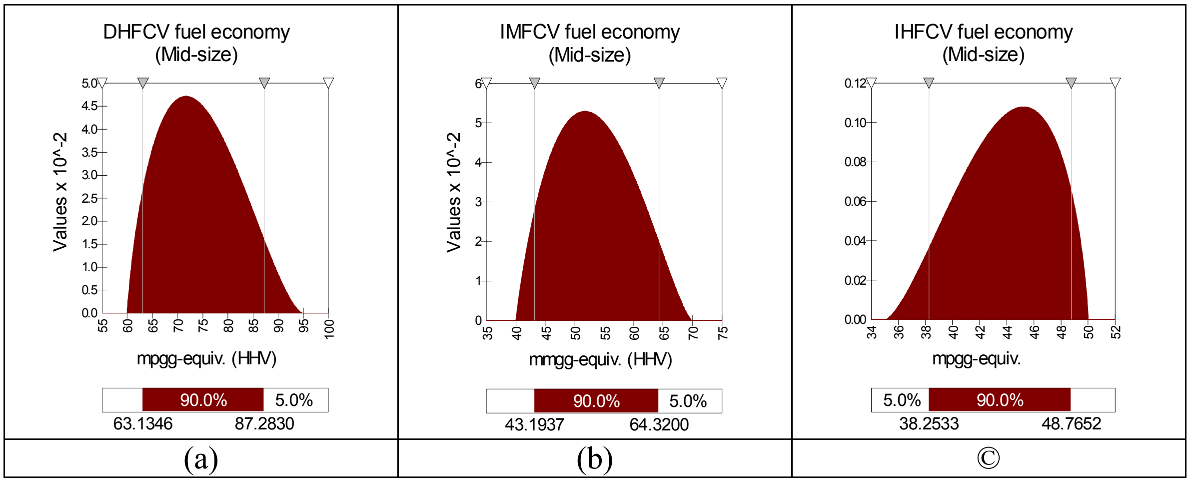
FUEL ECONOMY			**HHV - High Heating Value**									**Observation**
Vehicle technology			**Direct Hydrogen**			**Indirect Methanol**			**Indirect Hydrocarbon**			
Source	Drive Cycle	Class	mpgg-eq	miles/MBtu	km/MJ	mpgg-eq	miles/MBtu	km/MJ	mpgg-eq	miles/MBtu	km/MJ	
DTI (98) - probable case	comb/1.25	Mid-size	71.7	573.3	0.874	47.8	382.2	0.583	45.6	364.8	0.556	single H2-model
DTI (98) - best case	comb/1.25	Mid-size				53.2	407.1	0.621	31.5	240.9	0.367	estimated-liquids
Ogden (99)	Combined	Compac	106	810.4	1.236	69	527.5	0.805	65	496.9	0.758	single model
Greet 1.5a (2000)	generic	generic	77.9	623.4	0.951	59.7	477.9	0.729	51.9	415.6	0.634	estimated
Unnasch (00) - nominal	generic	generic	59.5	476.2	0.726	25.0	200.0	0.305				estimated
Unnasch (00) - aggressive	generic	generic				27.5	220.3	0.336				estimated
CARB (99)	FUDS	Compac				51.4	411.3	0.627	41.6	332.5	0.507	single model
Ford P2000 (in, CEC)	Combined	Mid-size	72.6	581.0	0.886							measured ?
Necar IV (in, CEC)	Combined ?	Compac	57.9	462.9	0.706							measured ?
CFCP,01 - Low value	comb/1.05	Compac	52.6	420.4	0.641	45.4	363.0	0.554	40.8	326.4	0.498	estimated
CFCP,01 - High value	comb/1.05	Compac	65.3	522.3	0.796	50.6	404.7	0.617	45.7	365.6	0.558	estimated
Methanex (2000)	comb/1.25	Mid-size	63.9	511.1	0.779	50.4	402.5	0.614	42.4	339.2	0.517	estimated
MIT (2000) - 2020 model	Combined	Mid-size	101.8	814.7	1.243	61.6	492.6	0.751	45.8	366.2	0.559	modeled
Pembina/Suzuki (2000)	Combined	Compac	91.5	731.4	1.116	61.1	488.2	0.745	41.8	334.4	0.510	estimated
ITS-Davis (2001)	Combined	Mid-size	67.5	539.9	0.823	48.4	386.8	0.590	42.1	336.6	0.513	robust model
ITS-Davis (2001)	US06	Mid-size	42.6	340.3	0.519	28.4	226.9	0.346	29.4	235.0	0.358	robust model

Table 5-2: Emissions of indirect methanol fuel cell passenger cars – data from the literature

EMISSIONS									
Methanol system	**(grams/mile)**		NMOG	NMOG	CO	CO	NOx	NOx	CH4
			(best)	(probable)	(best)	(probable)	(best)	(probable)	(probable)
Ballard (in Pembina, 00)	reformer	Autothermal	0.0024	0.0027					
DTI (98)	reformer	steam r. (cold).	0.006	0.007					
DTI (98)	reformer	steam r. (hot).	0.0024	0.0027	0.003	0.004	0	0	
ETSU (97)	reformer	SR (ss-hot)		0.0099		0.001		0.0002	
Mark (94)	reformer	steam r.		0.002		0.003		0.001	
CARB (99)	reformer	SR/membrane		0.0034		0.026		0.0025	0.0106
CARB (99)	reformer	SR/PROX/b		0.0069		0.016		0.0026	0.0096
CARB (99)	reformer	Autothermal		0.0021		0.017		0.0027	0.0096
DTI (98)	evaporative	no pressur.	0.018	0.02					
DeLuchi (91)	evaporative	no pressur.	0.087	0.13					
ETSU (97)	evaporative	no pressur.		0.0001					
Mark (94)	evaporative	no pressur.		0.07					

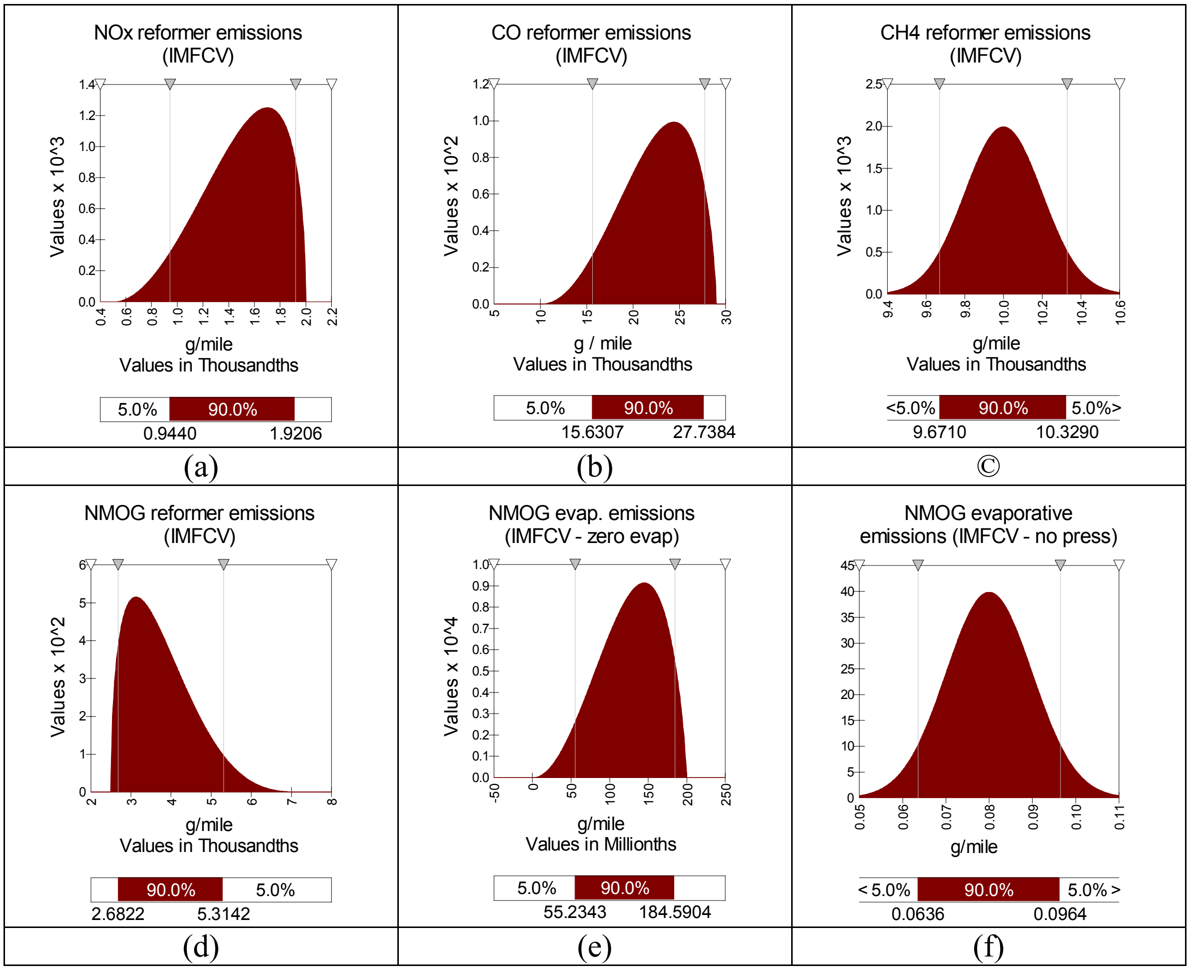
Table 5-3: Emissions of the indirect hydrocarbon fuel cell passenger cars – data from literature

EMISSIONS									
Hydrocarbon system	**(grams/mile)**		NMOG	NMOG	CO	CO	NOx	NOx	CH4
			(best)	(probable)	(best)	(probable)	(best)	(probable)	(probable)
DTI (98)	reformer	POX	0	0	0	0	0	0	
ETSU (98)	reformer	POX		0		0		0	
Epix (00)	reformer	POX (ss-extr)		0.017		0.013		0.003	
CARB (99) - load foll.	reformer	POX		0.0047		0.02		0.006	0.0106
CARB (99) - hybrid	reformer	POX		0.0032		0.017		0.0046	0.0067
DTI (98)	evaporative	no pressur.	0.262	0.378					



(a) (b) ©

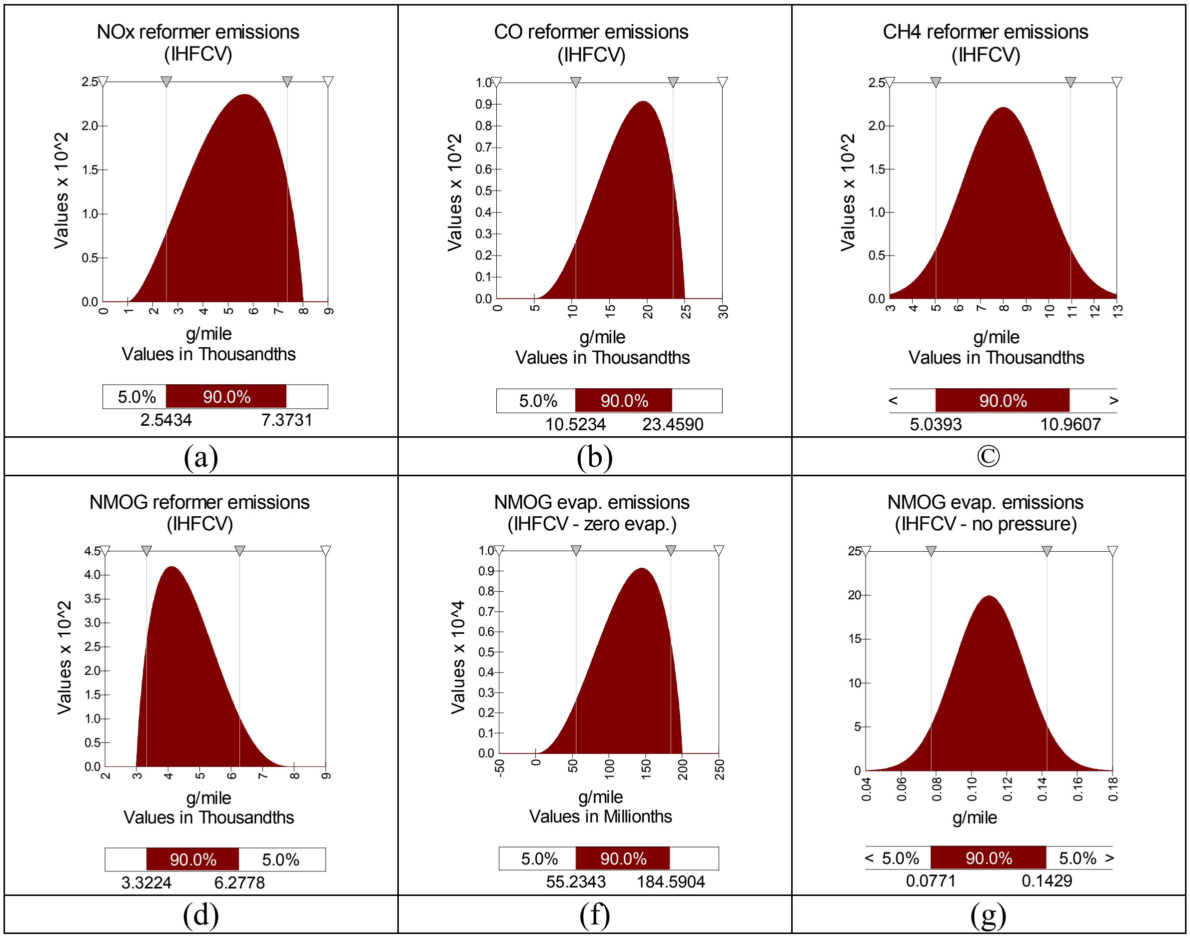
Figure 5-1: Vehicle fuel efficiency assumed



(a) (b) ©

(d) (e) (f)

Figure 5-2: Emissions assumed for the indirect methanol fuel cell vehicle (IMFCV)



(a) (b) ©

(d) (f) (g)

Figure 5-3: Emissions assumed for the indirect hydrocarbon fuel cell vehicle (IHFCV)

5.3 **Fuel upstream pathway scenarios**

The South Coast California Air Basin (SCAB) is a high emission control enforcement area and the chosen technologies placed inside the basin attempt to reflect these regional policies. Fuel transportation modes and distances, as well as the chosen pathway scenarios for feedstock and fuel production also reflect the regional characteristics. As explained before, we strongly discourage extrapolating the results to other areas or situations (see section 2.5).

For a specific pathway, in which the technologies are well defined, a consensus among the experts was achieved without problems. As explained before, there is also a consensus that in reality the probability of the fuel upstream activities being a mix of technologies is much greater than utilizing a single technology path (see section 3.1.2.1). Based on that, a combination of pathway scenarios should be a better way to calculate the final results for comparisons. However, it was very difficult to reach a consensus given the various possible combinations, the subjectivity of the section, the sensitivity of the variables, and the advocacy positions of several experts. The combined scenarios presented here are examples that represent the opinion of the majority of the experts but are not unanimous as are most of the other variables' inputs. In any case, the "bounding scenario" results presented here represent the edges of any possible combination.

For simplicity, some of the probabilistic curves discussed here are expressed with words such as " around," "about" or "approximately."

5.3.1 Gaseous Hydrogen

For a 3.45 x 10^4 kPa (5,000 psi) vehicle tank assumed, a fast refueling system will require a fuel station based, over-pressurized hydrogen storage at approximately 4.14x10^4 kPa (~6000 psi), which is about 6.90x10^3 kPa (~1000 psi) greater than the vehicle tank pressure. The fuel station storage system uses compressors in cascade powered by electric motors. The natural gas engine option to power the compressors is not considered due to concerns about emissions. Overall, around 4 kg of hydrogen per vehicle is considered for each instance of refueling activity.

The low density of gaseous hydrogen makes it difficult to store and to transport. The cheapest way to transport hydrogen is by using pipelines from a centralized plant; however, hydrogen pipelines require special design and are more expensive than natural gas pipelines. Based on this, centralized hydrogen plants are expected to be placed as close as possible to the market, using as much existing natural gas infrastructure as possible. On the other hand, the costs of building a centralized hydrogen plant and the necessary infrastructure are high and the hydrogen demand around 2010 is not expected to be high enough to justify huge investments. Therefore, mega-plants (270 MTPD - metric tons per day), which can be placed in rural areas to deliver hydrogen to several markets and may even sequester CO_2, require an extensive transmission pipeline network, and also a large and well established market demand. For the time frame of 2010 this option is not considered but, on the other hand, decentralized production at the fuel station can be used in the introductory phase and may remain until 2010.

Based on these considerations two pathways are used in this study, as explained below.

5.3.1.1 Pathway 1: Centralized production

This pathway assumes existing typical size plants (27 MTPD) located inside the market area (Los Angeles) and producing extra-steam for over-the-fence exportation. The plant uses a half-day production capacity storage at high pressure (around 23 MPa or 3350 psi) for a steady state operational guarantee. It recovers part of the compression energy with a turbo-compressor when the stored hydrogen is used. A pipeline distribution network of about 60 km (37 miles) is set to deliver hydrogen at 6.9 MPa (1000 psi) for the fuel stations. This assumption is an optimized pipeline design selected from an early analysis considering efficiency and safety issues (Contadini, 2000c). For emission control the plant uses a selective catalytic reduction (SCR) device and a continuous emission monitor system (CEMS). Figure 5-4 presents a graphical representation of the pathway's boundaries.

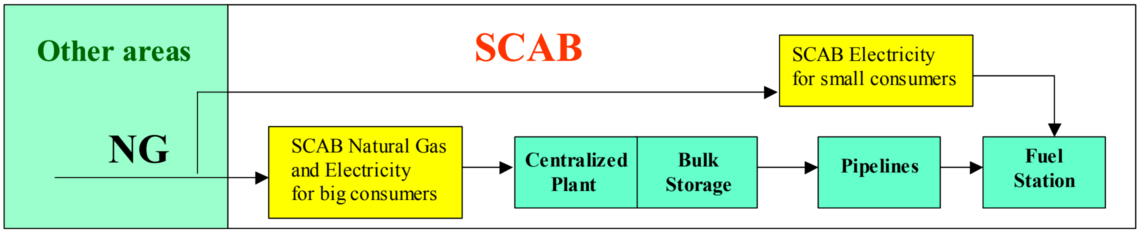


Figure 5-4: Boundaries definition for the hydrogen pathway 1

5.3.1.2 Pathway 2: Decentralized production

Hydrogen is produced at the fuel stations using small steam methane reformation (SMR) plants with production capacity of one MTPD. The plant uses natural gas (NG) from the local distribution system at an inlet pressure of 0.14 MPa (20 psi). The plant design has a pressure swing adsorption unit (PSA), with hydrogen output pressure of 1.6MPa (230 psi). For emission control it uses catalytic burners and SCR units. The boundaries are presented in Figure 5-5.

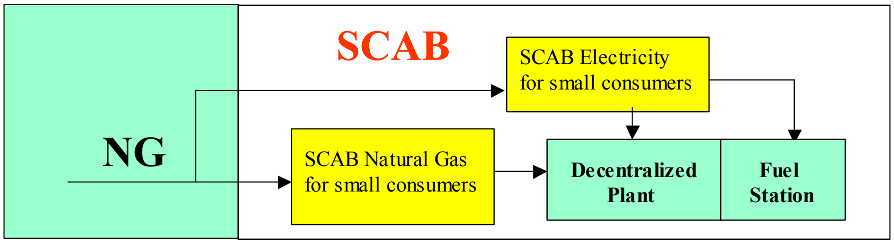


Figure 5-5: Boundaries definition for the hydrogen pathway 2

5.3.1.3 Combined Scenario

For a reduced fleet scenario, centralized plants, already established to supply hydrogen for chemical and petrochemical industries, can also supply hydrogen to the nearby fuel stations. In this situation a relatively high percentage of hydrogen fuel may come from decentralized plants to supply the fuel stations that are far from the industrialized area. With the increase in the number of hydrogen vehicles in the area, new typical size centralized plants can be built, reducing the relative percentage of decentralized plants in the area. Based on these ideas, the combined scenario considers a curve for the hydrogen production, establishing the hydrogen production coming from small plants (pathway 2) at between 20 to 50 % (see Figure 5-6). The remaining production comes from centralized plants (pathway 1).

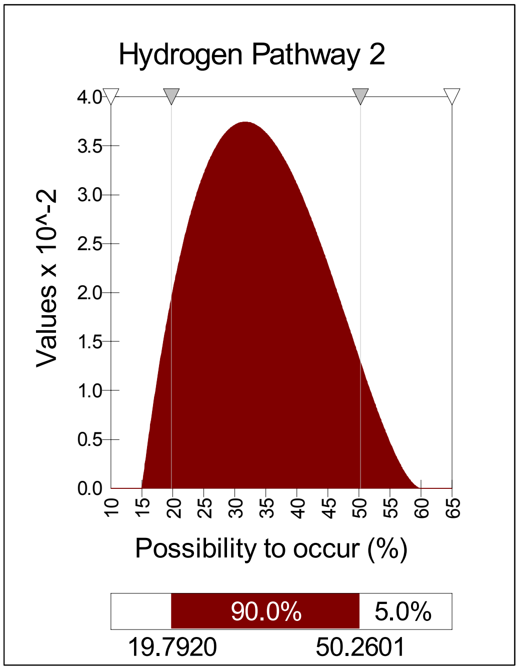


Figure 5-6: Share of the pathway 2 in the combination scenario.

