

Hydrogen production from rich combustion in porous media of methane and propane

Mario Toledo¹, Valeri Bubnovich², Alexei Saveliev³ and Lawrence Kennedy³

¹Department of Mechanical Engineering, Universidad Técnica Federico Santa María, Valparaíso, Chile, e-mail: mario.toledo@usm.cl

²Department of Chemical Engineering, Universidad de Santiago de Chile, Santiago, Chile

³Department of Mechanical and Industrial Engineering, University of Illinois at Chicago, Chicago, USA

ABSTRACT: This paper studies experimentally and numerically rich combustion of methane and propane inside inert porous media to examine the suitability of the concept for hydrogen production. Temperature velocities and chemical products of the combustion waves were recorder experimentally at the equivalence ratio range from stoichiometry ($\phi = 1.0$) to $\phi = 2.5$, at a filtration velocity of 12 cm/s. Two-temperature numerical model based on comprehensive heat transfer and chemical mechanisms was developed and found to be in a good agreement with experimental data. It is observed that the products of methane and propane partial oxidation (H_2 , CO, and C2 hydrocarbons) are dominant for ultrarich superadiabatic combustion where up to 60% and 55% of fuel, respectively, is converted to CO and H_2 . Propane conversion to hydrogen was significantly higher than for methane.

Keywords: Hydrogen production, Filtration combustion, Porous media.

1. INTRODUCTION

Hydrogen is considered the fuel of the future due to contains more energy per unit mass than any other fuel, produces minimum emissions when combusted and essentially no emissions when electrochemically converted to electricity in a fuel cell, and other characteristics. For the projected utilization of hydrogen, simpler and efficient processes will have to be found. One such solution is superadiabatic decomposition of light hydrocarbon in a porous media. During the past 20 years a variety of works has been published that describe gaseous fuel combustion in porous media [1,2]. Within this context, stationary and transient systems are the two major

design approaches commonly employed in porous combustion [3-5]. Filtration combustion at rich conditions create a situation in which partial oxidation and/or thermal cracking of hydrocarbons can occur [2] due to its superadiabatic temperatures. Multiple studies have shown that the conversion of methane to hydrogen occurs in two stages: initially through partial oxidation and then by steam reforming [3-5].

In this paper, the results for hydrogen production from rich combustion of methane/air and propane/air mixtures are presented. Temperature profiles and combustion wave velocities were measured experimentally and predicted numerically, as were the chemical product compositions.

2. EXPERIMENTAL SETUP

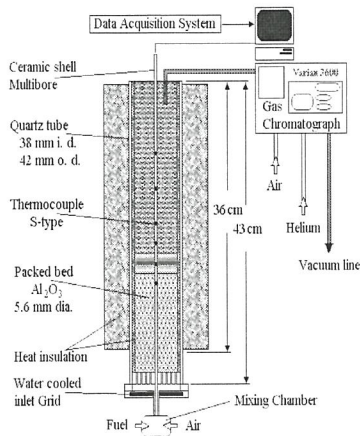


Figure 1: Schematic of the experimental setup.

Experiments on filtration combustion wave propagation were conducted using the setup schematically shown in Figure 1. The apparatus consisted of porous heating burner, a fuel and air supply system, a temperature measurement system, and gas emission analyzers. More information about the experiment can be found in Ref. [3].

3. NUMERICAL MODEL

Experimentally recorded negligible radial temperature gradients allow for a credible one-dimensional representation of the combustion wave. The volume-averaged model [6] is used to mathematically describe the filtration combustion. The flame zone is considered to be isobaric, steady, and quasi-one-dimensional. The velocity of the wave, u , is assumed to be at least three orders of magnitude less than interstitial velocity of gas mixture, v . A two-temperature approximation was formulated to describe a fully developed steady combustion wave in a system of coordinates moving with the reaction zone [2]. The numerical model [2,7] describes gas and solid as two phases

interacting via fluid dynamics and heat transfer.

The governing equations, describing fully developed steady combustion wave in a system of coordinates moving with the reaction zone are (e.g., see [2,7]):

Continuity Equation:

$$\frac{\partial(\rho v)}{\partial x} = 0$$

Gas Phase Energy Equation:

$$\varepsilon c_p \rho_g v \frac{\partial T_g}{\partial x} = \varepsilon \frac{\partial}{\partial x} \left([k_g + (c_p \rho_g) D_{ax}] \frac{\partial T_g}{\partial x} \right) - \varepsilon \sum_k \alpha_k h_k W_k - \varepsilon \sum_k \rho_g Y_k V_k c_{pk} \frac{\partial T_g}{\partial x} - h_v (T_g - T_s)$$

Solid Phase Energy Equation:

$$-(1 - \varepsilon) c_s \rho_s u \frac{\partial T_s}{\partial x} = \frac{\partial}{\partial x} \left([k_s + k_r] \frac{\partial T_s}{\partial x} \right) - \beta (T_s - T_0) - h_v (T_g - T_s)$$

Species Conservation Equation:

$$\rho_g v \frac{dY_k}{dx} + \frac{d}{dx} (\rho_g Y_k V_k) = \alpha_k W_k$$

Assuming thermal equilibrium between gas and solid at the limits of long computational domain, the following boundary conditions are imposed:

At the inlet ($x = 0$): $T_g = T_s = T_0$, $Y = Y_{k,0}$;

At the exit ($x = L$):

$$\partial Y_k / \partial x = 0; \quad T_g = T_s = T;$$

$$\partial T / \partial x = \beta (T - T_0) / (\varepsilon c_p \rho_g v - (1 - \varepsilon) c_s \rho_s u)$$

Downstream boundary condition for the wave temperature is imposed using an analytical solution of the above Equations. It is assumed that $\partial Y_k / \partial x = 0$; $T_g = T_s = T$;

$\alpha_k = 0$ and radiation is negligible at the cold interface far from the reaction zone. This allows temperature and species profiles calculations for combustion wave enclosed within a finite spatial domain ($L = 40$ cm).

