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Enhancing the Steam-Reforming Process with Acoustics: A Theoretical Investigation of Potential Benefits for Application in Fuel Cell Vehicles

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ABSTRACT

This paper provides a theoretical basis for the investigation of using acoustic waves as a means of enhancing performance in conjunction with the hydrocarbon fuel steam-reforming process for application in fuel cell vehicles. In order to minimize liabilities associated with steam-reforming, a novel reforming enhancement is being investigated.

A reformation process that utilizes acoustic fields in critical fluid paths is introduced. Potential benefits of using acoustic fields in the reformation process are decreased effective space velocity, an increase of convective heat transfer rates, and increased specie mixing that would help produce an increase in capacity and overall reaction rate for a given reformer volume. The proposed acoustic enhancement should result in some combination of quicker start up times, faster dynamic response, smaller size and lower weight.

INTRODUCTION

Fuel cells are low emission power sources that have the potential of replacing the internal combustion engine in the transportation sector. The problem of reforming liquid hydrocarbon fuels to hydrogen in fuel cell vehicles is currently one of the major technological hurdles delaying the introduction of liquid fueled fuel cell vehicles (Erickson and Roan, 1999). While it has been demonstrated that the endothermic steam-reforming process can be accomplished in a catalytic converter (Idem and Bakhshi, 1994: Ledjeff-Hey et al., 1998: Peppley et al., 1997), the process has liabilities of weight, size and complexity in addition to long start-up and transient response times (Ohl et al., 1996). In order to reduce these liabilities a novel reforming enhancement is being investigated.

A reformation process which utilizes acoustic fields in critical fluid paths is thought to have possible benefits of decreased effective space velocity, an increase of convective heat transfer rates, increased mass transfer rates, and increased specie mixing that may help produce an increase in effective mass flow capacity and overall reaction rate for a given reformer volume and mass. The benefits of using acoustics in combustion reactors have been shown in the literature as increased convective heat transfer rates (Yavuzkurt et al., 1991), increased mass transfer rates (Ha and Yavuzkurt, 1993), and increased specie mixing (Erickson et al., 1997). The acoustic enhancement of the reformation process with similar enhancement should result in some combination of quicker start up times, faster dynamic response, smaller size and lower weight.

Limiting Steps in the Reformation Process

For fuel cell vehicle applications, size, weight, and transient response are vital factors. In order to design an optimal reformer for fuel cell vehicles one would desire the smallest possible, lightweight reformer that would have enough catalyst surface area to react the fuel into a hydrogen rich stream at the maximum design flow. Steam-reforming of hydrocarbons can be limited by heat transfer rates, diffusion, and/or by chemical kinetics. These limitations are evidenced by restrictions in reformer capacity, and transient response.

Because of its endothermic nature, the reformation of liquid hydrocarbon fuels requires heat transfer to the reactants and catalyst. If the heat transfer rate is not high enough the reformer capacity will be limited. Heat transfer limitations can be compensated by an increased size of the reformer to increase the heat transfer area (Ohl et al., 1996). Such design results in undesirably large processors and corresponding high weight. The large size and thermal mass then further contribute to a lagging transient response.

Diffusion and chemical kinetics can also limit the reformation process. The hydrocarbon and steam mixture must first be transported to the surface of the catalyst. Next the mixture must diffuse to an open catalyst site to react. The reaction rate is governed by the chemical kinetics and then products of the reaction would diffuse back out to the bulk flow stream. Increasing the amount of catalyst sites available can compensate for limitations in diffusion or chemical kinetics. Normally this means increasing the amount of catalyst to provide enough reaction area and to allow for diffusion to the reaction site. This decrease of space velocity once again results in large reforming units.

Some of these limiting steps may be minimized by using acoustics in the reformation process by allowing an increase in effective surface area (by an effective decrease in space velocity by increased particle path length) for a given catalyst mass that would allow for a smaller size of the reforming unit along with other associated benefits in heat and mass transfer.