5.3.2 Liquid Fuels Marketing

The major benefits of liquid fuels are the higher energy density compared to gaseous fuels and the relative ease with which one can transport and store them. The benefits in the transportation and storage of liquid methanol and Fisher-Tropsch Naphtha (FTN) qualify them as possible hydrogen carrier fuels for FCVs. The rationale for these liquid fuels' marketing closely parallels that for gasoline. Figure 5-7 shows the pathway boundary details. Taking into account the high degree of air quality enforcement in areas such as SCAB and considering the transportation infrastructure in place, the established scenarios for all pathways take into account the following activities:

a. A balance control recovery system for the vehicle refueling and for the fuel station underground tank refueling. The system allows the tank fuel vapor displaced (by the refueled new fuel) to be transferred from tank to tank until reaching the fuel terminal, where the majority of the vapor is recovered.
b. Diesel truck tankers (US class 8b) equipped with a vapor collector are assumed for the retail distribution stages.
c. Internal floating roof tanks at the fuel terminals, which for the SCAB case are located close to the port.
d. The port activities include diesel engines for hotel loads and diesel tugboats.
e. The tanker ship size considered is the one equivalent to 150,000 dead weight tons of crude oil. The ship has no air emission control devices and uses bunker fuel (US residual oil 6). During the vessel's return trip, a water ballasting of around 30 % by weight is assumed

f. The bulk fuel storage tanks at the remote areas are dependent on the regional air quality enforcement policy assumed in each pathway. Several examples show that the remote plants are likely to be constructed in areas that already have some industrial activities, and concentrated industrialized areas are more likely to control local emissions. On the other hand, because of the industrial concentration the plants are able to export steam or electricity; therefore, in this analysis air control device requirements become associated with steam-exportation possibilities.

g. Finally, it is assumed that the fuel production plants in Malaysia are located next to ports.

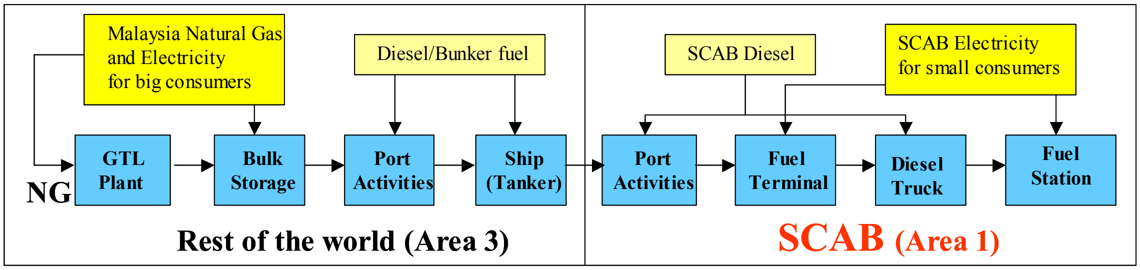


Figure 5-7: Liquid fuels pathway boundaries

5.3.3 Methanol

Four pathway scenarios are considered for the methanol analysis. Two different technologies are chosen to produce syngas for the methanol synthesis and also two different regional situations for steam exportation with air emission control device requirement. Figure 5-8 shows the pathway idea. All pathways consider the same fuel marketing activities explained in the previous section (section 5.3.2).

5.3.3.1 Pathway 1: Typical size plant within uncontrolled situation

This pathway considers a typical size methanol plant of 2,500 metric tons per day (MTPD) using steam methane reformation (SMR) for syngas production, constructed on a site without industrial concentration. The plant uses no air control device and uses fixed roof tanks for the fuel storage. No extra steam exportation is considered.

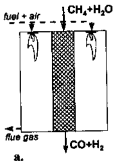
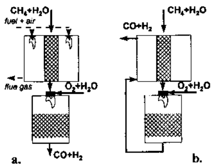
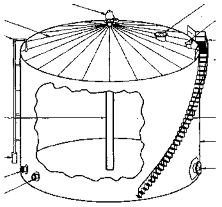
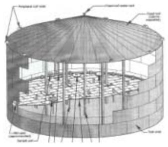
MeOH	**(uncontrolled situation)**	**(controlled situation)**	
Plant Design	**Pathway 1 :** • **Typical size (2,500 mtpd)** • **SMR syngas production** • **No extra-steam**	**Pathway 3 :** • **Typical size (2,500 mtpd)** • **SMR syngas production** • **Extra-steam** • **SCR**	
	Pathway 2 : • **Mega-size (10,000 mtpd)** • **SMR/POX syngas prod.** • **No extra-steam**	**Pathway 4 :** • **Mega-size (10,000 mtpd)** • **SMR/POX syngas prod.** • **Extra-steam** • **SCR**	
Storage	 **Fixed roof tank**	 **Internal floating roof tank**	

Figure 5-8: Methanol pathways representation

5.3.3.2 Pathway 2: Mega size plant within uncontrolled situation

This pathway considers a mega-size methanol plant of 10,000 metric tons per day (MTPD) using a combination of SMR and partial oxidation (POX) for the syngas production, constructed on a site without industrial concentration. The plant uses no air control device and uses fixed roof tanks for the fuel storage. No extra steam exportation is considered.

5.3.3.3 Pathway 3: Typical size plant within controlled situation

This pathway considers a typical size methanol plant of 2,500 MTPD using SMR for the syngas production, constructed on a site with industrial concentration. The plant uses selective catalytic reduction as an air control device and uses internal floating roof tanks for the fuel storage. Extra steam exportation is considered.

5.3.3.4 Pathway 4: Mega size plant within controlled situation

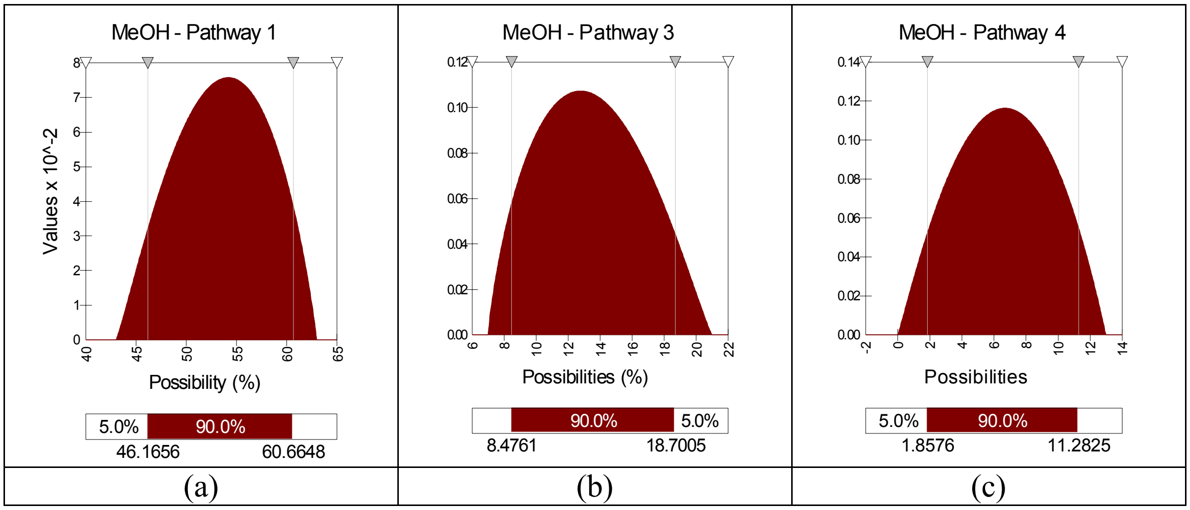
This pathway considers a mega-size methanol plant of 10,000 metric tons per day (MTPD) using a combination of SMR and partial oxidation (POX) for the syngas production, constructed in a site with industrial concentration. The plant uses selective catalytic reduction as an air control device and uses internal floating roof tanks for the fuel storage. Extra steam exportation is considered.

5.3.3.5 Combined Scenario

Currently the methanol industry has around 20 % to 30 % of over-capacity. The future for MTBE (an oxygenated additive for gasoline that uses methanol as feedstock) is controversial and creates a possibility of an even bigger over-capacity in the near future. Existing and relatively older plants use SMR in a less efficient way than the new SMR plants considered in this study. Some experts believe that these less efficient plants are going to be decommissioned by 2010 and that all methanol for FCVs will be produced in existing newer plants or in future built plants. In complement of that, some controversies exist as to what the new plant designs and market share will be by the year 2010. Mega-size plants (10,000 MTPD) using combined SMR/POX are more efficient, and according to some experts there are several projects already considering this option.

On the other hand, several experts, the majority in fact, disagree with this scenario, believing that short-term new plants (if any) will have similar characteristics (with small efficiency increments) as current typical size plants (2,500 MTPD) using SMR. Most believe that several of the existing plants can be temporarily deactivated and reactivated when the methanol demand increases around 2010. According to them this strategy has worked in the past and it has the benefit of using the capital already invested, avoiding investment in new plants.

Ultimately, the assumed pathway combination applies where the uncontrolled situation is expected to be more common than the controlled one, and where the typical size plants using SMR may prevail over the mega size plants by 2010. Figure 5-9 presents the assumed curves, representing the possibility of occurrences for pathway 1, 3 and 4. The possibility of pathway 2 is the difference to 100 %.



(a) (b) (c)

Figure 5-9: Possibilities of occurrences assumed for the methanol pathways

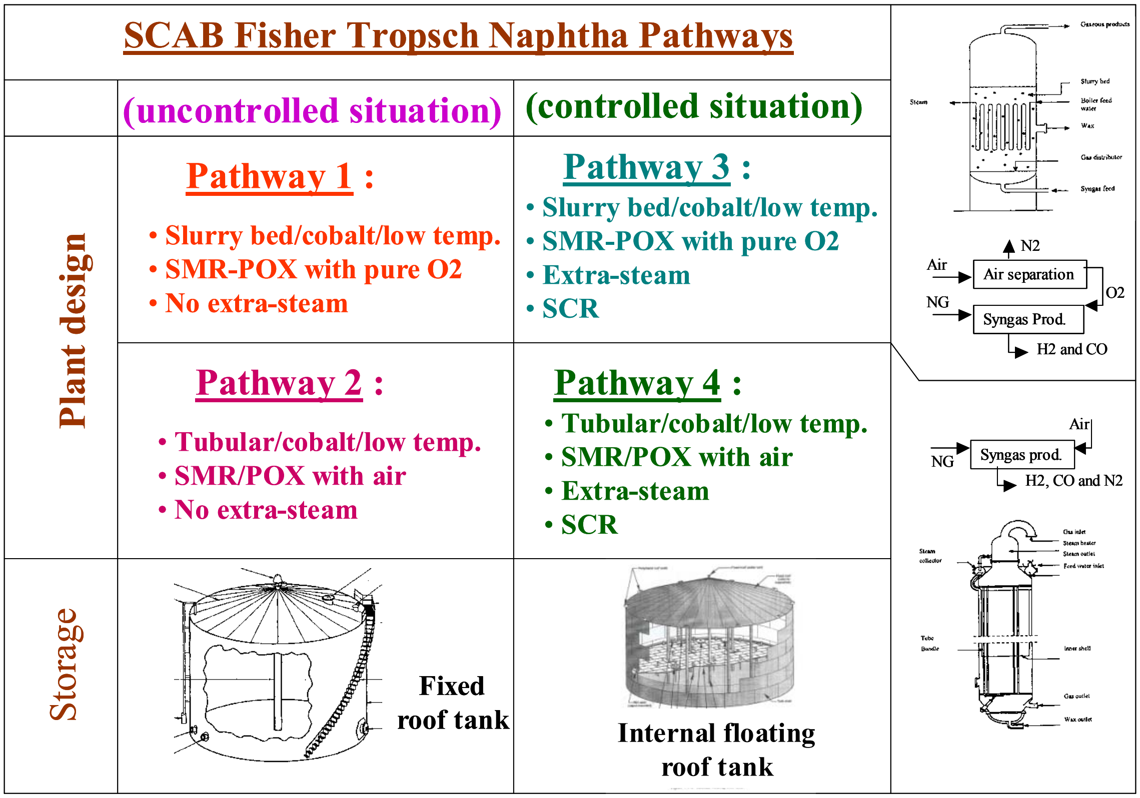
5.3.4 Fisher-Tropsch Naphtha (FTN)

As in the methanol analysis, four pathway scenarios are considered for the FTN analysis. Two different technologies are chosen to represent ways to manage the oxygen in the production of the syngas for the Fisher-Tropsch (FT) synthesis. Also, two different regional situations are considered for steam exportation and for the air emission control device requirement. The major problems of the FT process at present are the initial costs of the plant and the relatively small degree that the plants can be scaled up, compared to mega size methanol plant alternative. A great part of the plant capital investment is related to oxygen production, and the potential solution adopted by the methanol industry - scaling the production and diluting the cost - does not apply. One way to reduce the initial cost of the Fisher Tropsch plants is to use air injection instead of pure oxygen. This design has a trade-off with plant efficiency, because of the amount of nitrogen (inert) that must be carried over in the pressurized system. A possible extra benefit, according to some experts, is the added safety of having no pure oxygen in the plant.

On the other hand, several experts believe that oxygen safety is not an issue and that the economy of the air system, in most cases, does not compensate for the efficiency losses. High temperature FT synthesis (300 to 350 ^{o}C) using alkalized iron or fused iron oxide catalysts is not considered in this analysis due to the mix of non-paraffinic components (olefins, aromatics, etc.) that they tend to produce. All of the pathways consider the same fuel marketing activities explained earlier in the section on liquid fuels marketing (section 5.3.2). Figure 5-10 shows the pathways idea that is explained in the following sections.

5.3.4.1 Pathway 1: Slurry and pure O_2 within an uncontrolled situation

This pathway considers a Fisher Tropsch plant with a capacity of 5,000 MTPD constructed on a site without industrial concentration. The plant design assumes a slurry bed low temperature reactor (220 to 270 °C) and cobalt catalyst. The plant also uses combined SMR/POX syngas production with pure oxygen injection. It has hydrotreating and hydrocraking stages with final cuts around 60% of diesel, 18% of kerosene and 22% of naphtha (by weight). The plant uses no air control device and uses fixed roof tanks for the fuel storage. No extra steam exportation is considered.



SCAB Fisher Tropsch Naphtha Pathways

	(uncontrolled situation)	(controlled situation)
Plant design	**Pathway 1 :** • Slurry bed/cobalt/low temp. • SMR-POX with pure O2 • No extra-steam	**Pathway 3 :** • Slurry bed/cobalt/low temp. • SMR-POX with pure O2 • Extra-steam • SCR
	Pathway 2 : • Tubular/cobalt/low temp. • SMR/POX with air • No extra-steam	**Pathway 4 :** • Tubular/cobalt/low temp. • SMR/POX with air • Extra-steam • SCR
Storage	Fixed roof tank	Internal floating roof tank

Figure 5-10: Fisher Tropsch Naphtha pathways representation

5.3.4.2 Pathway 2: Tubular and air within an uncontrolled situation

This pathway considers an FT plant with capacity of 5,000 MTPD constructed on a site without industrial concentration. The plant design assumes a multi-tubular low temperature reactor (220 to 270 ^{o}C) and cobalt catalyst. The plant also uses combined SMR/POX syngas production with air injection instead of pure oxygen. It has hydrotreating and hydrocraking stages with final cuts around 50% of diesel, 20% of kerosene and 30% of naphtha (by weight). The plant uses no air control device and uses fixed roof tanks for the fuel storage. No extra steam exportation is considered.

5.3.4.3 Pathway 3: Slurry and pure O_2 within a controlled situation

This pathway considers the same FT plant design assumed in pathway 1 but constructed on a site with industrial concentration. The plant uses selective catalytic reduction as an air control device and uses internal floating roof tanks for the fuel storage. Extra steam exportation is considered. The plant design has a capacity of 5,000 MTPD and uses a slurry bed low temperature reactor (220 to 270 ^{o}C) with cobalt catalyst. The plant also uses combined SMR/POX syngas production with pure oxygen injection. It has hydrotreating and hydrocraking stages with final cuts around 60% of diesel, 18% of kerosene and 22% of naphtha (by weight).

5.3.4.4 Pathway 4: Tubular and air within a controlled situation

This pathway considers the same FT plant design assumed in pathway 2 but constructed on a site with industrial concentration. The plant uses selective catalytic reduction as an air control device and uses internal floating roof tanks for the fuel storage.

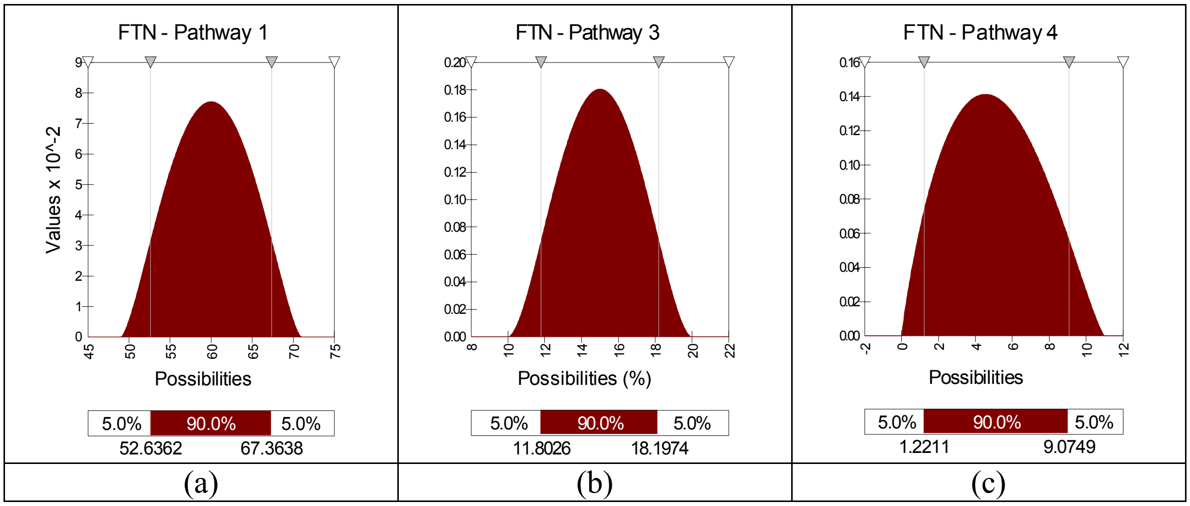
Extra steam exportation is considered. The plant design has a capacity of 5,000 MTPD and uses a multi-tubular low temperature reactor (220 to 270 ^{o}C) and cobalt catalyst. The plant also uses combined SMR/POX syngas production with air injection instead of pure oxygen. It has hydrotreating and hydrocraking stages with final cuts around 50% of diesel, 20% of kerosene and 30% of naphtha (by weight).

5.3.4.5 Combined scenario

Cost effective Fisher Tropsch plants are still at a stage of development similar to fuel cell vehicles, where the companies that are developing the technology do not provide much information, and for strategic reasons they aggressively defend their technological approach as the only one, in economical terms, that makes sense.

The use of air instead of pure oxygen in the syngas production has extreme positions among the experts, but the majority agreed that a possible continuum between the two approaches is more likely. In other words, there is a possibility of plant designs using from 100 % pure oxygen and 0 % air up to 0 % pure oxygen and 100 % air. However, the shape of this continuum did not get a consensus. The most probable pathway combination according to the majority of experts (not a consensus) is where an uncontrolled situation is expected to be more common than the controlled one, and where the slurry bed reactors with pure oxygen syngas production may prevail over the air use and tubular reactors. Figure 5-11 presents the assumed curves, representing the possibility of occurrence for pathway 1, 3 and 4. The possibility of occurrence of pathway 2 is the difference to 100 %.

It is important to point out also that the possibility of exporting extra steam in remote areas creates another controversy, since the water produced at the plant, and the desalinization of external water using extra-energy produced at the plant, can be a solution that benefits arid areas.



(a) (b) (c)

Figure 5-11: Possibilities of occurrences assumed for the Fisher Tropsch naphtha pathways.

5.3.5 Natural Gas Feedstock

In this analysis, natural gas is consumed in different locations and by different consumer sizes. In the South Coast Air Basin (SCAB), natural gas will be used for electricity production and for centralized and decentralized hydrogen production. In Malaysia, the natural gas will be used to produce electricity, methanol and Fisher Tropsch naphtha. In both cases, natural gas is consumed in its own production as well.

5.3.5.1 For Gas-to-Liquids Production

Gas-to-liquids fuels (methanol and Fisher-Tropsch) have the benefit of being able to use the cheapest (sometimes with negative values) natural gas reservoirs located in remote areas (far from the markets). Being liquids at the ambient temperature, methanol and Fisher-Tropsch naphtha (FTN) can easily be transported by sea tankers and sold as a hydrogen carrier for fuel cell application in developed markets.

Australia, Qatar, Malaysia, Chile and Trinidad/Tobago are examples of relatively inexpensive natural gas reservoirs where new gas-to-liquid plants have been proposed. In most cases these sites have featured some industrial development supported by the local natural gas industry. This study considers Malaysia, as an example of a source at an intermediate distance, in order to facilitate comparison with a previous study (Unnasch, 1996). The maritime distance between Malaysia and Los Angeles (about 15500 nautical miles – round trip) can be considered as a conservative assumption compared to the other sites (Chile and Trinidad Tobago). The transportation energy requirement for the Malaysia site represents about 2% of the total energy requirement, and 1.3% of the total for the Chile and Trinidad Tobago sites.

The natural gas extraction characteristics in Malaysia can also be assumed as being representative of the other optional sites. Around 30% of the natural gas is extracted in wells associated with light oil and 70% comes from the non-associated gas wells. One interesting characteristic of these natural gas sites is that, in general, they are close to the coast and most of the industrial complexes have been developed near port areas. This study assumes a 20-mile pipeline transporting natural gas from the processing plants to the gas-to-liquid plants. Natural gas turbines drive the pipeline.

5.3.5.2 For Hydrogen Production

For the hydrogen case the situation is completely different. Bulk liquid hydrogen is not an economical solution due to the high-energy requirement of the liquefying process and also due to the necessary use of special ships to maintain cryogenic temperatures and to consume hydrogen boil-off.

Being unable to benefit from the inexpensive natural gas from abroad, the hydrogen plants are forced to use the much more expensive gas of the California market. By 2010 it is assumed that around 50% of the marginal demand will be supplied by pipelines from Texas and 50% by pipelines from Canada. This assumption is similar to the one used by the California Energy Commission (in Unnasch, 1996) and is consistent with the projections made by the DOE/EIA (2000). The DOE/EIA report states: "liquefied natural gas imported from the remote areas is not expected to become a major source of U.S. supply between 1999 and 2020". The report also states that the majority of the U.S. increment of natural gas supply by 2020 will come as gas from western Canada and from offshore production in the Gulf of Mexico.

The Canada NG characteristic is around 60 % produced in non-associated wells, 15 % produced in wells associated with light oil, and 25 % produced in wells associated with heavy oil. Pipelines along with the compressors (50 % reciprocating engines and 50 % turbines) take care of the gas transportation and distribution. The length of the pipeline inside the basin (SCAB) is around 80 Km (50 miles). Around 640 Km (400 miles) are placed in California and around 2,170 Km (1,350 miles) are placed in the rest of the world (USA and Canada).

The Texas NG characteristic is as follows: 85 % produced in non-associated wells, 14.7 % produced in wells associated with light oil, and 0.3 % produced in wells associated with heavy oil. Pipelines along with the compressors (50 % reciprocating engines and 50 % turbines) take care of the gas transportation and distribution. The length of the pipeline inside the basin (SCAB) is around 80 Km (50 miles) and around 2,170 Km (1,350 miles) are placed in the rest of the world (USA crossing the California state border directly into SCAB). For small consumers such as fuel stations a distribution pipeline of around 60 Km (37 miles) is also added.

5.3.6 Electricity

All the system upgrades and new generator implementation to produce electrical energy in the South Coast Air Basin (SCAB) has been considered by the California Energy Commission (CEC) using natural gas combined cycle turbines. This technology has been assumed in this analysis for SCAB and also for electricity used in Malaysia where the gas-to-liquid plants are considered. For the California state electricity mix, the probabilistic curves were extrapolated from the literature and the production technology share is around 19 % coming from coal, 31 % coming from natural gas, and 3 % from oil. For the USA mix the share is around 52 % coming from coal, 22 % from natural gas, and 2 % from oil. For the Canada mix the share is around 16 % coming from coal, 5 % from natural gas, and 2 % from oil. The high voltage transmission line losses are between 3 to 7%. For short distances and small consumers such as fuel stations a low voltage distribution line is considered with losses between 2 and 4 %.

5.4 Analysis Results

The following results are based on the assumptions and scenarios developed by the FUEEM expert network for fuel cell vehicles (middle-size passenger cars) which hypothetically start running in SCAB (Los Angeles area) by 2010. It is important to point out again that extrapolating these results to other situations is not recommended. The main goal here is to demonstrate the life cycle analysis method suggested in this dissertation.

The method proposed was fully used in the fuel upstream analysis ("well to tank"), but because the analysis of total energy requirement and greenhouse gases only makes sense when the entire life cycle is analyzed ("well to wheels"), the vehicle assumptions (section 5.2) are included here as well, in spite of the fact that those are my educated guesses only. To calibrate the vehicle curves and reach consensus about them it is necessary to establish a new expert network with more car-manufacturers involved and to use the same data input treatment methodology explained in section 3. In other words, the results presented here are entirely my responsibility.

It is also important to point out several assumptions made in this dissertation. All the uncertainties are represented in the calculations with probabilistic curves using the confidence interval of 90 %; however, when a technology comparison is done, the entire interval (100 %) is considered. The combined scenarios of the fuel upstream pathway are always assumed unless stated otherwise. Finally, the fuel energy content is based on the higher heating values (HHV).

5.4.1 Total energy requirement (TE_{req})

In general terms, the operation of a direct hydrogen fuel cell vehicle (DHFCV) has a higher possibility of requiring (or consuming) less energy in the entire life cycle than the other technologies considered – the indirect methanol fuel cell vehicle (IMFCV) and the indirect Fisher Tropsch naphtha fuel cell vehicle, here simplified as indirect hydrocarbon (IHFCV).

On the other hand, based on the uncertainty analysis done, only 37.6 % of the direct hydrogen (DH) scenarios are more efficient, or consume less energy in the life cycle ($1.41\ MJ_{req}/km \leq DH\text{-}TE_{req} < 1.85\ MJ_{req}/km$) than any of the indirect methanol (IM) scenarios considered. For the rest of the hydrogen scenarios (62.4 %) it is possible to find at least one methanol scenario that consumes equal or less energy ($1.85\ MJ_{req}/km \leq DH\text{-}TE_{req} \leq 2.49\ MJ_{req}/km$) than the hydrogen scenarios. The analyses also show that 44.7 % of the indirect methanol scenarios are less efficient, or consume more energy in the life cycle than any hydrogen scenario considered ($2.49\ MJ_{req}/km < IM\text{-}TE_{req} \leq 3.25\ MJ_{req}/km$). For all scenarios the direct hydrogen cycles are more efficient (or consume less energy) than the indirect hydrocarbon cycles. See Figure 5-12 for a graphical representation of the curves.

The same discussion applies to the indirect methanol fuel cell vehicle (IMFCV) and the indirect hydrocarbon (IHFCV) scenarios. As shown in Figure 5-12, 78.2 % of the indirect methanol scenarios consume less energy ($1.85\ MJ_{req}/km \leq IM\text{-}TE_{req} < 2.73\ MJ_{req}/km$) than any indirect hydrocarbon (IH) scenario considered. For the other 21.8 % of the methanol scenarios ($2.73\ MJ_{req}/km \leq IM\text{-}TE_{req} \leq 3.25\ MJ_{req}/km$) it is possible to find at least one hydrocarbon scenario that consumes equal or less energy than the methanol scenarios. In the same way, 48.3 % of the indirect hydrocarbon scenarios are less efficient, or consume more energy in the life cycle (3.25 MJ_{req}/km < IH-$TE_{req} \leq$ 4.13 MJ_{req}/km) than any methanol scenario considered.

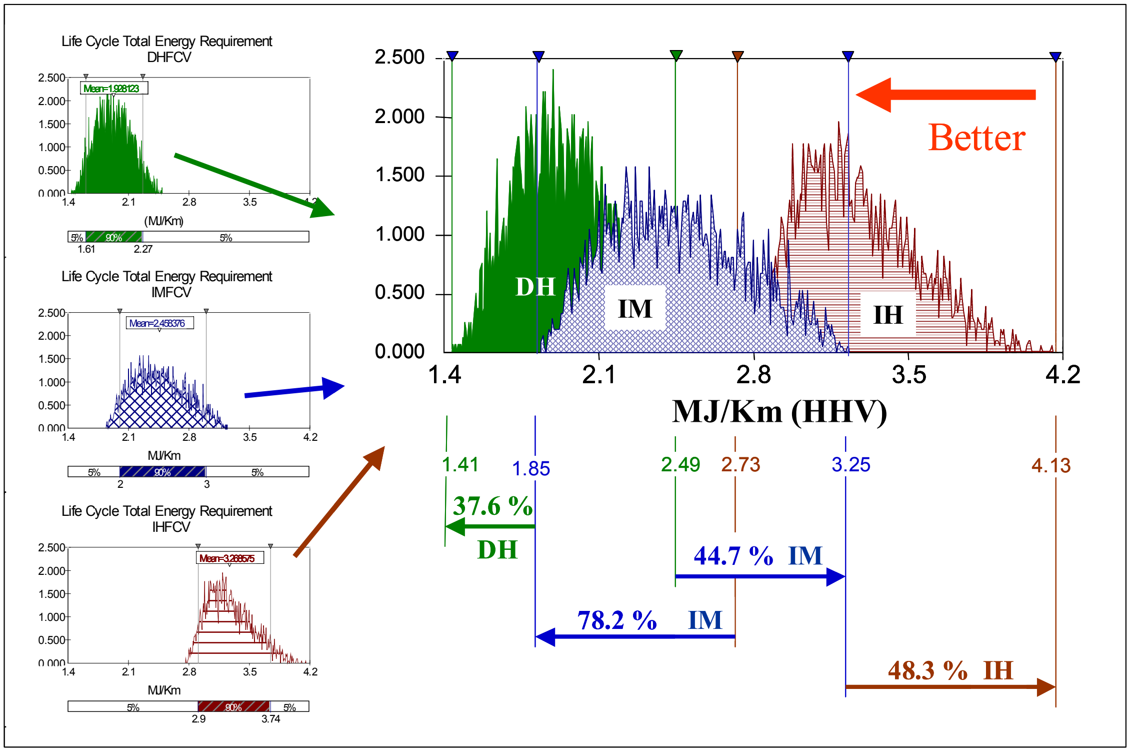


Figure 5-12: Life cycle result of the total energy requirement

5.4.1.1 Bounding scenarios

As discussed previously, a majority vote was used to combine the different scenarios, as opposed to the consensus established in all other variables. The idea of carrying on the “bounding scenarios” through the results was suggested for “extreme cases” analysis and accepted. An example of this alternative analysis is presented in Figure 5-13, as a critical case – the DHFCV and IMFCV comparison.

Basically, it shows that if one considers only pathway 2 for the hydrogen fuel (decentralized production at the fuel station) and pathway 4 for the methanol fuel (mega size plant with extra-steam exportation), practically no difference in efficiency is shown. It is important to keep in mind that, in the real world, it is unlikely that only one technology will occur, but it can be analyzed and FUEEM allows it to occur.

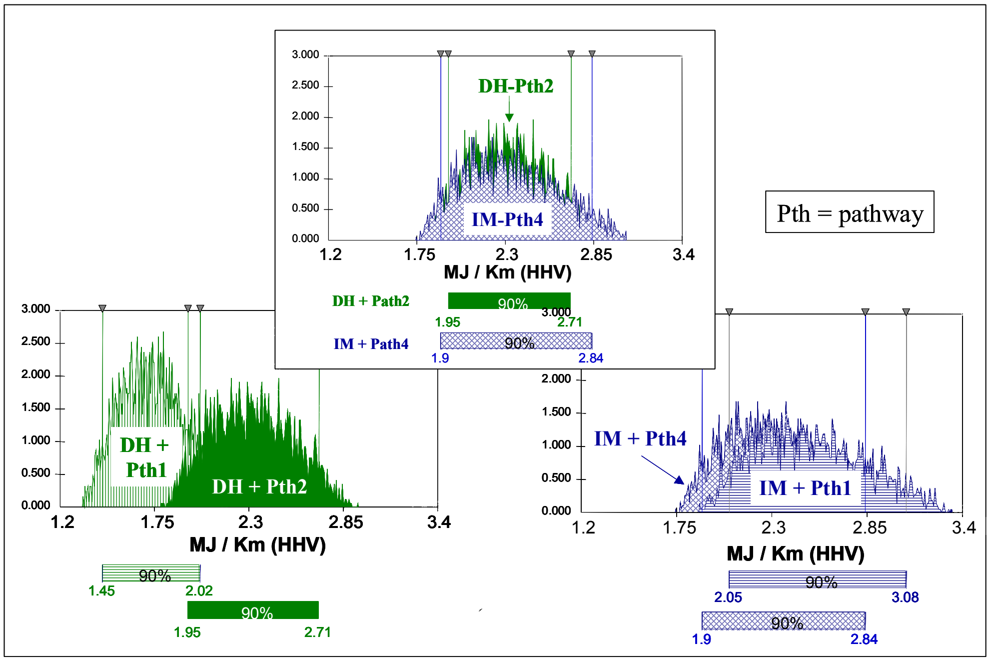


Figure 5-13: Example of "bounding scenarios" analysis for the total energy requirement of DHFCV and IMFCV cycles

5.4.1.2 Fuel upstream analysis

From the FUEEM pathways worksheets it is possible to do an analysis for the fuel upstream part only. Different vehicles' technologies consuming the same fuel in SCAB can be analyzed using those values. Figure 5-14 presents an example for the total energy consumed in the fuel upstream activities in terms of Giga Joule of energy consumed upstream per Giga Joule of fuel delivered to the vehicle at the fuel station.

5.4.1.3 Secondary fuel calculation

Another example is presented here to reinforce the idea of the secondary fuel calculation: the diesel energy consumed to run a truck that is transporting methanol is considered primary energy consumption and it is accounted for in the FUEEM process energy. On the other hand, the energy consumed to produce that diesel is considered in the secondary fuel calculation. Having the results of these calculations disaggregated in the model allow us to investigate the importance of the secondary fuel calculation in the final result.

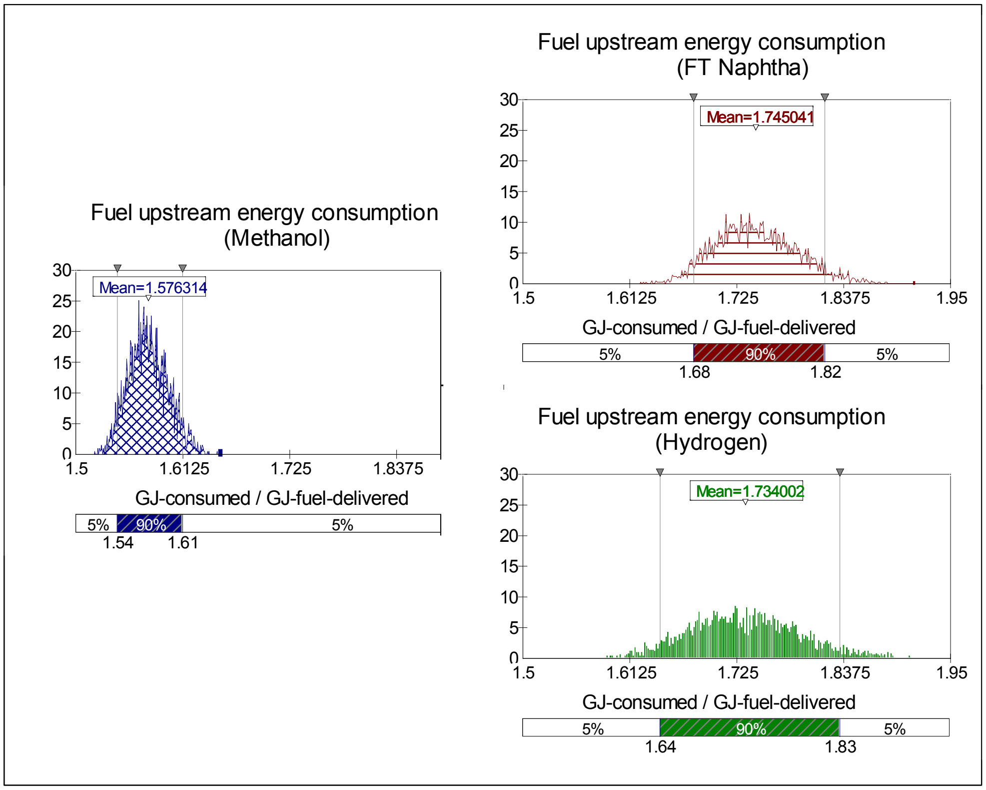


Figure 5-14: Example of fuel upstream analysis for the energy requirement

Using the means of the total energy requirement of each technology (see Figure 5-15) as an example, it can be said that, for the three analyzed technologies and several fuel pathways considered, the secondary fuel calculation is, in most cases, not significant. The only exceptions are the secondary fuel values in electric power generation. This is why the DHFCV, which has a more intense electric energy consumption cycle (to compress the gas and, partially, to produce the fuel), presents a much higher value in the figure.

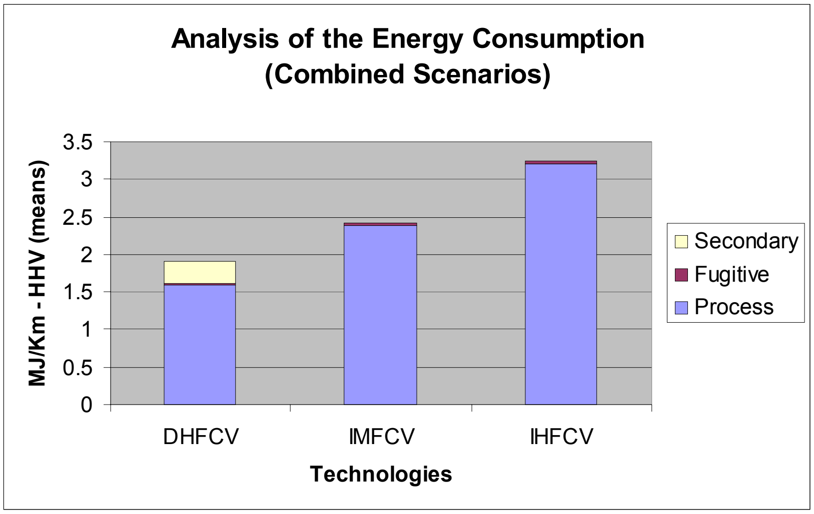


Figure 5-15: Example of the secondary fuel calculation share.

5.4.1.4 Non-renewable fuels and petroleum dependency

As explained earlier, FUEEM carries on the energy requirement calculation disaggregated, to allow the analysis of the amount of non-renewable fuel consumed, and the dependency over petroleum use, as well as the total energy. Figure 5-16 confirms the expectation that fuel cell vehicles in SCAB help reduces the dependency on petroleum, but it also may maintain, for the 2010 time-frame, the dependency of the system on non-renewable sources (fossil-fuels), since all “most probable” scenarios selected for this demonstration analysis are natural gas based fuels.

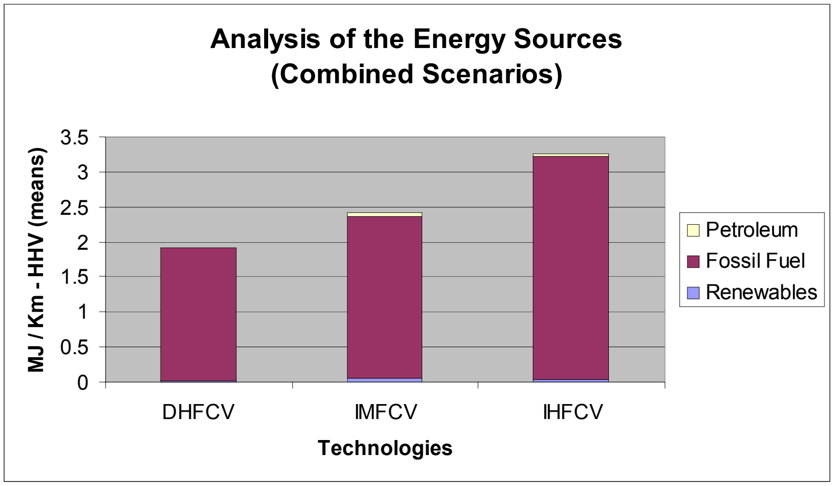


Figure 5-16: Example of non-renewable fuel and petroleum dependency

5.4.2 Assessment of global warming

FUEEM provides the opportunity to assess the impact of greenhouse gases emissions by using two different sets of factors: one set is the deterministic hundred year global warming potential (GWP) factors developed by IPCC (2001), and the second set is the probabilistic curves based on the economic damage index (EDI) factors developed by several authors and discussed by Delucchi (1997).

An initial comparison was made, for the DHFCV case, between the use of the GWP factors and the EDI ones. Figure 5-17 shows the result. It turns out that, practically speaking, there is no difference in using one or the other set. The reason is that the amount of CO_2 released to the atmosphere is much higher than the other greenhouse gases (CH_4 and N_2O), even in the EDI case that also considers the greenhouse effect of other gases (NO_x, NMOG and CO). For the three technologies analyzed, Figure 5-18 shows this proportion in terms of milligrams of pollutant emitted everywhere per kilometer driven.