STEAM-REFORMING IN COMBINATION WITH ACOUSTICS

Superimposing an oscillating flow in the axial direction of the reformer (also referred to as organ pipe oscillations) with the steady flow component is proposed. High acoustic pressures could be achieved by establishing resonance in the reactor. The use of acoustics results in increased particle path length, so that to the reactants the reformer appears "longer." The steady flow component carries the overall flow forward and the oscillating flow portion incrementally steps the fluid forward and backward across portions of the catalyst bed allowing for a "shearing" of the boundary layer along the reactor walls and past the catalyst particles. Under the proper conditions, increased heat transfer and diffusion rates also would occur as a result of the thinned boundary layers and acoustic-induced mixing in the reactor. The projected effects of acoustics on particle path length, heat transfer rate, mass transfer and chemical kinetics of the overall process are discussed below.

Increased Particle Path Length due to Acoustics

A simplified model of the acoustics shows a significant increase in the particle path length resulting in a decreased effective space velocity without changing the overall bulk residence time. In order to illustrate

$$Y_m = \frac{P_m}{2\pi f \rho c} \tag{1}$$

this effect, consider an empty open-ended pipe (without obstruction from the catalyst). Acoustic displacement amplitude is given in Eq. 1, (Halliday and Resnick, 1986) where Y_m is the maximum acoustic displacement amplitude (m), P_m is the maximum acoustic pressure (Pa), f is frequency (Hz), ρ is density of the gas (kg/m^3), and c is the sonic

$$U_m = \frac{P_m}{\rho c} \tag{2}$$

velocity in the gas (m/sec). For sinusoidal fluctuations the spatial averaged amplitude Y_{avg} is 0.64 times the maximum. The equation for maximum particle velocity due to acoustic oscillation U_m (Kinsler et al., 1982) is shown in Eq. 2. This particle velocity is subsequently referred to as acoustic velocity. In order to derive the total path length seen by a particle traveling through the reactor (effective particle path length), one must consider the length of the reactor (original particle path length with no acoustic oscillation) and distance traveled by a particle due to acoustic oscillation. Adding the original particle path length L to the acoustic path length of the particle during residence in the reactor yields the equation of the effective particle path length. This equation is shown in

$$D_{eff} = L + (4) \times \frac{P_m}{2\pi f \rho c} \times 0.64 \times \frac{L}{V_s} f \tag{3}$$

$$D_{eff} = L + (0.407) \frac{P_m}{\rho c} \frac{L}{V_s} \tag{4}$$

Eq. 3 and further simplified in Eq. 4 where D_{eff} is effective particle path length (m), L is the length of the reactor (m), and V_s is the steady flow component of the reactor (m/s). One can see that the effective particle path length is independent of frequency in this model. This results from the fact that while an increased frequency does cause more oscillations during the residence time the amplitude of those oscillations is decreased proportionally.

Non-dimensionalizing this result by dividing by reactor length L and plotting with respect to the acoustic pressure over the steady or average velocity component V_s yields Fig. 1. As Fig. 1 shows, this model

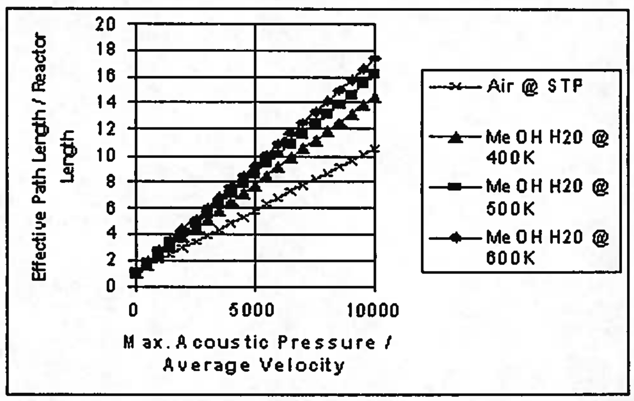

Figure 1 Dimensionless particle path length versus maximum acoustic pressure (Pa) over average velocity (m/s) for air at standard temperature and pressure and 1:1 methanol-steam mixtures at various temperatures.