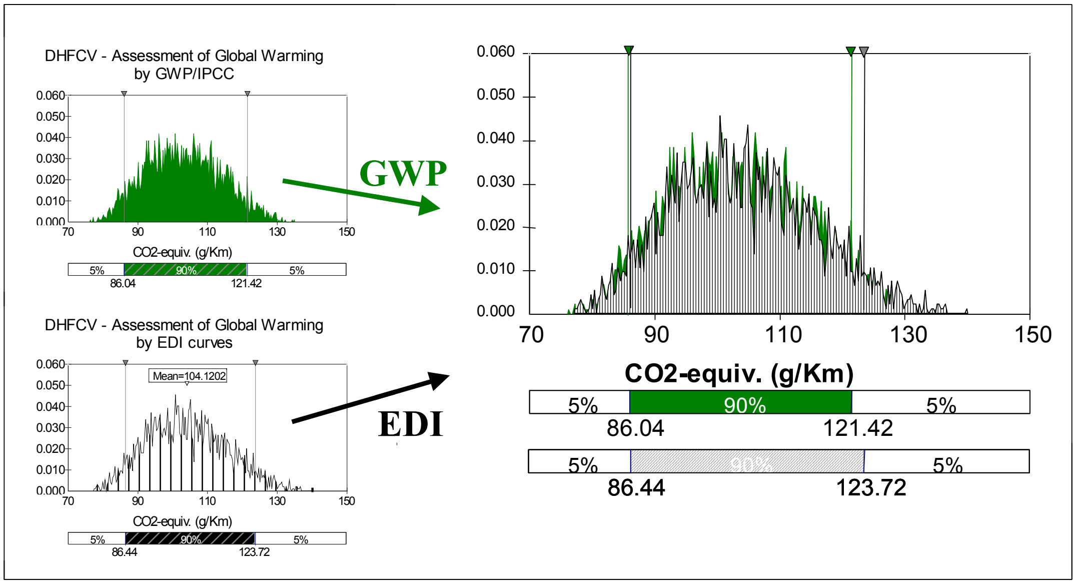


Figure 5-17: Global warming potential versus economic damage index - comparison for the DHFCV case

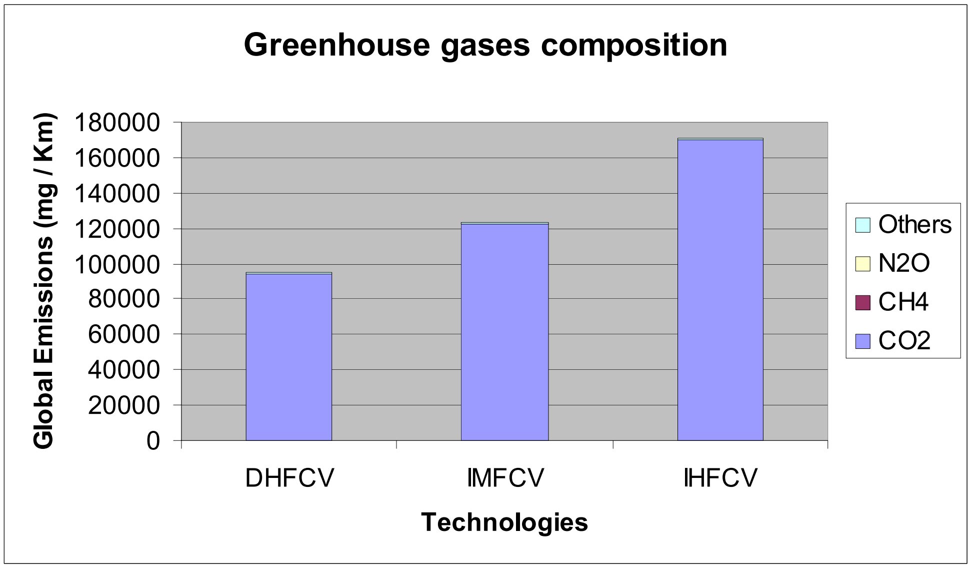


Figure 5-18: Greenhouse gases emissions (means).

Since the two factor sets are relative values compared to the CO_2 impact potential ($CO_{2\text{-equivalent}}$), in both cases the CO_2 reference factor is the deterministic value of one (1), minimizing any potential differences caused by the factors of the other pollutants.

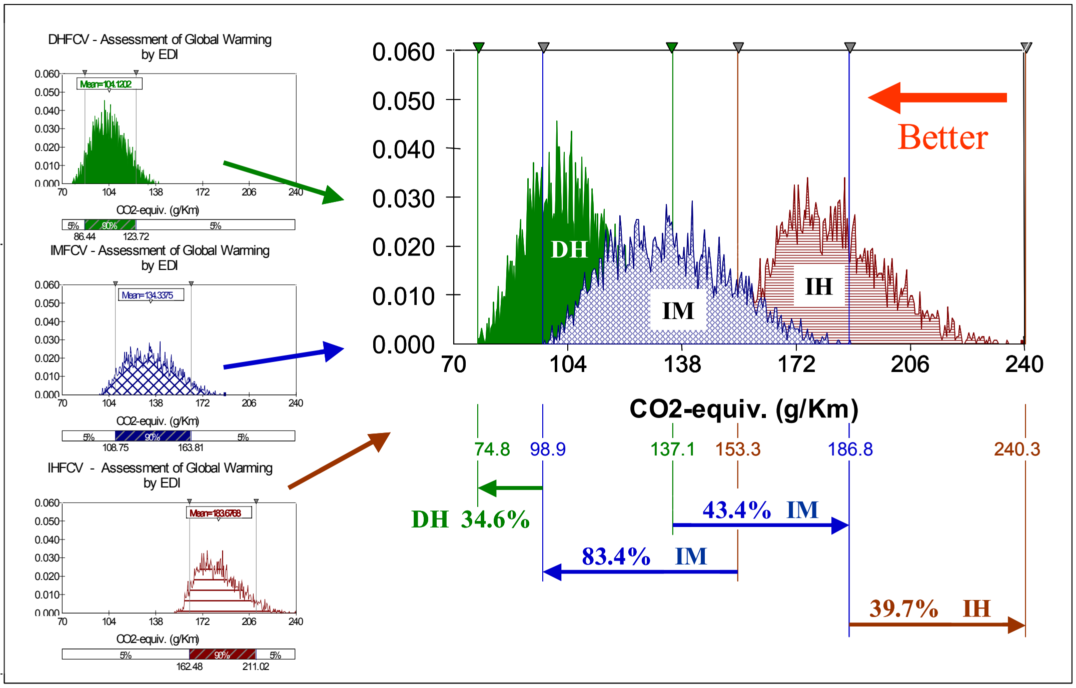


Figure 5-19: Assessment of global warming using EDI factors.

Since the EDI set assumes probabilistic curves as input, it was selected to show the assessment results of the SCAB demonstration analysis. Figure 5-19 presents the comparison in terms of grams of $CO_{2\text{-equivalent}}$ per kilometer driven. The results of the greenhouse gases assessment are very similar to the total energy requirement results. The reason is that the bulk of the energy consumption is fossil fuel consumption which produces CO_2 when combusted. For comparison, the global CO_2 emissions calculated by Unnasch *et al*. (1996) in the case of methanol fuel delivered at SCAB is 87 g/mi. It translate into 20.6 kg of CO_2 per Giga Joule adjusted for high heating values and the comparable result in the FUEEM analysis is a curve from 17.71 kg/GJ (5 %) to 21.19 kg/GJ (95 %) and mean of 19.34 kg/GJ.

5.4.3 Criteria Pollutants

5.4.3.1 Global Emissions

In general, the concern about criteria pollutant emissions (NO_x, NMOG, CO, PM_{10} and SO_x) is related to air quality in urban areas. Global emissions of these pollutants may play a rule in some environmental impact assessments. The greenhouse potential of NO_x, NMOG and CO were discussed in a previous section and SO_x and NO_x can also be associated with acid rain. For the analyzed cycles, Figure 5-20 shows the share of global emissions of criteria pollutants per area of occurrence. The idea is to show that the bulk of these emissions occur outside of the SCAB area. In Figure 5-20 only the means of the result curves are used, but, if necessary, the entire curve can be analyzed as well.

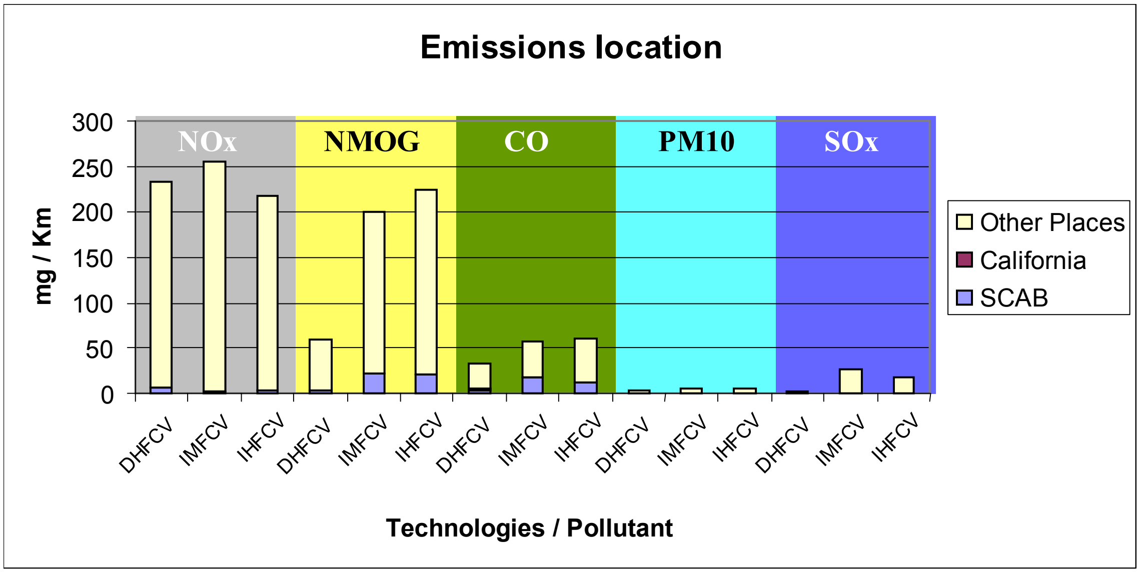


Figure 5-20: Global emission share of criteria pollutants

5.4.3.2 NO_x emissions within SCAB

The emissions of nitrogen oxides (NO_x) inside SCAB area are low for the three cycles analyzed. In general terms, the operation of the indirect methanol fuel cell vehicle (IMFCV) may have the highest probability for the lowest life cycle emissions ($1.3 \text{ mg/km} \leq \text{IM-NO}_{x\text{-SCAB}} \leq 2.8$ mg/km), followed by the indirect hydrocarbon fuel cell vehicle (IHFCV) operation ($1.4 \text{ mg/km} \leq \text{IH-NO}_{x\text{-SCAB}} \leq 5.78$ mg/km), and then by the direct hydrogen fuel cell vehicle (DHFCV) operation ($4.74 \text{ mg/km} \leq \text{DH-NO}_{x\text{-SCAB}} \leq 13.0$ mg/km). The uncertainty analysis shows that, if on one hand, in 99.2 % of the methanol scenarios (100 – 0.8) it is possible to find at least one hydrocarbon scenario that emits equal or less NO_x within SCAB, on the other hand, that 85.6 % of the hydrocarbon scenarios ($2.8 \text{ mg/km} < \text{IH-NO}_{x\text{-SCAB}} \leq 5.78$ mg/km) emit more NO_x than any methanol scenario. Figure 5-21 presents these curves.

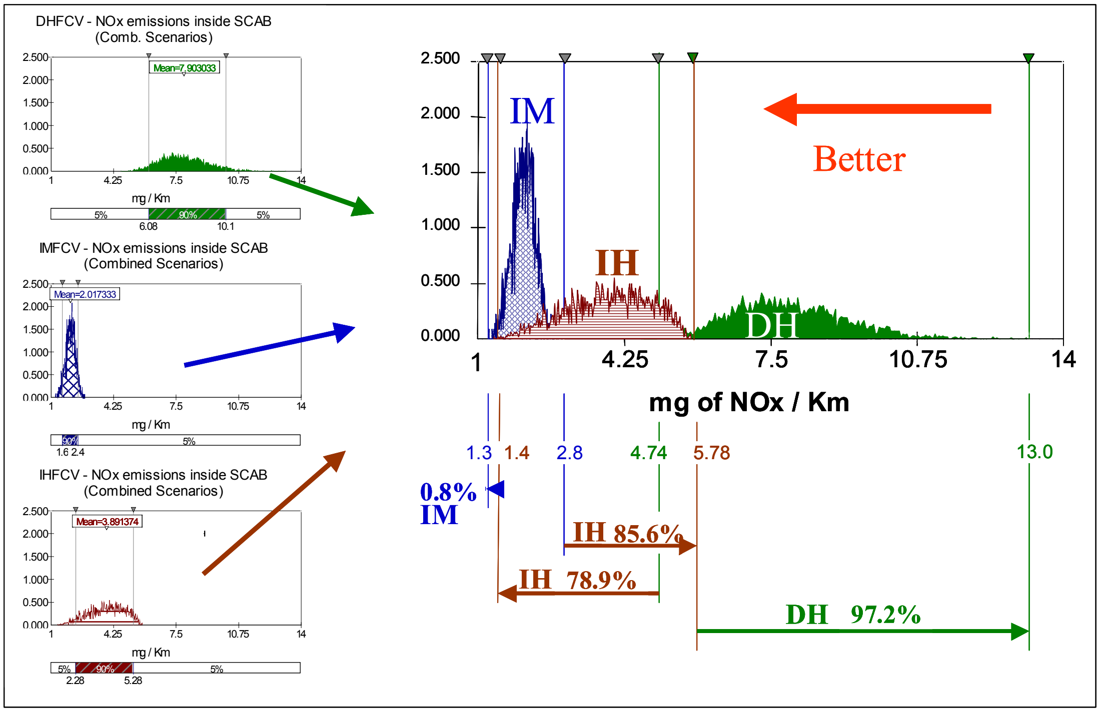


Figure 5-21: Life cycle result of the NO_x emissions within SCAB

The majority of these emissions come from the activities that burn natural gas (power generation and compression station equipment) and diesel (trucks and port activities) and, in the hydrogen case, they are also related to the scenarios selected by the expert network, where the hydrogen production plants are most likely placed close to the end-user retail market, and thus within SCAB.

5.4.3.3 NMOG emissions within SCAB

The operational life cycle of DHFCV will possibly emit less non-methane organic gases (NMOG) within SCAB than the other two alternatives analyzed. As presented in Figure 5-22, the DHFCV emissions may be in the range of 0.7 mg/km to 9.2 mg/km. These values are better than any IMFCV scenario ($11.5 \text{ mg/km} \leq \text{IM-NMOG}_{SCAB} \leq 204 \text{ mg/km}$) and any IHFCV scenario ($13.1 \text{ mg/km} \leq \text{IH-NMOG}_{SCAB} \leq 116 \text{ mg/km}$). It is important to point out that around 90 % of the direct hydrogen emissions come from natural gas (NG) leaking and venting in the hydrogen production plants and in the NG pipeline systems.

On the other hand, the figure also shows that the indirect hydrocarbon scenarios have a higher probability to be more concentrated towards the lower values than the indirect methanol scenarios. The main reason for that is the vapor pressure characteristic of the fuels. However, it also shows that for any IH scenario considered it is possible to find an IM scenario that emits equal or less NMOG than the IH case. A detailed investigation shows that a great part of these emissions (in the liquid fuel scenarios) comes from fugitive emissions in the upstream activities. See steps 1 and 2 of the analysis in Figure 5-23. Steps 3 and 4 show that the refueling process makes the largest contribution to the emissions, followed by the port activities. The evaporative emissions from the wet nozzle, from spillage, and from the vehicle tank (when it is opened to refuel) are the activities concerned.

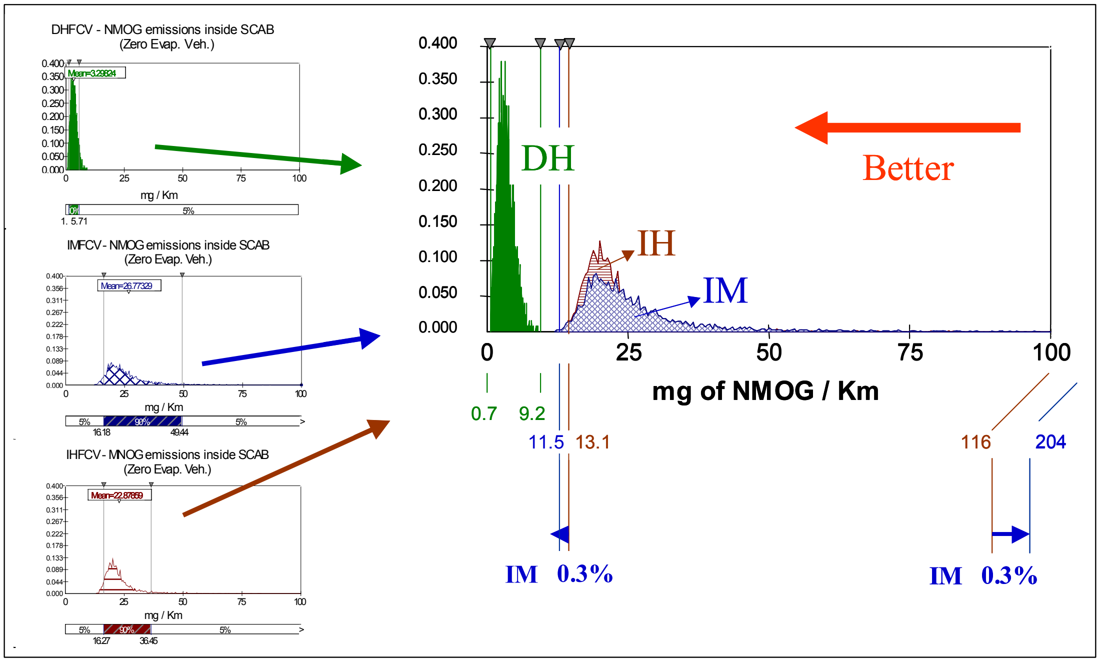


Figure 5-22: Life cycle result of NMOG emissions within SCAB

The chosen scenarios for the FUEEM demonstration analysis consider that the vehicles technologies using liquid fuels will comply with a proposed California law requiring that new vehicles have almost zero evaporative emissions. These vehicles are called "zero-evap" vehicles. According to the expert network this means a sealed and somehow pressurized fuel system in the vehicle. The sensitivity of this scenario assumption was tested in the case of a vehicle with "normal" fuel system still in place in 2010. I called this option "non-zero-evap." As an example, Figure 5-24 shows that, in the methanol case, NMOG emissions can increase, moving the curve to the range between 60.45 mg/km and 100.45 mg/km.

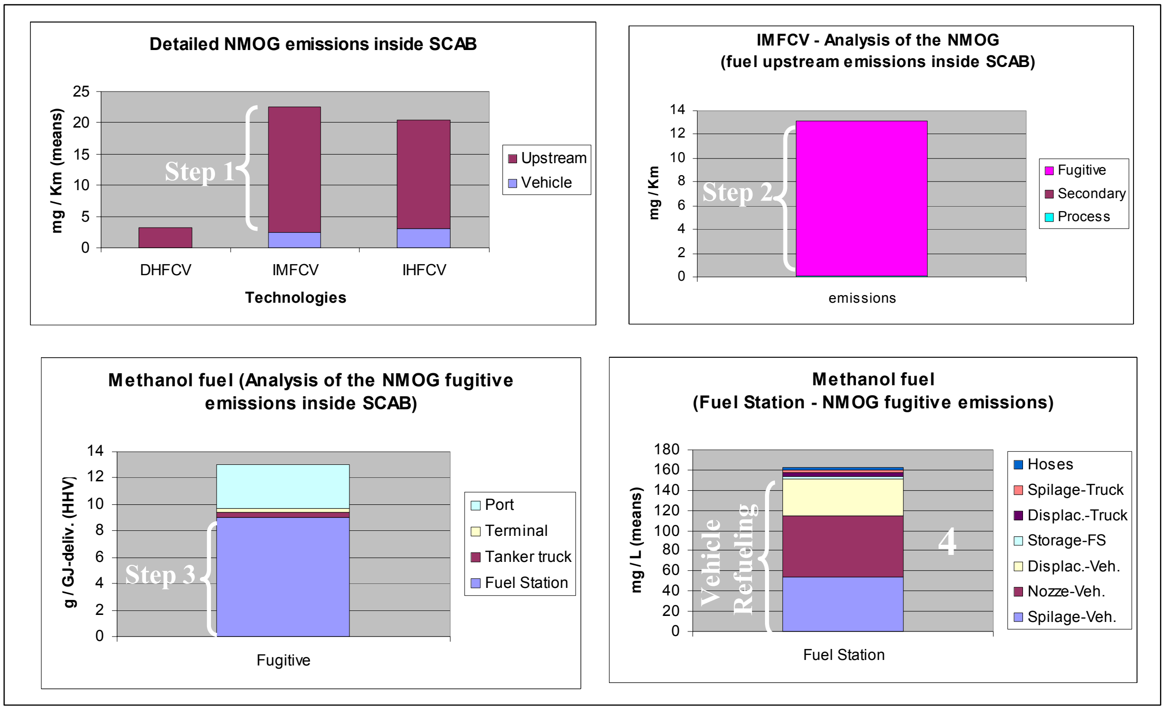


Figure 5-23: Details of the NMOG emissions within SCAB (IMFCV example)

The scenario also assumed that the refueling system would be similar to the controlled system existing today (with balance system control to capture the displacement emissions of the vehicle tank) that does not take care of problems like wet nozzle exposure, spillage, or the collection of vehicle emissions as soon as the tank is opened. However, since we are talking about a new refueling fuel infrastructure (for methanol or FT-naphtha) and new vehicle fuel system ("zero-evap"), there was a general consensus that a new system could be developed to minimize these problems. The potential benefit of this virtual "new refueling system" was also considered in the sensitivity analysis presented in Figure 5-24. This "new system" can greatly reduce the emissions and uncertainties in liquid fuel refueling (from 10.31 mg/km to 17.87 mg/km, in the methanol case), but those emissions may still be worse than the emissions in the hydrogen case.

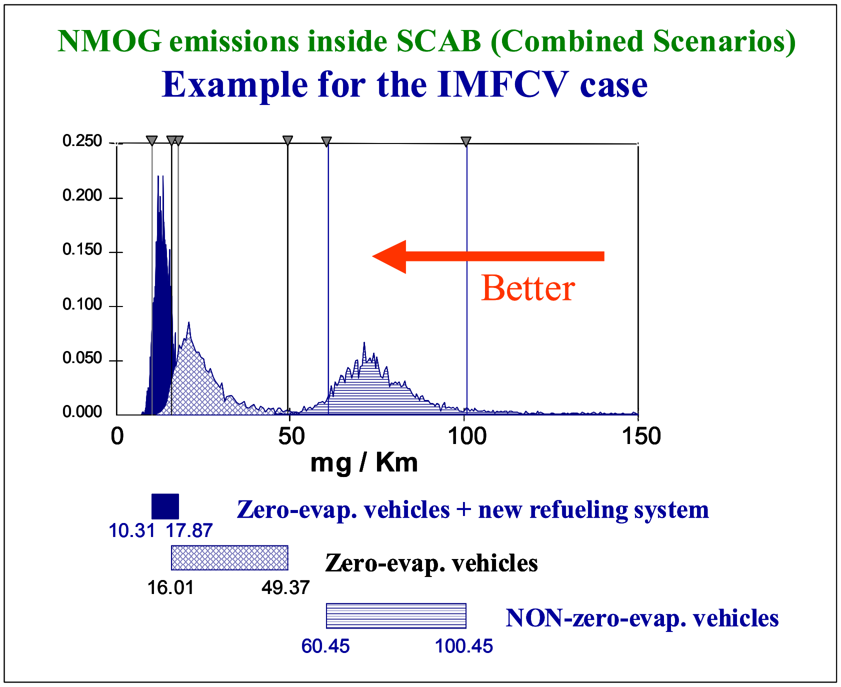


Figure 5-24: Sensitivity analysis over the "zero-evap" vehicle assumption (90 % confidence interval)

5.4.3.4 CO emissions within SCAB

The fuel cell vehicle life cycle emissions of carbon monoxide (CO) within SCAB are even lower compared with current technologies. By analyzing only the upstream activities it can be said that the emissions follow the same logic described for the NO_x emissions (section 5.4.3.2). However, for the overall cycle, the vehicular occurrences for the indirect technologies (IMFCV and IHFCV) are significantly higher compared with the upstream emission occurrences. Therefore, the operation of DHFCV will possibly emit less CO (from 1.2 mg/km to 7.3 mg/km) than the liquid fuel technologies, and the differences in the liquid fuel technology results are related to the vehicle onboard reformer emissions (see section 5.2). Figure 5-25 presents the results.

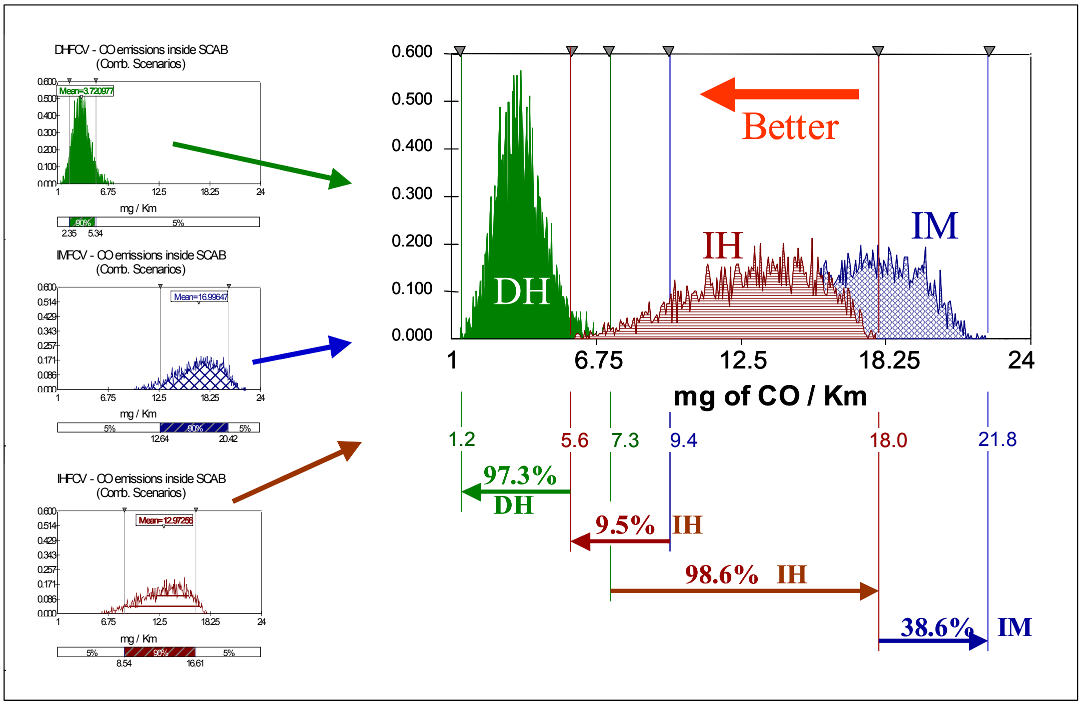


Figure 5-25: Life cycle result of CO emissions within SCAB

5.4.3.5 PM_{10} emissions within SCAB

The life cycle emission results of particulate matter smaller than 10 microns (PM_{10}) are so low for the three technologies analyzed that they can be considered negligible for all. Based on this fact, no attempt to compare their differences was made. Figure 5-26 presents the results.

5.4.3.6 SO_x emissions within SCAB

Similar to the PM_{10} case, the life cycle emission results of sulfur oxides (SO_x) are so low for the three technologies analyzed that they can be considered negligible for all. Based on this fact, no attempt to compare their differences was made. Figure 5-27 presents the results.

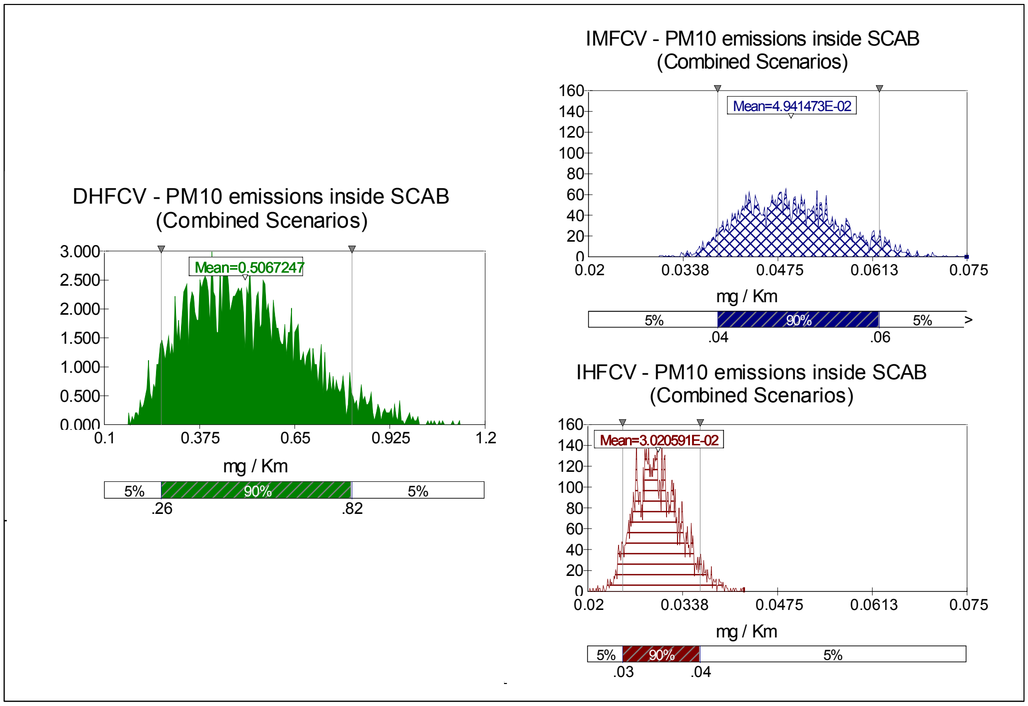


Figure 5-26: Life cycle result of the PM_{10} emissions within SCAB

5.5 Regression Sensitivity Analysis

As stated before, the Monte Carlo simulation approach is similar to performing several analyses at once (in fact, 3,000 interaction analyses were considered in this demonstration study), with the advantage of establishing the importance of each scenario at the end. This importance is expressed in the occurrence probability, and if the input variables are well discussed and accepted, uncertainty analysis calculation should suffice.

On the other hand, the alternatives of “bounding scenarios” or “sensitivity analysis” (in the refueling system case) were presented, if the detail of some extreme cases interested people or, if for some reason, a pathway that may have some small possibility of occurring was not included in the calculation, as was the case of the new “virtual” refueling system associated with the “zero-evap” vehicles. These alternatives are, in fact, single pathway calculation results that should be interpreted as “what if” cases. For example, *what if* all methanol were produced in mega-size plants with extra-steam exportation? Or, *what if* all fuel pumps had a new system that takes care of the spillage and wet nozzle problems?

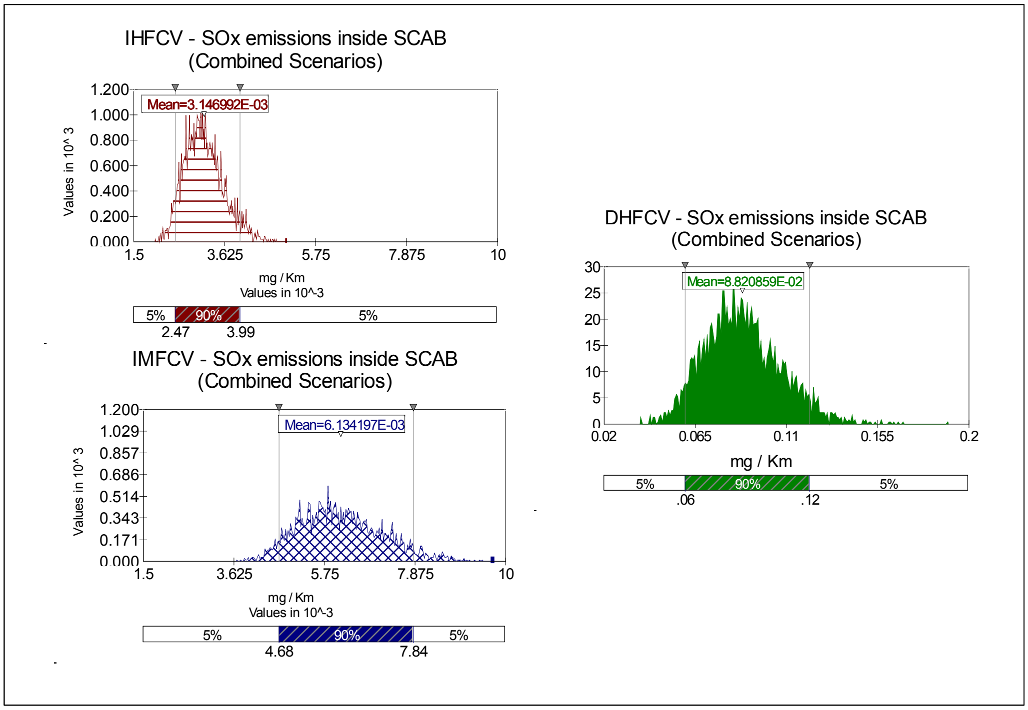


Figure 5-27: Life cycle result of the SOx emissions within SCAB

Another, and interesting, analysis that is suggested here is the "regression sensitivity" of the input variables assumed. By performing multivariate stepwise regression the @Risk ® software allows the investigation of the importance of each variable in the result. The most important variables identified can be revisited in future studies when new information is available, or revisited in future discussion rounds of the expert network for studies is not yet completed.

A regression value of "1" and "-1" indicates that a variation in the standard deviation of the input variable will provoke a similar variation (in the opposite direction for the negative case) in the output variable considered. A regression value of zero (0) means there is no significant relationship between the input and output variable.

As example, Figure 5-28, Figure 5-29 and Figure 5-30 present the regression sensitivity of the total energy requirement result of the three vehicle technologies analyzed. They show that vehicle fuel economy is a very sensitive variable as are the possibilities of occurrence of each pathway analyzed. This more general result reinforces the necessity for future studies to concentrate efforts on both variables, since, to complement the sensitivity, the vehicle fuel economies did not yet follow the FUEEM data treatment methodology, and the fuel pathway combination scenarios are the only fuel upstream variables that did not have consensus among the expert network.

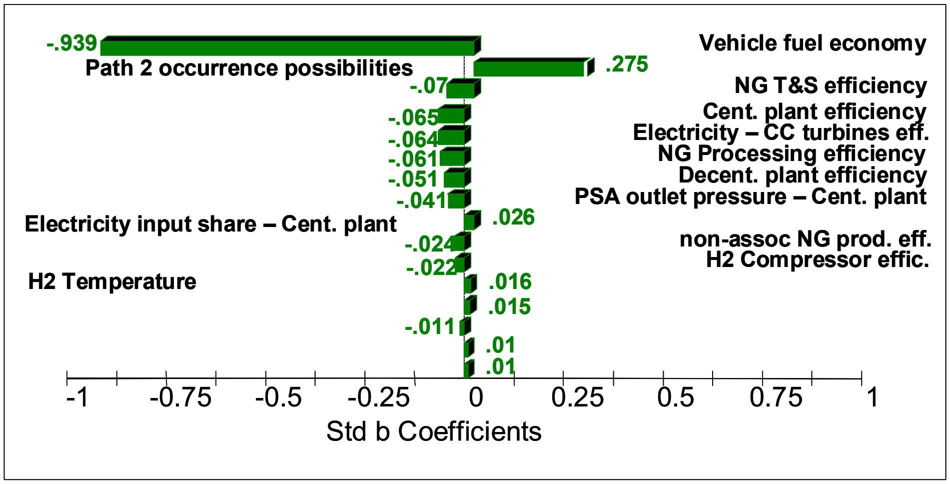


Figure 5-28: Regression sensitivity for the DHFCV - Total energy requirement

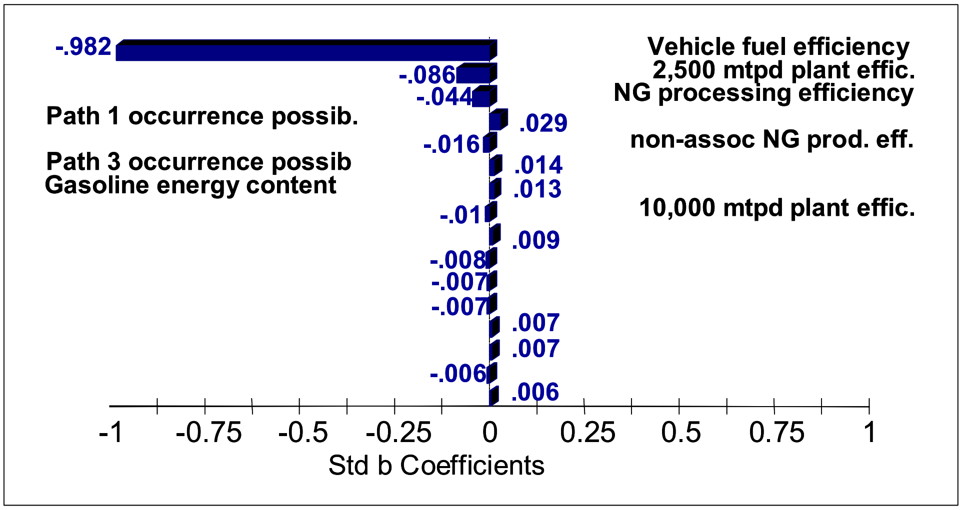


Figure 5-29: Regression sensitivity for the IMFCV - Total energy requirement

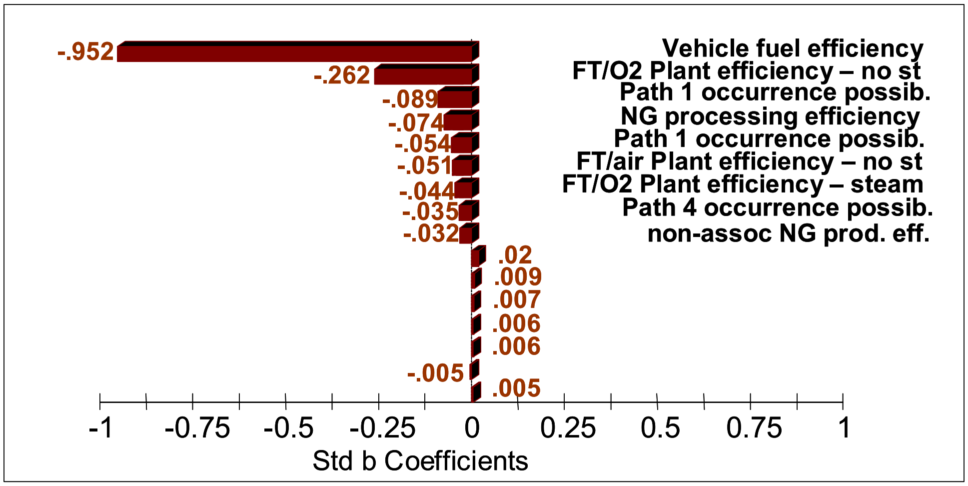


Figure 5-30: Regression sensitivity for the IHFCV - Total energy requirement

To eliminate the effect that the vehicle fuel economy provokes in the graphic, facilitating the analysis of the other variables, the regression sensitivity can be done only at the fuel upstream result level. As examples of this Figure 5-31 and Figure 5-32 are presented, showing how informative the results can be.

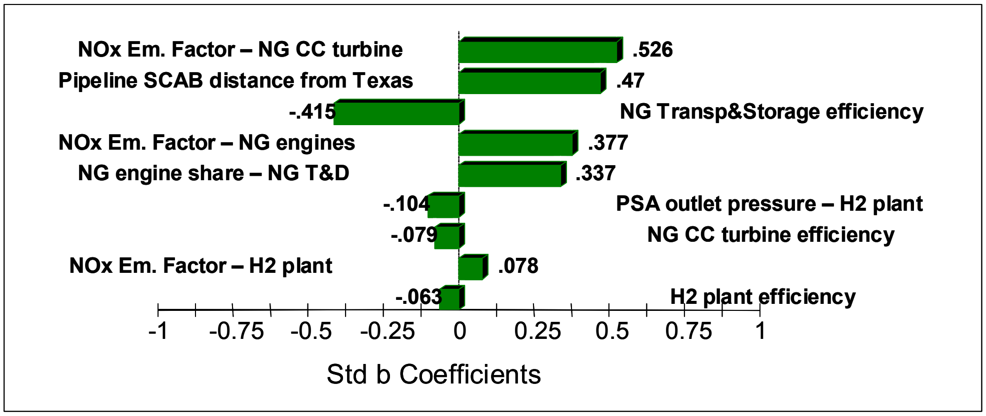


Figure 5-31: Regression sensitivity for the H2 pathway 1 - NOx emissions within SCAB

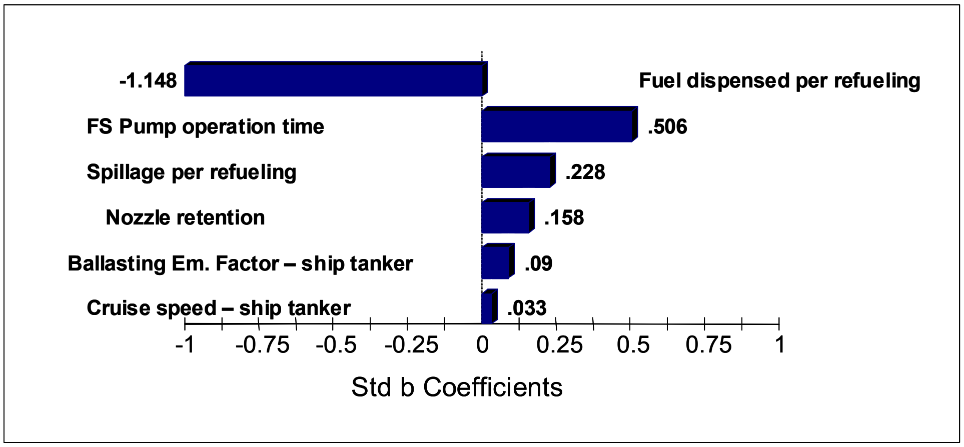


Figure 5-32: Regression sensitivity for the MeOH pathway 1 - NMOG emissions within SCAB

5.6 Analysis of the use of dependency among variables

To deal with the eventual dependency among some of the variables not previously correlated within mathematical expressions, the FUEEM was set using rank order correlation techniques and an envelope technique in the hydrogen production case. To understand the importance and influence of this decision in the final result, a parallel model was modified. All the rank correlations were disabled and the envelope method at the hydrogen production worksheet was replaced by regular probabilistic curves.

The results of both models with and without correlations among variables were compared. Contradicting the initial expectation, no large differences were encountered nor even some pattern or tendency, though the correlations would decrease the uncertainties as suggested in Figure 5-33. Figure 5-34 shows the opposite situation where the uncertainty appears to increase with the dependency assumption and, finally, Figure 5-35 shows an example where the values were moved to the left side only.