predicts large increases in particle path length for decreasing average velocity or increasing particle acoustic velocity by higher acoustic pressure levels. For a reasonable example, a sound pressure level of 150 dB (re 20μPa) in air and a steady flow component of 0.1 m/s yields a particle path length of 9 times the particle path length with non-oscillating flow. If employed in a reforming process the effective space velocity would be 9 times smaller than the space velocity without acoustics.

Increased Heat Transfer Rate due to Acoustics

Heat transfer rate is seen as a fundamental resistive step in the fuel reformation process. Recent papers have addressed this issue (Ohl et al., 1996: Düsterwald et al., 1997) and certain methods of increasing heat transfer have been reported, including the use of fins to increase the heat transfer area (Shiizaki et al., 1999). However, increasing heat transfer rates with acoustic fields for other applications has been well documented over the years (Fraenkel et al., 1998: Erickson et al., 1997: Zinn, 1992: Yavuzkurt et al., 1991: Kurzweg, 1986).

Space and time averaged Nusselt numbers have been shown by Ha and Yavuzkurt (1993), for a single spherical particle in a pulsating flow with a steady flow component, to be represented by Eqs. 5 and 6. In these equations, V_r is velocity ratio (defined as acoustic velocity U_m

$$\text{for } V_r < 1 \quad \frac{Nu_p}{Nu_s} = 1 + 0.009608\,V_r - 0.109608\,V_r^2 \qquad (5)$$

$$\text{for } V_r > 1 \quad \frac{Nu_p}{Nu_s} = 0.73839\,V_r^{0.578} + 0.16161 \qquad (6)$$

divided by average velocity V_s), Nu_p is the Nusselt number due to pulsating flow, and Nu_s is the steady flow Nusselt number. Figure 2 is a plotted representation of these two equations. While interactions between particles in a reformer reactor are clearly much more complex than the single particle example, Fig. 2 shows the potential for drastically

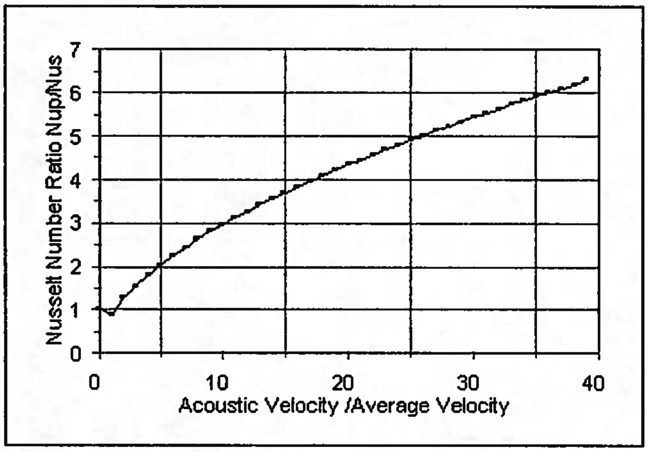

Figure 2 Graphical Representation of Eqs. 5 and 6 Nusselt Number Ratio versus Velocity Ratio.

increasing heat transfer rates with acoustic fields. For the previous example of a SPL of 150 dB and a 0.1 m/s steady component the heat transfer rate is increased by a factor of 4. Fraenkel et al. (1998) have found similar results for velocity ratios above 1 when flow oscillations are used in grain drying.

An increase in heat transfer rates should help the reformation process in two separate ways: 1) Increased reformer capacity because of the endothermic nature of reformation; and 2) Decreased response time when changing power levels. The decrease in response time would be further enhanced by use of a smaller reactor size and thermal mass associated with an increased capacity.