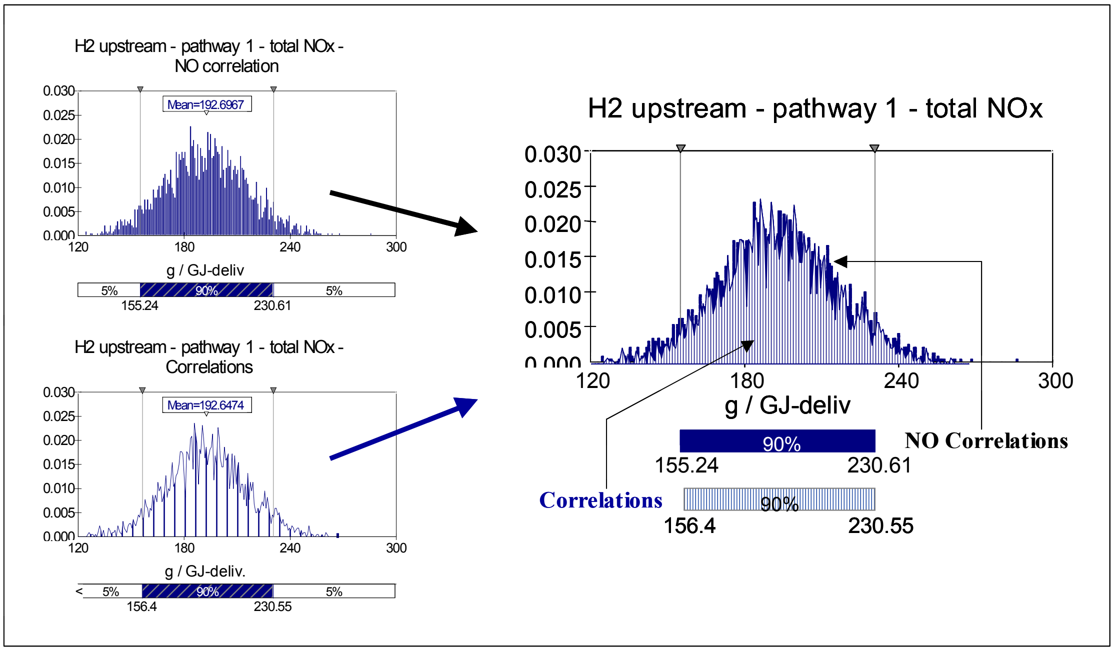


Figure 5-33: Comparison example of the models assuming independent and dependent variables – total NOx emissions for the hydrogen pathway 1.

It should be noted that we used two models for this analysis and considering that new probabilistic curves were input without correlations – in order to remove the envelope technique – the Monte Carlo sampling sequence could be different (even maintaining the same seed). Therefore, part of these small differences encountered in the results could be due to this possible variation in the model sampling.

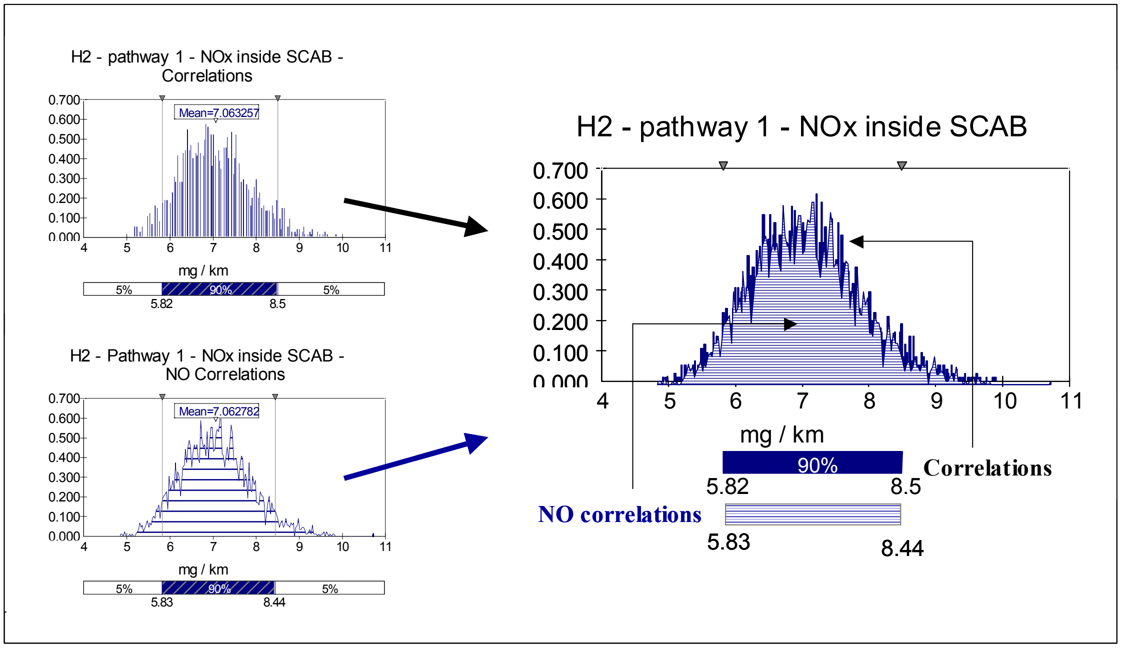


Figure 5-34: Comparison example of the models assuming independent and dependent variables – NO_x emissions within SCAB for the hydrogen pathway 1.

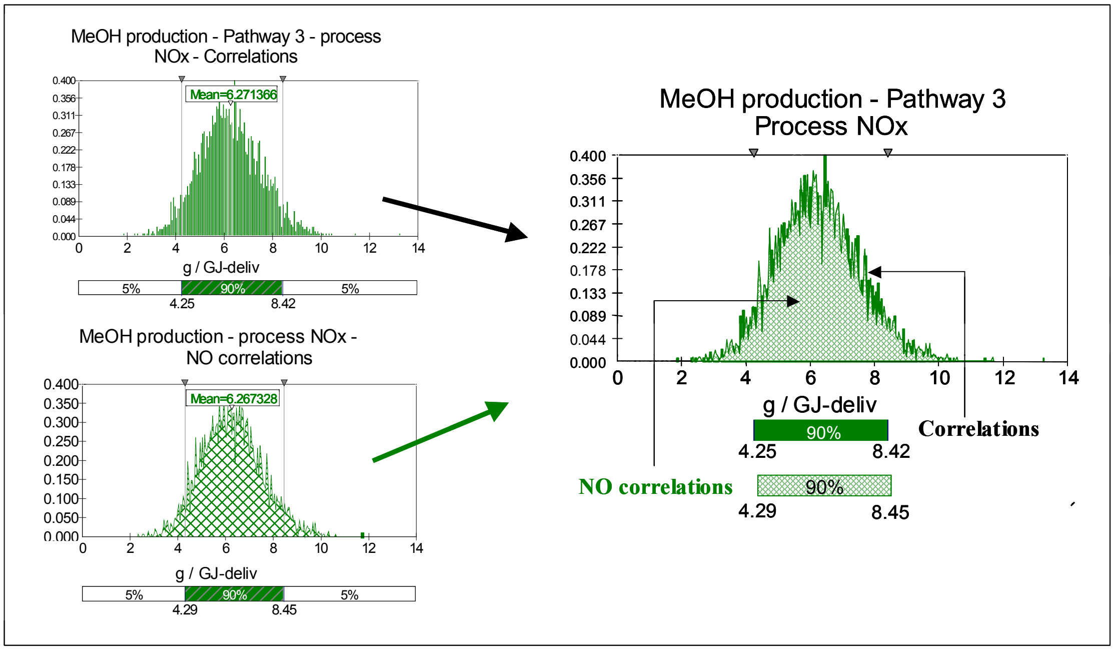


Figure 5-35: Comparison example of the models assuming independent and dependent variables – process NOx emissions for the methanol pathway 3.

6 CONCLUSIONS AND SUGGESTIONS

6.1 Input Data Treatment Methodology

Life Cycle Assessment (LCA) will always have some level of subjectivity and uncertainty, especially for the impact assessment phase of any LCA and also for the inventory analysis phase of future technologies, products, and services. The FUEEM project developed a robust methodology to deal with uncertainties and to forecast activities of fuel for fuel cell vehicles in the year 2010, with the involvement of the interested parties. In this case study, subjective estimates were necessary because of the lack of data, the context of a completely new situation relative to special future fuels and vehicles, and the necessity of assumptions to obtain probabilistic curves and correlations among them.

The involvement of the interested parties in all phases of the study as opposed to only as reviewers at the end of the study suggests that it is possible to obtain a higher level of technical credibility in LCA through a more participatory process. In the case of technical information on common and specific activities (such as, for example, hydrogen production in a 27 metric tons per day steam reformation plant), the participatory process associated with probabilistic curves to represent them can generate consensus among the different economic sectors and players. Future studies and new correlation data (such as the plant efficiency related to the natural gas composition) can create a very respectable database, removing even the regional differences. Petroleum extraction, natural gas pipelines, and electricity production are examples of common activities that should have this kind of consensus because they may appear in several kinds of life cycle studies. A necessary step in this direction is to stimulate the “data collectors” such as EPA (Environmental Protection Agency) and CARB (California Air Resources Board) to move towards better information on data uncertainties.

Another benefit of generating a consensus at this technical level is to reduce the space for manipulation when an organization attempts to use LCA to push its agenda. The FUEEM method, using a modified Delphi technique coupled with data search and industry surveys, appears to be very effective in this sense. The focus on the technical comments of the experts in the Delphi rounds was fundamental to generating the consensus. Further studies should confirm if this method generates consensus towards the real value, as it is supposed to do.

For the scenario construction, the method also appears to be very efficient, especially by eliminating ideas that are far from the possible reality. A well-conducted process, leading to a good group learning process, can screen the best solution and perhaps even improve it. A future study to check the consistency and general applicability of this statement would be interesting. The consensus of the expert network is that the decision of the group in most cases would be superior to the decision of a single modeler or single organization.

On the other hand, the FUEEM method was not able to perform well for the extreme cases of the scenario combination, in which no consensus was reached and the majority’s result was used. The scenario combination is the part of the study in which the most subjectivity was present. It was also the final opportunity for some organizations to try to influence the final result. The scenario combination, using the majority value, can be very sensitive to the expert network formation. The FUEEM expert network formation tried to be as representative as possible but it is hard to claim an absence of bias since some industries were represented more than others. An alternative solution adopted for the scenario combination was to present the results of the extreme cases as “bounding scenarios.” This solution brought much more information to the final answer. As the use of probabilistic curves is similar to performing several sensitivity analyses in the study, it provides more and richer information. The quantity of information presented when both solutions are put together can be excessive and its usefulness should be further investigated.

The major drawback of the FUEEM method is the relative higher cost in terms of time and resources necessary to perform a good investigation when compared with studies using the decisions of a single modeler and only a few data points collected from the published literature. From the reaction of the internal and external public to the initial FUEEM results, as well as from the perseverance of the expert participation during the long process, it can be said that the benefits may compensate for the costs. Future studies could try to quantify these benefits. On the other hand, if this method generates information that has a general consensus so that several studies can benefit from them, then the relative cost can be much less, while the benefit in each study will be greater.

Finally, according to Sullivan and Claycombe (1977), “no forecast should be accepted as final,” especially in the area of advanced technology, where development occurs very quickly and there is considerable interest. The FUEEM method should be viewed as an additional and interesting tool to help the improvement of LCA, and as a basis for constant improvement.

6.2 Fuel cell vehicle life cycle assessment

Life cycle assessment (LCA) of future fuel cell vehicles (FCV) can be performed at national average level or at local and more specific level. The uncertainties in the assessment result increase with the breadth (e.g., national as opposed to local) of the study due to the increment of pathways necessary in the scenario combination.

In complement to that, the analysis of the environmental aspects of criteria pollutants is more concerned with the emissions released within urban areas. These emissions are strongly related to the specificities of each urban area that would hardly be captured in a broad national study.

To demonstrate the methodology proposed, this study performed a local life cycle assessment to compare three mid-size fuel cell passenger vehicle technologies supposedly running in the South Coast Air Basin (Los Angeles area) around 2010. The vehicle technologies considered were:

1. DHFCV: Direct hydrogen fuel cell system with an on-board compressed gaseous tank at 34.5 MPa (5,000 psi).
2. IMFCV: Indirect methanol fuel cell system with an on-board steam reformation fuel processor.
3. IHFCV: Indirect hydrocarbon fuel cell system with an on-board autothermal fuel processor.

The special fuel cell fuels (sulfur-free) are all based on natural gas feedstock. Fisher-Tropsch naphtha was the choice for the hydrocarbon case.

For the most-probable scenario selected (for the SCAB area), it can be said that:

1. The DHFCV has 37.6 % of the scenarios with a better efficient energy cycle requirement than any of the IMFCV scenarios. The results also show that 44.7 % of the IMFCV scenarios are less efficient than any DHFCV scenario. All the DHFCV scenarios are more efficient than any IHFCV scenario and 48.3 % of the IHFCV scenarios are less efficient than any IMFCV scenario.
2. Similar pattern and results are observed for the greenhouse gases assessment in terms of $CO_{2\text{-equivalent}}$ where the impacts are driven by CO_2 production from fossil fuel combustion processes.
3. The hydrogen case (DHFCV) will also emit less NMOG within SCAB than the liquid fuel cases (IMFCV and IHFCV). Evaporative emissions in the fuel marketing activities are the main reason for the liquid fuel case's emissions. A new refueling system may minimize the emissions, even though the DHFCV will still emit less.
4. NO_x emissions within SCAB are low for the life cycle of all the technologies analyzed and the DHFCV will emit more than the indirect technologies (IMFCV and IHFCV) because of the consideration to produce hydrogen near to the end-user retail market (within SCAB) and also because this process consumes more electricity than the others, which is also considered to be generated within SCAB.
5. CO emissions within SCAB are almost negligible for the three technologies analyzed. In this case, the vehicular emissions of the technologies using on-board reformers (IMFCV and IHFCV) are more significant than the fuel upstream emissions.

6. PM_{10} and SO_x life cycle emissions within SCAB can be considered negligible for the three technologies.

6.3 Suggestions for future improvements and studies

In complement to the suggestions presented in section 6.1, about the data treatment methodology, it is important to mention some further suggestions about the LCA of fuel cell vehicles and about the model software.

Apparently, the use of rank correlations to deal with the dependency among variables did not provide significant differences in the final results. More effort should be put into this section to investigate the possible existence of some other correlations not included in the current model. Another problem to be investigated further is the forced input value of the rank correlation coefficient in the correlation matrix due to inconsistency test performed automatically by @Risk software.

If necessary, to minimize time and modeling effort, the secondary fuel calculation could be restricted to power generation fuels. In doing so an underestimation up to 1 % in the final results should be considered.

The spreadsheet platform used by @Risk software is not amenable to change or creating new pathways for analysis. It would be different if the component models were developed in Simulink/Matlab ® blocks that can be more easily rearranged in the graphical platform, making the model much more flexible. In order to do that some development in the Simulink codes is necessary to allow for most of the Monte Carlo simulation features presented in the @Risk software. Also a better database system than the spreadsheet platform used should be interesting for easier search of existing data, as well as for easier input of new data.

In terms of the life cycle assessment of fuel cell vehicles, one of the priorities for future studies should be the use of the FUEEM data treatment methodology for the vehicle input assumptions. Considerations about hybridization alternatives, controls, vehicle class size, vehicle body designs, and materials used should be interesting to analyze.

In terms of fuel upstream analysis, should be interesting to prioritize the study of petroleum pathway options. It would allow the investigation of a refined naphtha pathway option for the hydrocarbon fuel cell vehicle analysis, as well as work towards a future comparison with internal combustion engine alternatives (regular and hybrid versions of gasoline and diesel engines).

Finally, it should be very interesting to carry through all the uncertainty analysis of emissions and energy requirement associated with an uncertainty analysis of cost, making possible a cost-effectiveness analysis in the future.

7 REFERENCES

Ackerson M. D., Clausen E. C., Gaddy J. L. (1993). The Use of Biofuels to Mitigate Global Warming. A Global Warming forum: Scientific, Economic and Legal Overview. CRC Press, Boca Raton – Florida.

Acurex Environmental Corporation (1996). Evaluation of Fuel-Cycle Emissions on a Reactivity Basis. 2 volumes. Prepared for CARB. A166-134. Principal Authors: Unnasch, S.; Browning, L. and Montano, M.

Adamson, K-A and Pearson, P. (2000). Hydrogen and Methanol: A Comparison on Safety, Economics, Efficiencies and Emissions. Journal of Power Sources, 86, pp. 548-555.

ADL - Arthur D. Little Inc. (1996). Energy Efficiency and Emissions of Transportation Fuel Chains, Technical Report to Ford Motor Company. Reference 455333.

Al-Alawi, S. M. and Islam, S. M. (1996). Principles of Electricity Demand Forecasting. Part 1: Methodologies. Power Engineering Journal. June, pp. 139 – 143.

Allard, Mark. (2000). Issues Associated with Widespread Utilization of Methanol. Society of Automotive Engineers. Technical Paper Series 2000-01-0005.

AMI – American Methanol Institute (1998). Looking Beyond the Internal Combustion Engine. The Promise of Methanol Fuel Cell Vehicles. by Gregory P. Nowell.

Anderson, Robert B. (1984). The Fischer-Tropsch Synthesis. Academic Press, Inc.

Andress, David (1998). Comparison of Ethanol Fuel Cycles in the GHG Models developed by Michael Wang and Mark Delucchi. Prepared for DOE, Office of Fuel Development and Office of Transportation Technologies, Energy Efficiency and Renewable Energy. DE-AC05-96OR22464.

ANL – Argonne National Laboratory (1998). Total Energy Cycle Assessment of Electric and Conventional Vehicles: An Energy and Environmental Analysis. Volume I and II, Technical Report and Appendices. Prepared for the Department of Energy, office of Energy Efficiency and Renewable Energy.

API – American Petroleum Institute (1989). A Survey and Analysis of Liquid Gasoline Released to the Environment During Vehicle Refueling at Service Station. Publication no. 4498. June. Washington, DC.

Armstrong, A. P. and Akhurst, M. A. (1999). Alternative Fuels: Well-to-Wheels Energy Use & CO_2 Comparisons. BP Amoco, Fuels Technology Group. Presented at the IIR Fuel Cell Vehicles Conference.

Armstrong, J. Scott (1985). Long Range Forecasting: From Crystal Ball to Computer. Second edition. Wiley-Interscience Publication. New York.

Armstrong, J. Scott (1999). Introduction to Paper and Commentaries on the Delphi Technique. International Journal of Forecasting. 15, pp. 351 – 352.

Armstrong, J. S. and Collopy, F. (1993). Causal Forces: Structuring Knowledge for Time Series Extrapolation. Journal of Forecasting, 12, pp. 103-115.

Asif, F.; Weaver, C. S. and Walsh, M. P. (1996). Air Pollution From Motor Vehicles – Standards and Technologies for Controlling Emissions. The International Bank for Reconstruction and Development – The World Bank. Washington DC.

Asregadoo, Ray (1992). Gasoline Dispensing Facilities – Petroleum Production and Marketing. Section 4.10 – Emission Inventory Codes and Description. California Air Resource Board. March.

Ayres, Robert U. (1995). Life cycle analysis: A critique. Resource, Conservation and Recycling. Vol. 14, pp. 199-223.

Ayton, P.; Ferrel, W. R. and Stewart, T. R. (1999). Commentaries On "The Delphi Technique as a Forecasting Tool: Issues and Analysis" by Rowe and Wright. International Journal of Forecasting. 15, pp. 377 – 381.

Balentine, H. W.; Dickson, R. J. and Oliver, W. R. (1994). Development of Uncertainty Estimates for the Grand Canyon Visibility Transport Commission Emission Inventory. Radian Corporation Technical Memorandum, Sacramento – CA.

Barry, Timothy M. (1996). Recommendations on the Testing and Use of Pseudo-Random Number Generators Used in Monte Carlo Analysis for Risk Assessment. Risk Analysis. Vol. 16, No 1, pp. 93 – 105

Beckmann G., Klopries B. (1991). CO_2 Increase: Questions Beyond Climatic Change. Energy Vol. 16, No. 11/12, pp. 1317-1330.

Belson, William A. (1981). The Design and Understanding of Survey Questions. Gower Publishing Co., Aldershot, England.

Benkovitz, C. M. and Oden, N. L. (1985). Framework for Uncertainty Analysis of the NAPAP Emissions Inventory. U. S. Environmental Protection Agency, Air and Energy Engineering Research Laboratory. EPA/6000/7-85/036.

Bentley, J. M. *et al.* (1992). The Impact of Electric Vehicles on CO_2 Emissions. Arthur D. Little. Inc., Urbana-Champaign, Ill., May.

Berry, Gene D. (1996). Hydrogen as a Transportation Fuel: Costs and Benefits. Lawrence Livermore National Laboratory. UCRL-ID-123465.

Bhattacharya, Alak (1995). Catalyst Components Team Up for Shift-gas Reaction. Chemical Engineering. September, 1995. pp. 23.

Blinge, M. and Lumsden, K. (1995). Energy Logistic Model – Life Cycle Assessment of Motor Fuels. 28th ISATA – International Symposium on Automotive Technology and Automation. 18th – 22nd September, Stuttgart, Germany.

Borroni-Bird, Christopher E. (1996). Fuel Cell commercialization issue for ligth-duty vehicle applications. Journal of Power Source, vol. 61, p 33 – 48, Elsevier Science S.A.

Boustead, I.; Fink, P.; Langowski, H. and Sundstrom, G. (1992). Eco-balance: Methodology for Commodity Thermoplastic. A Report for The European Centre for Plastics in the Environment (PWMI), Brussels, December.

Boustead, Ian (1994). The Boustead Model For Life Cycle Inventory Calculations. Operating Manual. Boustead Consulting Ltd. August.

Braun, Henry I. (1988). Empirical Bayes Methods: A Tool for Exploratory Analysis. Program Statistics Research Technical Report, no. 88-82. Educational Testing Service. Princeton, New Jersey.

Brockhoff, Klaus (1984). Forecasting Quality and Information. Journal of Forecasting, Vol. 3, pp. 417-428.

California Air Resources Board (1997a). Marine Petroleum Unloading. Emission Inventory Sources. Section 4.9. California Environmental Protection Agency. October.

California Air Resources Board (1997b). Marine Petroleum Loading Tankers & Barges. Emission Inventory Sources. Section 4.8. California Environmental Protection Agency. October.

California Air Resources Board (1999). Evaluation of Fuel Cell Reformer Emissions. California Environmental Protection Agency. Research Division. Prepared by Unnasch, S. and Drunert, V.; Contract 95-313.

California Energy Commission (1996). Methanol Fueling System – Installation and Maintenance Manual. P500-96-002. Main author: Mark Rawson.

California Energy Commission (2000). Fuel Cycle Energy Conversion Efficiency, Status Report. Prepared by Unnasch, S. and Browning, L.; May.

California Fuel Cell Partnership (2001). Bringing Fuel Cell Vehicle to Market: Scenarios and Challenges with Fuel Alternatives. Appendix B: Fuel Economy Comparisons for FCVs. October.

Carlin, B. P. and Louis, T. A. (1996). Bayes and Empirical Bayes Methods for Data Analysis. 1st ed., Chapman & Hall, New York.

Carlson, T. R. and Austin, T. C. (1997). Development of Speed Correction Cycle. Sierra Research, Inc. – prepared for U. S. Environmental Protection Agency. SR97-04-01.

Carpetis, C. (1988). Storage, Transport and Distribution of Hydrogen. Hydrogen as an Energy Carrier: Technologies, Systems and Economy. Chapter 9. Translated by Peter R. and Sarah B. Hoffmann. Springer-Verlag. Berlin.

Chang, T. Y.; Hammerle, R. H.; Japar, S. M. and Salmeen, I. T. (1991). Alternative Transportation Fuels and Air Quality. Environmental Science Technology, Vol. 25, No. 7, pp. 1190-1197.

Chemical Economics Handbook (1996). Methyl Alcohol. By Larisa Gorbaty, SRI – Stanford Research Institute. January, 674.5000.

Cheng, W. H. and Kung, H. H. (1994). Methanol Production and Use. Marcel Dekker, Inc.

Christiansen, K. (1993). Life Cycle Assessment in a Historical Perspective. Chapter 1. Environmental Assessment of Products, 2nd Edition, Edited by Bo P. Weidema. UETP-EEE publishing. Helsinki, Finland.

Clemen, Robert T. (1985). Extraneous Expert Information. Journal of Forecasting. Vol. 4, pp. 329 – 348.

Consoli, F.; Allen, D.; Boustead, I.; de Oude, N.; Fava, J.; Franklin, W.; Quay, B. Parrish, R.; Postlethwaite, D.; Seguin, J. and Vigon, B. (1993). Guideleines for Life Cycle Assessment: A "Code of Practice." Brussels and Pensacola: Society for Environment Toxicology and Chemistry (SETAC).

Contadini, J. F.; Moore R. M.; Sperling, D. and Sundaresan, M. (2000a). Life-cycle Emissions of Alternative Fuels for Transportation: Dealing with Uncertainties. Society of Automotive Engineers, Inc.; SAE 2000-01-0597.

Contadini, J. F.;. Diniz, C. V; Sperling, D. and Moore R. M. (2000b). Hydrogen Production Plants: Emissions and Thermal Efficiency Analysis. Proceedings of the Second International Symposium on Technological and Environmental Sections in Transports. Milan, October.

Contadini, J. F.;. Diniz, C. V; Sperling, D. and Moore R. M. (2000c). Design and Energy Requirements for Future Marketing Activities of Gaseous Hydrogen Fuel for Fuel Cell Vehicles. Proceedings of the Second International Symposium on Technological and Environmental Sections in Transports. Milan, October.

Contadini, J. Fernando (2000d). Social Cost Comparison Among Fuel Cell Vehicle Alternatives. Published by the American Institute of Aeronautics and Astronautics, Inc., AIAA-2000-3043.
Coogee Chemicals (2001). Methanol Process Description. www.coogee.com.au.

Cullinane, K. and Khanna, M. (1999). Economies of Scale in Large Container Ships. Journal of Transportation Economics and Policies 33(2). pp 185-208.

Dalkey, N. and Helmer, O. (1963). An experimental Application of the Delphi Method to the use of Experts. Journal of the Institute of Management Science, Vol. 9, pp. 458-467.

Darrow, K. G. (1994). Light Duty Vehicle Full Fuel Cycle Emissions Analysis. Gas Research Institute. Prepared by Energy International, Inc. Report No. 9333R440.

Davis, Stacy C. (2000). Transportation Energy Data Book. Edition 20. Center for Transportation Analysis. Oak Ridge National Laboratory. U.S. Department of Energy. ORNL – 6959.

Delbecq, A. L. and Van de Ven, A. H. (1971). A Group Process Model for Problem Identification and Program Planning. Journal of Applied Behavioral Science, vol. 7, No. 4, pp. 466-498.

Delbecq, A. L.; Van de Ven, A. H. and Gustafson, D. H. (1975). Group Technique for Program Planning: A Guide to Nominal Group and Delphi Process. Scott Foresman and Company. Glenview, IL.

Delucchi, Mark A. (1991). Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity. Volume 1: Main Text. Center for Transportation Research. Argonne National Laboratory. ANL/ESD/TM-22, Vol. 1.

Delucchi, Mark A. (1993). Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity. Volume 2: Appendixes A-S. Center for Transportation Research. Argonne National Laboratory. ANL/ESD/TM-22, Vol. 2.

Delucchi, Mark A. (1997). A Revised Model of Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity. Institute of Transportation Studies, University of California at Davis. UCD-ITS-RR-97-22.

Denison, R. A. (1993). Towards a Code of Ethical Conduct for Life Cycle Assessment. Chapter 4, Environmental Assessment of Products, 2nd Edition, Edited by Bo P. Weidema. UETP-EEE publishing. Helsinki, Finland.

Derenne, Benoit (1995). Life Cycle Analysis: Usefulness and Limitations. Consumption and Environment. Ecodecision. Spring.

DOC - U.S. Department of Commerce (1976). Methanol: Its Synthesis, Use as a Fuel Economics, and Hazards. David Leroy Hagen, NP-21727.

DOC - U.S. Department of Commerce (1985). A Competitive Assessment of the U.S. Methanol Industry. Prepared by the Office of Chemicals and Allied Products.

DOE - U.S. Department of Energy (1989). Assessment of Cost and Benefits of Flexible and Alternative Fuel Use in the U.S. Transportation Sector. Technical Report Three: Methanol Production and Transportation Costs. DOE/PE-0093

DOE - U.S. Department of Energy (1997). Direct-Hydrogen-Fueled-Proton-Exchange-Membrane Fuel Cell System for Transportation Applications (DOE/CE/50390-9).

DOE – U.S. Department of Energy (1999). Emissions of Greenhouse Gases in the United States, 1998. Energy Information Administration, Washington, DC.

DOE/EIA – U.S. Department of Energy – Energy Information Administration (2000). Annual Energy Outlook 2001. With Projections to 2020. DOE/EIA-0383(2001).

Dransfeld, H.; Pemberton, J. and Jacobs, G. (2000). Quantifying Weighted Expert Opinion: The Future of Interactive Television and Retailing. Technological Forecasting and Social Changes. 63, pp. 81 – 90.

Dry, M. E. (1981). The Fischer-Tropsch Synthesis. Chapter 4, Catalysis Science and Technology. Volume 1, Edited by Anderson, J. R. and Boudart, M.; Springer-Verlag. Berlin.

DTI – Directed Technologies, Inc. (1997). Hydrogen Infrastructure Report. By Thomas, C. E., Ira F. Kuhn, Jr., Brian D. James, Franklin D. Lomax, Jr. and George N. Baum. Prepared for the U. S. DOE by Ford Motor Company and Direct Technologies, Inc., Report no. DOE/CE/50389-504, July.

DTI – Directed Technologies, Inc. (1998a). Fuel Options for the Fuel Cell Vehicles: Hydrogen, Methanol or Gasoline? By C. E. Thomas, B. D. James, F. D. Lomax and I. F. Kuhn. Presented at the Fuel Cell Reformer Conference, SCAQMD, Diamond Bar, CA.

DTI – Directed Technologies, Inc. (1998b). Integrated Analysis of Hydrogen Passenger Vehicle Transportation Pathways. By Thomas, C. E., Ira F. Kuhn, Jr., Brian D. James and Franklin D. Lomax, Jr. Prepared for the National Renewable Energy Laboratory. Subcontract No. AXE-6-16685-01. U. S. DOE. Golden, Colorado.

Ecobilan (1996). Overview of Life-Cycle Assessment Studies in the Automotive Sector. European Commission. Joint Research Centre. IPTS Technical Report Series, Seville. EUR 17674 EN.

Effa, R. C. and Larsen, L. C. (1993). Development of Real-World Driving Cycles for Estimating Facility-Specific Emissions from Light-Duty Vehicles. California Environmental Protection Agency – Air Resource Board – Technical Support Division.

EIIP – Emission Inventory Improvement Program, (1996). Evaluating the Uncertainty of Emission Estimates. Volume VI: Chapter 4. Prepared by Radian Corporation for U. S. EPA Quality Assurance Committee. July.

EIIP – Emission Inventory Improvement Program, (1997). Gasoline Marketing (Stage I and Stage II). Volume III: Chapter 11. Prepared by TRC Environmental Corporation for U. S. EPA Area Source Committee. September.

EIIP – Emission Inventory Improvement Program, (1998). Methods for Estimating Methane and Nitrous Oxide Emissions from Stationary Combustion. Volume VIII: Chapter 14. Prepared by ICF Incorporated for Greenhouse Gas Committee. U. S. EPA. December.

EIIP – Emission Inventory Improvement Program, (1999). Source Contributions to PM-2.5 in Ambient Air. Volume IX: Chapter 1 – Getting Started: PM-2.5 Emission Inventory. U. S. EPA. September.

Eisenberg, B.; Fiato, R. A.; Mauldin, C. H.; Say, G. R. and Soled, S. L. (1998). Exxon's Advanced Gas-to-Liquids Technology. Natural Gas Conversion V. Studies in Surface Science and Catalysis, Vol. 119. A. Parmaliana *et al*. (Editors).

Ekdunge, P. and Raberg, M. (1998). The Fuel Cell Vehicle Analysis of Energy Use, Emissions and Cost. International Journal of Hydrogen Energy. Vol. 23, No. 5, pp. 381-385.

Ekvall, T. (1992). Life Cycle Analyses of Corrugated Cardboard. A Comparative Analysis of Two Existing Studies. Chalmers Industriteknik 1992: 3, Göteborg.

EMFAC 2000 – CARB, California Air Resource Board (2000). Heavy-Duty Trucks Emission Factors Development. Section 10.0. Technical Support Documentation.

EPA-U.S. Environmental Protection Agency (1992). National Air Pollutant Emission Estimates 1990/1991. EPA-454/R-92-013.

EPA-AP42, U.S. Environmental Protection Agency, (1995). Compilation of Air Pollutant Emission Factors, Stationary Point and Area Sources, Fifth Edition, volume I. EP-4.9:42/995/V1.

EPA-AP42, U.S. Environmental Protection Agency, (1996). Liquid Storage Tanks - Emission Factors, Chapter 7. EP-4.9:42/995/V1.

EPA/MOBILE-6, U.S. Environmental Protection Agency, (1998). Update Heavy-Duty Engine Emission Conversion Factors for MOBILE6: Analysis of Fuel Economy, Non-Engine Fuel Economy Improvements, and Fuel Densities. EPA420-P-98-014. May.

EPA/MOBILE-6, U.S. Environmental Protection Agency, (1999). Update Heavy-Duty Emission Levels (Model Years 1988-2004+) for Use in MOBILE6. Air and Radiation. EPA420-R-99-010.

EPA, U.S. Environmental Protection Agency, (2000). Analysis of Commercial Marine Vessels Emissions and Fuel Consumption Data, EPA420-R-00-002.

Epyx Corporation (2000). Emissions from Fuel Processor / Fuel Cell Power Systems. Bowers, B. J.; Hagan, M.; Rumsey, J. and Prabhu, S.; SAE Technical Paper Series. 2000-01-0375.

Espinoza, R. L.; Steynberg, A. P.; Jager, B. and Vosloo, A. C. (1999). Low Temperature Fisher-Tropsch Synthesis from Sasol Perspective. Applied Catalysis A: General, **186**, pp. 13-26.

ETSU – Energy Technology Support Unit (1996). Alternative Road Transport Fuels – A Preliminary Lyfe-cycle Study for UK. Volume 1 and 2. By Gover, M. P.; Collings, S. A.; Hitchcock, G. S.; Moon D. P. and Wilkins, G. T.; London: HMSO.

ETSU – Energy Technology Support Unit (1997). “Environmental Characteristics of Fuel Cell and Competing Technologies.” Initial Assessment, Volume 1. Prepared by D. Hart and G. Hormandinger. Department of Trade and Industry, UK. ETSU F/02/00111 /REP/1.

ETSU - Energy Technology Support Unit (1998). Further Assessment of the Environmental Characteristics of Fuel Cells and Competing Technologies. By Hart, D. and Bauen, A., for DTI (Department of Trade and Industry), ETSU F /02/00153/REP.

Farrauto, R. J. and Bartholomew, C. H. (1997). Fundamentals of Industrial Catalytic Processes. Chapman & Hall. Blackie Academic & Professional. London.

Farshchi, M.; Brodrick, C. J. and Dwyer, H. A. (2001). Dynamometer Testing of Heavy Duty Diesel Engine Equipped with a Urea-SCR System. Society of Automotive Engineers, Inc.; SAE 2001-01-0516.

Franklin, W. E. and Hoffsommer, K. K. (1992). The use of Life Cycle Analysis to Evaluate the Energy and Environmental Profile of Plastic Products. Presented at Recycle 92. Davos, Switzerland.

Fox, Bennett L. (1999). Strategies for Quasi-Monte Carlo. Kluwer Academic Publishers. Norwell, MA

Gaines, L.; Stodolsky, F.; Cuenca, R. and Eberhardt, J. (1998). Life-Cycle Analysis for Heavy Vehicles. Argonne National Laboratory, Transportation Technology R&D Center. Conference paper: Air & Waste Management Ass. Annual Meeting.

Geerlings, J. J. C.; Wilson, J. H.; Kramer, G. J.; Kuipers, H. P. C. E.; Hoek, A. and Huisman, H. M. (1999). Fischer-Tropsch Technology – From Active Site to Comercial Process. Applied Catalysis A: General, **186**, pp. 27 – 40.

Giacomazzi, G. (1981). Seaborne Energy Transportation – An analysis of Costs and Energy Requirements. Energy Storage and Transportation. Edited by G. Beghi. D. Reidel Publishing Company. London. pp. 375-420.

GM (2001). Well-to-Wheel Energy Use and Greenhouse Gas Emissions of Advanced Fuel Vehicles Systems – North American Analysis. General Motors Corporation. Program Manager: Wallace III, James P.

Goedkoop, M. (1995). The Eco-Indicator 95. Final Report. Pre Consultants, Amersfoort.

Gordon, Debora (1991). Steering a New Course: Transportation, Energy, and the Environment. Union of Concerned Scientists. Island Press, Washington, DC.

Gover *et al*. (1996). See ETSU (1996).

Graedel, Thomas E. (1998). Streamlined Life-Cycle Assessment. Published by Prentice-Hall, Inc. New Jersey.

Greene, David L. (1996). Transportation & Energy. Eno Transportation Foundation, Inc. Lansdowne, VA.

Greet, Wang, M. Q. (1996). Greet 1.0 - Transportation Fuel Cycles Model: Methodology and Use, ANL/ESD-33, Argonne National Laboratory.

Greet, Wang, M. Q. (1998). Greet 1.4 – Transportation Fuel-Cycle Model: Methodology, Use, and Results. Center for Transportation Research, Energy System Division, Argonne National Laboratory.

Greet, Wang, M. Q. (1999). Greet 1.5 – Transportation Fuel-Cycle Model. Volume 1: Methodology, Development, Use and Results. Volume 2: Appendices of Data and Results. Center for Transportation Research, Energy System Division, Argonne National Lab. ANL/ESD-39.

Greet, Wang, M.Q. (2000). Greet 1.5a: Changes from Greet 1.5, Center for Transportation Research, Energy System Division, Argonne National Lab.

Gupta, U. G. and Clarke, R. E. (1996). Theory and Applications of the Delphi Technique: A Bibliography (1975 – 1994). Technological Forecasting and Social Change. 53, pp. 185 – 211.

Hart, D. and Bauen, A. (1998). See ETSU (1998).

Harrison, M. R.; Theresa M. Shires; Wessels, J. K. and Cowgill, R. M. (1997). Methane Emissions from the Natural Gas Industry. Project Summary. United States Environmental Protection Agency – EPA/600/SR-96/080. June.

Harvey, L.D.D. (1995). Solar Hydrogen Electricity Generation in the Context of Global CO2 Emission Reduction. Climate Change, 29, pp-53-89.

Hastings, N. A. J. (1975). Statistical Distributions. Butterworth & Co (Publishers) Ltd. London.

Hauer, Karl-Heinz (2001). Analysis Tool for Fuel Cell Vehicle Hardware and Software (Controls) with an Application to Fuel Economy Comparisons of Alternative System Design. Ph. D. Dissertation. Transportation Technology and Policy. University of California at Davis.

He, D. and Wang, M. (2000). Contribution of Feedstock and Fuel Transportation to Total Fuel-Cycle Energy Use and Emissions. Society of Automotive Engineers, Inc.; SAE 2000-01-2976.

Heijungs, R.; Guinee, J. B.; Huppes, G.; Lankreijer, R. M.; Ansems, A. M. M.; Eggels, P. G.; van Duin, R. and de Goede, H. P. (1991). Manual for the Environmental Lyfe Cycle Analysis of Product. Center of Environmental Science, Leiden University, Leiden.

Heintz, B. and Baisnee, R. (1991). System boundaries in life cycle assessment. SETAC Life Cycle Assessment Workshop, Leiden, December 2nd. Society for Environmental Chemistry and Toxicology. pp. 35 – 52.

Hendrickson, C. T.; Horvath, A.; Joshi, S.; Klausner, M.; Lave, L. B. and McMichael, F. C. (1997). IEEE – Institute of Electrical and Electronics Engineers, ISEE – International Symposium on Electronics and the Environment. May 5 – 7. San Francisco, CA.

Humphreys, K. K.; Placet M. and Singh, M. (1996). Life-Cycle Assessment of Electric Vehicles in the United States. Institute of Electrical and Electronics Engineers, IEEE 96530. pp. 2124 – 2127.

Hunt, R. G.; Franklin, W. E.; Welch, R. O.; Cross, J. A. and Wooddall, A. E. (1974). Resource and Environmental Profile Analysis of Nine Beverage Container Alternatives. U. S. Environmental Protection Agency, Office of Solid Waste Management Programs (EPA/530/SW-91c). Washington D. C.

Hunt, R. G.; Sellers, J. D. and Franklin, W. E. (1992). Resource and Environmental Profile Analysis: A Life Cycle Environmental Assessment for Products and Procedures. Environmental Impact Assessment Rev., 12, pp. 245 – 269.

Iman, R. L.; Davenport, J. M. and Zeigler, D. K. (1980). Latin Hypercube Sampling: Program User's Guide. Sandia Laboratories, SAND79-1473. Albuquerque, NM.

Iman, R. L.; Helton, J. C. and Campbell, J. E. (1981). An Approach to Sensitivity Analysis of Computer Models: Part I – Introduction, Input Variable Selection and Preliminary Variable Assessment. Journal of Quality Technology, Vol. 13, No. 3, pp 174-183.

Iman, R. L. and Conover, W. J. (1982). A Distribution-Free Approach to Inducing Rank Correlation Among Input Variables. Communications in Statistics: Simulation and Computation. Volume 11, number 3, pp. 311-334.

Iman, R. L. and Davenport, J. M. (1982). Rank Correlation Plots for Use With Correlated Input Variables. Communications in Statistics: Simulation and Computation. Volume 11, number 3, pp. 335-360.

International Standard ISO 14040 (1997). Environmental Management – Life cycle assessment – Principles and framework. First edition, International Organization for Standardization. Reference number: ISO 14040:1997(E).

International Standard ISO 14041 (1998). Environmental Management – Life cycle assessment – Goal and Scope Definition and Inventory Analysis. First edition, International Organization for Standardization. Reference number: ISO 14041:1998(E).

IPCC – Intergovernmental Panel on Climate Change (1996). Climate Change 1995: Impacts, Adaptations and Mitigation of Climate Change – Scientific-Technical Analyses. Ed. by Watson, R. T.; Cambridge University Press, Cambridge.

IPCC – Intergovernmental Panel on Climate Change (2000). IPCC Special Report – Emissions Scenarios – Summary for Policymakers. ISBN: 92-9169-113-5.

IPCC – Intergovernmental Panel on Climate Change (2001). Technical Summary – A Report of Working Group I. Coordinating lead authors: Albritton, D. L. and Meira Filho, L. G..

ITS - Institute of Transportation Studies (1999). A Direct-Hydrogen Fuel Cell Vehicle Simulation and Comparison using the FCVSim Tool. Fuel Cell Vehicle Modeling Group. UCDavis. February.

Jager, B. (1998). Developments in Fischer-Tropsch Technology. Natural Gas Conversion V. Studies in Surface Science and Catalysis, Vol. 119. A. Parmaliana *et al.* (Editors).

Jones, H. and Twiss, B. C. (1978). Forecasting Technology for Planning Decisions. A Petrocelli Book publication. New York.

Kendall, M. and Gibbons, J. D. (1990). Rank Correlation Methods. 5th ed., Edward Arnold. London.

Kennedy, W. J., Jr. and Gentle, J. E. (1980). Statistical Computing. Marcel Dekker, New York.