From an energy balance in the reformer (taking into account convective heat transfer from the walls to the catalyst bed), allowable reactant mass flow rate is directly proportional to the heat transfer rate as

$$\dot{m} = \frac{hA(T_{wall} - T_{reformer})}{\Delta H} \qquad (7)$$

shown in Eq. 7 where $\dot{m}$ is mass flow rate, h is the convective heat transfer rate coefficient, A is the heat transfer area, T is temperature, and ΔH is the change in enthalpy between reactants and products. This relation applies for heat transfer limited cases that are not limited by diffusion or chemical reaction rates.

Increased Overall Reaction Rate due to Acoustics

With a higher heat transfer rate, the rate limiting steps of diffusion and chemical kinetics become more important to the reformation process. Although mass transfer rate has not been a perceived limitation in previous work (Asprey et al., 1999: Peppley et al., 1997), smaller reactors with high flow rates would deviate from the plug flow reactor assumption. As described and quantified by Ha and Yazavkurt (1993), acoustic mixing increases the mass flow rate at the surface of a particle; thus in a reformer, acoustics would reduce the diffusion time of a mixture to reach the outside of a catalyst. Internal diffusion or mass transfer into the core catalyst area is not expected to be significantly affected by the acoustic waves, thus overall diffusion rate enhancement by acoustics may be limited. If the internal diffusion is not the limiting factor, but rather the process is limited by external diffusion, acoustics would have significant effect.

While increased mixing from acoustics may decrease a rate limiting diffusion step to a catalyst surface, there is a possibility that the chemical kinetics will be increased as well. Tonkovich et al. (1999) have found that for the water gas shift reaction, intrinsic reaction times are on the order of milliseconds rather than the observed reaction times of 6-9 seconds. They exploit the fast intrinsic reaction times by using micro-channel reactors where fast heat and mass transfer rates govern. In a similar approach, acoustic vibrations will increase mass transfer rates at the exposed catalyst surface and thus decrease the required contact time on that catalyst surface.

Although it is obvious that not all of the area in a catalyst would be affected by the acoustic wave (due to internal pores etc.), bounds of the reaction rate can be established. The lower bound would be the case where the reaction rate is limited only by internal diffusion rate and thus overall reaction rate would not change when acoustics are applied. The upper bound would be where the rate is wholly limited by diffusion rates at the surface and the total effective area would be used in the reaction rate equation. It is expected that with catalyst pellets, internal area and diffusion to those sites would dominate and thus the lower bound of reaction rate would be followed. Use of the higher bound of reaction rate would be more correct for screen or monolith type catalysts, where acoustic waves would have more of an effect on the active reaction sites.

Practical Limitations of Employing Acoustics

While the theory developed points toward enhancement of the reforming process, such enhancement does not come without some difficulty and limitations. Perceived limitations and possible drawbacks of using this system, which need quantification, are as follows: The acoustic wave must be generated by a power source. Does the enhancement justify the use of that power? Can resonance be established in the reactor? If the reformer system is acoustically dispersive, resonance may not be possible and lower acoustic pressure levels may actually reduce the heat and mass transfer (see drop in Fig. 2). While benefits may arise from being able to "tune the reformer" to the desired hydrogen output, the acoustic system and control of it will add to the complexity of the system. Other limitations are sure to be found as experimentation occurs.

CONCLUSIONS

In theory, the possible benefits which arise from employing acoustic waves in the reforming process are an increase in capacity for a given catalyst mass, a decrease in transient response, and an increase in the overall efficiency of the reformation process. While the acoustic field may not significantly affect diffusion and chemical kinetics for all catalysts, and all effects still need to be quantified in an actual reformer, the theoretical investigation points toward potential for enhancing overall reformation processes with acoustic waves. The authors are actively pursuing research in this novel application of acoustical fields at the University of Florida Fuel Cell Research and Training Laboratory.

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