Kordesch K. V., Simader G. R. (1995). Environmental Impact of Fuel Cell Technology. Chemical Review. Vol. 95, p: 191 – 207. American Chemical Society.

Kruse, R. E. and Huls, T. A. (1973). Development of the Federal Urban Driving Cycle. Society of Automotive Engineers – Technical Paper Series. 730553.

Kuhler, M. and Karstens D. (1978). Improved Driving Cycle for Testing Automotive Exhaust Emissions. Society of Automotive Engineers – Technical Paper Series. 780650.

Lange, Jean Paul (2001). Methanol synthesis: a short review of technology improvements. Catalysis Today, **64**, pp. 3-8.

Lange, J. P. and Tijm, P. J. A. (1996). Processes for Converting Methane to Liquid Fuels: Economic Screening Trough Energy Management. Chemical Engineering Science, Vol. **51**, No **10**, pp. 2379-2387.

Law, A. M. and Kelton, W. D. (2000). Simulation Modeling and Analysis. 3rd ed., McGraw-Hill Companies, Inc.

LeBlanc, J. R.; Schneider, R. V. and Strait, R. B. (1994). Production of Methanol. Edited by Cheng, W. H. and Kung, H. H., Methanol Production and Use. Marcel Dekker, Inc.

Lee, J. J.; Callaghan, P. O. and Allen, D. (1995). Critical Review of Life Cycle Analysis and Assessment Techniques and their Application to Commercial Activities. Resource, Conservation and Recycling. Vol. 13, pp. 37-56.

Lee, Sunggyu (1990). Methanol Synthesis Technology. CRC Press, Inc.

Lee, Sunggyu (1997). Methane and Its Derivatives. Marcel Dekker, Inc.

Leeth, G.G. (1977). Transmission of Gaseous Hydrogen, Hydrogen: Its Technology & Implications. Volume 2. Transmission & Storage, pp. 03-10.

Leventon, Engineering Ltd. (1999). Alternative and Future Fuels and Energy Sources for Road Vehicles. Prepared for Transportation Issue Table, National (Canadian) Climate Change Process. File: 499-0171.

Lipman, Timothy E. (1999). “Zero-Emission Vehicle Scenario Cost Analysis Using a Fuzzy Set-Based Framework.” Institute of Transportation Study. UCDavis. UCD-ITS-RR-99-18

Linstone, H. A. and Turoff, M. (1975). The Delphi Method: Techniques and Applications. Addison & Wesley. Reading, MA.

Louis, J. J. J. (2001). Well-To-Wheel Energy Use and Greenhouse Gas Emissions for Various Vehicle Technologies. Society of Automotive Engineers, Inc.; Technical Paper Series. SAE 2001-01-1343.

Lunsford, Jack H. (2000). Catalytic conversion of methane to more useful chemical and fuels: a challenge for the 21st century. Catalysis Today, **63**, pp 165-174.

Mann, M. K. and Spath, P. L. (1997). Life Cycle Assessment of a Biomass Gasification Combined-Cycle Power System. NREL – National Renewable Energy Laboratory, Golden, CO. TP-430-23076.

Mark J., Ohi J. M. and Hudson Jr. D. V. (1994). Fuel Savings and Emissions Reductions from Light Duty Fuel Cell Vehicles. National Renewable Energy Laboratory. NREL/TP-463-6157.

Mark, Jason (1996a). Zeroing Out Pollution: The Promise of Fuel Cell Vehicle. Union of Concerned Scientist. May.

Mark, Jason (1996b). Getting from Here to There: Infrastructure Requirements or Hydrogen-Vehicle Future, Union of Concerned Scientists.

Mark, Jason (1998). Upstream Emissions from Hydrogen Production and Delivery. Union of Concerned Scientists. Presented at Fuel Cell Vehicle Technology Conference. ITS, UCDavis.

Martino, J. P. (1983). Technological Forecasting for Decision Making. 2nd Edition. North-Holland. New York.

Mathis, D.A. (1976). Gaseous Hydrogen, Hydrogen Technology for Energy, pp. 21-48.

McAuliffe, C. A. (1980). Storage of Hydrogen, Hydrogen and Energy, Chapter 4, pp. 55-60.

McKay, M. D.; Conover, W. J. and Beckman, R. J. (1979). A Comparison of Three Methods for Selecting Values of Input Variables in the Analysis of Output from a Computer Code. Technometrics, 21, pp. 239-245.

Methanex Corporation (2000). Assessment of Net Emissions of Greenhouse Gases from Fuel Cell Vehicles. Prepared by $(S\&T)^2$ Consultants Inc. Delta, BC, Canada.

Methanex Responsible Care (1997). Methanol. Material Safety Data Sheet 3 – Methanol Physical Properties. Revised September/97. Methanex Corporation. Vancouver, Canada.

Mikhailov, G. A.(1991). Minimization of Computational Cost of Non-Analogue Monte Carlo Methods. World Scientific Publishing Co. Pte. Ltd. London.

Mikhailov, G. A.(1995). New Monte Carlo Methods with Estimating Derivatives. VSP. Utrecht, The Netherlands.

MIT (2000). See Weiss *et al*. (2000).

Mooney, Christopher Z. (1997). Monte Carlo Simulation. Sage Publications, Inc.; Thousand Oaks, CA.

Moore, R.B. and Raman, V. (1998). Hydrogen Infrastructure for Fuel Cell Transportation, Int. Journal of Hydrogen Energy, 23 (7), pp. 617-620.

Moore, R. M. (1999). Cell, Stack, System Interactions and System Optimization for Direct Methanol Fuel Cell. Gordon Research Conference on Fuel Cells, 27 June – 2 July, Plymouth, New Hampshire.

Moore, R. M.; Gottesfeld, S. and Zelenay, P. (1998). Comparison of a Direct-Methanol and a Direct-Hydrogen Fuel Cell System for Automotive Applications. Presented at the Second International Symposium on PEM Fuel Cell. Eletrochemical Society – 194 Meeting, Boston-MA.

Morgan, M. G. and Henrion, M. (1990). Uncertainty: A Guide to Dealing with Uncertainty in Quantitative Risk and Policy Analysis. Cambridge University Press, Cambridge.

Morgester, J. J.; Fricker, R. L. and Jordan, G. H. (1992). Comparison of Spill Frequencies and Amounts at Vapor Recovery and Conventional Service Stations in California. Journal of Air & Waste Management Association. 42: 284-289.

NREL - National Renewable Energy Laboratory (1991). A Comparative Analysis of the Environmental Outputs of Future Biomass-Ethanol Production Cycles and Crude Oil/Reformulated Gasoline Production Cycles. Appendices. Prepared for U. S. DOE, Office of Transportation Technologies. Golden, CO.

NREL - National Renewable Energy Laboratory (1992). Fuel Cycle Evaluations of Biomass-Ethanol and Reformulated Gasoline. Prepared for U. S. DOE, Office of Transportation Technologies. Golden, CO.

NREL - National Renewable Energy Laboratory (1997). See Mann and Spath (1997)

NREL - National Renewable Energy Laboratory (2000). See Spath and Mann (2000)

Ogden, J.M., Larson, E.D. and Delucchi, M.A. (1994). A Technical and Economic Assessment of Renewable Transportation Fuels and Technologies (UCD-ITS-RR-94-31).

Ogden, J. M.; Dennis, E.; Steinbugler, M. and Strohbehn, J. W. (1995). Hydrogen Energy Systems Studies. USDOE report, contract No. XR-11265-2.

Ogden, J. M.; Kreutz, T. G. and Steinbugler M. (1998). Fuels for Fuel Cell Vehicles: Vehicle Design and Infrastructure Issues. SAE Technical Paper Series. 982500.

Ogden, J.M. (1999). Developing an Infrastructure for Hydrogen Vehicles: a Southern California Case Study, Int. Journal of Hydrogen Energy, 24, 709-730.

Ohyama, Seiichi (1999). Low-temperature methanol synthesis in catalytic systems composed of nickel compounds and alkali alkoxides in liquid phases. Applied Catalysis A: General, **180**, pp. 217-225.

Parenté, F. J.; Anderson, J. K.; Myers, P. and O'Brien, T. (1984). An Examination of Factors Contributing to Delphi Accuracy. Journal of Forecasting. Vol. 3, pp. 173-182.

Patel, N.M., Davis, R.A., Eaton, N., Carlson, D.L., Kessler, F. and Khurana, V. (1994). Across-the-Fence Hydrogen Plant Starts up at California Refinery, Oil & Gas Journal, October.

Patel, N. M., Wang, Shoou-I and Raman, V. (1999). Hydrogen Supply, Transportation, and Bulk Storage for Fuel Cell Vehicles. Presentation at the FUEEM – Fuel Cell Modeling Workshop, University of California, Davis. September, 23 1999.

Pearson, R. (1988). Container Ships and Shipping. Fairplay Publications, London, England.

Pedersen, B. and Christiansen, K. (1992). A Meta-review on Product Life Assessment. In Product Life Cycle Assessment. Nordic Council of Ministers & The Nordic Council, Copenhagen & Stockholm (NORD: 1992:9).

Pembina-Suzuki (2000). Climate-Friendly Hydrogen Fuel: A Comparison of the Life-Cycle Greenhouse Gas Emissions for Selected Fuel Cell Vehicles Hydrogen Production Systems. Prepared by Pembina Institute with David Suzuki Foundation support. Primary authors: Jamin, Y. and Raynolds, M.

Peramanu, S.; Cox, B. G. and Pruden, B. B. (1999). Economics of hydrogen recovery processes for the purification of hydroprocessor purge and off-gases. International Journal of Hydrogen Energy, 24, pp. 405-424.

Porter, A. L. and Rossini, F. A. (1987). Technological Forecasting, in Singh, M. G. (ed) Encyclopedia of System and Control. Pp. 4823 – 4828. Oxford: Pergamon.

Porter, A. L.; Roper, A. T.; Mason, T. W.; Rossini, F. A. and Banks, J. (1991). Forecasting and Management of Technology. Wiley Series in Engineering & Technology Management. Wiley Interscience publication. New York.

Pottier, J. (1982). Hydrogen - Energy Source of the Future, Gas Heat International, 31(6), 271-279.

Pottier, J.D. (1995). Hydrogen Transmission for Future Energy Systems, Hydrogen Energy System – Utilization of Hydrogen and Future Aspects, pp. 181-193.

Pottier, J.D. and Blondin, E. (1995). Mass Storage of Hydrogen, Hydrogen Energy System – Utilization of Hydrogen and Future Aspects, pp. 167-179.

Press, W. H.; Teukolsky, S. A.; Vetterling, W. T. and Flannery, B. P. (1992). Numerical Recipes in C: The Art of Scientific Computing, 2d ed., Cambridge University Press, Cambridge.

Radler, M. (1996). 1996 Worldwide Refining Survey. Oil & Gas Journal, December, pp. 49-94.

Ramaswamy, S.; Sundaresan, M.; Eggert, A. and Moore, R. M. (2000). System Dynamics and Efficiency of the Fuel Processor for an Indirect Methanol Fuel Cell Vehicle. Proced. of the 35th International Energy Conversion Engineering Conference, American Institute of Aeronautics and Astronautics, Vol. 2, pp. 1372-1377.

Ramaswamy, S.; Sundaresan, M.; Diniz, C. V. and Moore, R. M. (2001). On-board Fuel Processor for an Indirect Hydrocarbon Fuel Cell Vehicle", Electric Vehicle Symposium, Berlin, October.

Roper, A. T. (1988). A Technique for the Early Stage of an Assessment. Procedings of the International Workshop on Impact Assessment for International Development. International Association for Impact Assessment. Barbados, West Indies.

Ross, Sheldon M. (1985). Introduction to Probability Models. 3rd ed., Academic Press, Inc. Orlando, Florida.

Ross, Sheldon M. (1997). Simulation. 2nd ed. Academic Press, Inc., Chestnut Hill, MA.

Rowe, G. and Wright, G. (1999). The Delphi Technique as a Forecasting Tool: Issues and Analysis. International Journal of Forecasting. 15, pp. 353-375.

Rubinstein, Reuven Y. (1981). Simulation and the Monte Carlo Method. John Wiley & Sons, Inc. New York, NY.

Scheuer, E. M. and Stoller, D. S. (1962). On the Generation of Normal Vectors. Technometrics. Vol. 4, no 3, pp. 278-281. The Rand Corporation.

Schulz, Hans. (1999). Short History and Present Trends of Fischer-Tropsch Synthesis. Applied Catalysis A: General, **186**, pp. 3-12.

SETAC – Society of Environmental Toxicology and Chemistry (1993). Guidelines for Life-Cycle Assessment: A “Code of Practice.” Edited by Frank Consoli *et al*.

Shahani, G. H., Garodz, L. J., Murphy, K. J., Baade, W. F. and Sharma, P. (1998). Hydrogen and Utility Supply Optimization. Hydrocarbon Processing, September, pp. 143-150.

Shanley, A. and Ondrey, G. (1996). Ammonia’s On the Upswing. Chemical Engineering, November. pp. 30-35.

Shearer, D. F. and Gilson, D. F. (1994). Underground Storage Tank Vent Line Emissions from Retail Gasoline Outlets. Prepared for Western States Petroleum Association. AV-FR-92-01-204R2.

Shelef, M. and Kukkonen, C. A. (1994). Prospects of Hydrogen-Fueled Vehicles. Prog. Energy Combust. Sci. Vol. 20, pp. 138-148.

Shreider, Yu. A.; Buslenko, N. P.; Golenko, D. I.; Sobol, I. M. and Sragovich, V. G. (1966). The Monte Method – The Methodof Statistical Trial. Edited by Shreider, translated from the Russian by Tee, G. J.; Pergamon Press.

Sie, S. T. and Krishna, R. (1999). Fundamentals and Selection of Advanced Fischer-Tropsch Reactors. Applied Catalysis A: General, **186**, pp. 55-70.

Sie, S. T.; Eilers, J. and Minderhout, J. K. (1988). Consequences of Fischer-Tropsch Chain Growth Kinetics for Process Mode Selection and Product Selectivity. Proceedings 9th International Congress on Catalysis, Calgary, Alberta, Canada. pp. 743-750.

Smith, P. N. (1994). Application of Fuzzy Sets in the Environmental Evaluation of Projects. Journal of Environmental Management, 42, pp. 365-388.

Socolow, R. (1997). Fuel Decarbonization and Carbon Sequestration: Report of a Workshop, Center of Energy and Environmental Studies. School of Engineering and Applied Science, Princeton University.

Spath, P. L. and Mann, M. K. (2000). Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming. National Renewable Energy Laboratory. NREL/TP-570-27637. August.

Specht, M.; Staiss, F.; Bandi, A. and Weimer, T. (1998). Comparison of the Renewable Transportation Fuels, Liquid Hydrogen and Methanol, with Gasoline – Energetic and Economic Aspects. International Journal of Hydrogen Energy, Vol. 23, No. 5, pp. 387-396.

Sperling, Daniel (1988). New Transportation Fuels: A Strategic Approach to Technological Change. University of California Press. Berkeley, CA.

Sperling, D. and Delucchi, M. A. (1989). Transportation Energy Futures. Annual Review of Energy. 14, pp. 375-424, October.

Spirinckx, C. and Ceuterick, D. (1996). Comparative Life Cycle Assessment of Fossil Diesel and Biodiesel. Presented at Eco-Informa 96: Global network for environmental information. Lake Buena Vista, November.

Steynberg, A. P.; Espinoza, R. L.; Jager, B. and Vosloo, A. C. (1999). High Temperature Fisher-Tropsch Synthesis in Commercial Practice. Applied Catalysis A: General, **186**, pp. 41-54.

Sudman, S. and Bradburn, N. M. (1982). Asking Questions: A Practical Guide to Questionnaire Design, 1st ed., Jossey-Bass. San Francisco

Sullivan, W. G. and Claycombe, W. W. (1977). Fundamentals of Forecasting. Reston Publishing Company. Reston, Virginia.

Sweeney, Graeme (1998). Fuel Cells – Threat or Opportunity for the Oil Industry. Shell International Petroleum Conference. Presented at IQPC Fuel Cell Conference. London, September.

Taylor, J.B., Alderson, J.E.A., Kalyanam, K.M., Lyle, A.B. and Phillips, L.A. (1986). Technical and Economic Assessment of Methods for the Storage of Large Quantities of Hydrogen. Int. Journal of Hydrogen Energy, volume 11, pp. 05-22.

TEDB (2000). See Davis (2000).

The World Bank (1996). See Asif *et al*. (1996)

Thomas *et al*. (1997 and 1998). See DTI (1997 and 1998).

Thompson, A. W. (1979). Materials for Hydrogen Service, in Kenneth, E.C. and Williamson, K. D. (eds.), Hydrogen: Its Technology and Implications, CRC Press, Cleveland, pp. 85-124.

Tijm, P. J. A.; Marriott, J. M.; Hasenack, H.; Senden, M. M. G. and Herwijnen, T. (1995). The Markets for Shell Middle Distillate Synthesis Products. Proceedings of the Alternate Energy – 1995. Vancouver, Canada. pp. 228 – 242.

Trommsdorff, G. (1982). Group Influences on Judgments Concerning the Future. Chapter 5. Studies in Decision Making. Editor: Martin Irle. De Gruyter. New York.

Thompson, A. W. (1979). Materials for Hydrogen Service, in Kenneth, E.C. and Williamson, K. D. (eds.), Hydrogen: Its Technology and Implications, CRC Press, Cleveland, pp. 85-124.

UETP-EEE, Environmental Engineering Education (1996). Life Cycle Assessment. Module 5. Environmental Management Course. Helsinki University of Technology.

UNDP – United Nations Development Program (2000). Energy and the Challenge of Sustainability. World Energy Assessment. Bureau of Development Policy. New York.

Unnasch, S and Drunert, V. (1999). Evaluation of Fuel Cell Reformer Emissions. Prepared by Arcadis Geraghty and Miller, Inc. for California Air Resource Board. Contract No. 95-313.

Unnash *et al*. (1996). See Acurex (1996)

Unnash, Stefan (2000). Refinement of Selected Fuel-Cycle Emission Analyses. Prepared for California Air Resource Board, Research Division. Final Report FR-00-101. Volume 1.

Van Der Drift, A. (1996). Low-NOx Hydrogen Burner. International Journal of Hydrogen Energy, Vol. 21, No. 6, pp. 445-449, 1996.

Van Der Lugt, W. A. (1986). A Time Saving Method to Determine Calorific Value and Density of Natural Gas with a Modified ISO 6976. Gas Quality. Edited by G. J. van Rossum. Elsevier, Amsterdam.

Van Dijk, J. (1990). Delphi Questionnaires versus Individual and Group Interview: A Comparison Case. Technological Forecasting and Social Change. Vol. 37, pp. 293-304.

Vigon, B. W.; Tolle, D. A.; Cornaby, B. W.; Latham, H. C.; Harrison, C. L.; Boguski, T. L.; Hunt, R. G. and Sellers, J. D. (1993). Life Cycle Assessment: Inventory guidelines and principles. U. S. Environmental Protection Agency, EPA/600/R-92/245.

Vose, David (1996). Quantitative Risk Analysis: A Guide to Monte Carlo Simulation Modelling. John Wiley & Sons Ltd, England.

Walsh M. P. (1993). Vehicle Activity Trends and Their Implications for Global Warming: The US in an International Context. In Transportation and Global Climate Change. Chapter 1. American Council for an Energy-Efficient Economy, Berkeley – CA.

Wang, M.Q., (1996, 1998, 1999 and 2000). See Greet (1996, 1998, 1999 and 2000).

Wang, M. Q.; Saricks Christopher and Wu May (1997). Fuel-Cycle Fossil Energy Use and Greenhouse Gas Emissions of Fuel Ethanol Produced from U.S. Midwest Corn. Center for Transportation Research, Argone National Laboratory.

Weidema, Pedersen (1993). Quality Criteria for Product Life Cycle Assessments. Chapter 5, Environmental Assessment of Products, 2nd Edition, Edited by Bo P. Weidema. UETP-EEE publishing. Helsinki, Finland.

Weiss, M. A.; Heywood, J. B.; Drake, E. M.; Schafer, A. and AuYeung, F. F. (2000). On the Road in 2020 – A life-cycle analysis of new automobile technologies. Massachusetts Institute of Technology - Energy Laboratory. MIT EL 00-003.

Welch, E.; Bretschneider, S. and Rohrbaugh, J. (1998). Accuracy of Judgmental Extrapolation of Time Series Data: Characteristics, Causes, and Remediation Strategies for Forecasting. International Journal of Forecasting, 14, pp. 95-110.

White, F.M. (1994). Fluid Mechanics, third edition, McGraw-Hill Inc.

Whitlock, P. A. and Kalos, M. H. (1986). Monte Carlo Methods. Volume I: Basics. John Wiley & Sons, Inc. New York, NY.

Winkler, R. L. and Makridakis, S. (1983). The Combination of Forecasts. Journal of the Royal Statistical Society. Series A (General), Volume 146, Issue 2, pp. 150 – 157.

Workman, G.S., Adams, R.G. and Shareef, G.S. (1996). Criteria Pollutant Emissions from Internal Combustion Engines in the Natural Gas Industry, Technical Report - volume I.

Yu, D. and Park, W. S. (2000). Combination and Evaluation of Expert Opinions Characterized in Terms of Fuzzy Probabilities. Annals of Nuclear Energy, 27, pp. 713-726.

Zimmermann, Henry J. (1990). Fuzzy Set Theory and its Applications. 2nd Edition. Kluwer Academic Publisher.