The volumetric convective heat transfer coefficient is found as: $h_v = (6\varepsilon/d^2) Nu k_g$.

The correlation for Nu number is given by [15] as: $Nu = 2 + 1.1 Pr^{1/3} Re^{0.6}$.

Radiation is treated with radiant conductivity model [6]; k_r is represented

by $k_R = 4F\sigma T_s^3$, where F is the radiation exchange factor. In the considered conditions, F depends upon the value of the conductivity of the solid state (alumina). The values of F from 0.3 to 0.6 are used.

The contribution of turbulent flow to the effective mass diffusion is described by the axial gas dispersion coefficient, D_{ax} , based on unit void area. It is given by $D_{ax} = 0.5dv$ [8]. According to a heat-mass transfer analogy the dispersive thermal diffusivity is the same as the mass diffusivity and the respective dispersion coefficients are equal. Similar to Henneke and Ellzey [7], we represent effective diffusion as a sum of molecular diffusion and dispersion.

Finally, the thermophysical properties, i.e. alumina conductivity, heat capacity, and radiative properties were obtained from published data [9] and verified against data of ceramic manufacturer (Coors, Inc.). Effective conductivity of the packed bed and its porosity were estimated as $k_e = 0.005k_s$, $\varepsilon = 0.4$.

The GRI 3.0 [10], an extensively validated chemical kinetic mechanism with inclusive NOx chemistry, was used along with the Chemkin [11] package of corresponding subroutines and databases. While this mechanism is not directly applicable to ultralean and ultrarich mixtures, it serves as a good first approximation for combustion mechanisms in these areas. It was also found that it adequately reproduces the combustion in ultralean region [2]. The calculations were performed for a given value of the interstitial velocity and the implemented numerical algorithm in the modified PREMIX [12] code was used to find the wave propagation velocity.

4. RESULTS AND DISCUSSION

Data were collected at filtration velocity of 12 cm/s and equivalence ratio range from

stoichiometry ($\phi = 1.0$) to $\phi = 2.5$. The experiments were identical for two fuel/air mixtures in procedure and apparatus. Solid phase temperatures as well as product compositions were measured and the propagation rate was calculated.

4.1 Hydrogen production from methane combustion

4.1.1 Combustion wave temperature and propagation rate

Downstream, upstream, and standing waves were observed, depending on experimental parameters, mainly the equivalence ratio. Fig. 2 displays the experimental (symbols) and numerical predictions (lines) combustion temperatures; the calculated adiabatic temperatures are provided for reference. From the origin (experimental temperature = 1352 K, adiabatic temperature = 2240 K), the combustion temperature rose to 1616 K at the equivalence ratio $\phi = 1.4$ maintaining this value practically constant for $\phi > 1.4$.

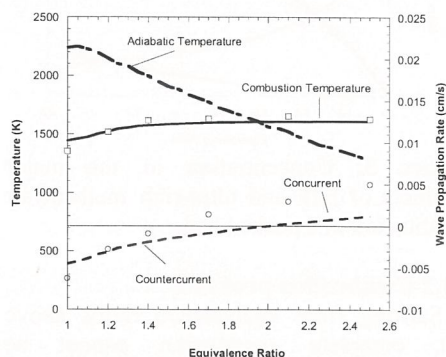


Figure 2: Combustion temperature and wave velocity of methane-air mixture.

The result of the numerical model presents good agreement with the experimental data. Equivalence ratio 1.9 marks the crossing point where the combustion temperature begins to exceed the adiabatic temperature.

The regimes of under and superadiabatic combustion are also manifested in the

direction of the wave propagation. Low velocity regime (LVR) is observed in all the range of equivalence ratios and for $\phi = 1.0$ a maximum experimental absolute value of velocity (0.0063 cm/s) is observed. Upstream underadiabatic regime of propagation is observed for the range of equivalence ratios from 1.0 to 1.6 and to 1.9, and a rich standing wave for $\phi \approx 1.6$ and $\phi \approx 1.9$ for respectively experimental and numerical predictions. The downstream superadiabatic propagation occurs in the ultrarich region, where the speed increases with methane content. The numerical deviation observed at the region of ultrarich mixtures is probably related to limited applicability of GRI mechanism in this range.

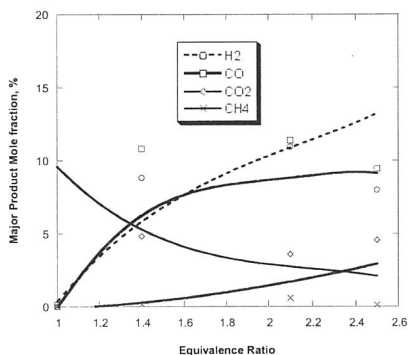


Figure 3: Concentration of the major products of rich and ultra-rich methane/air combustion in a packed bed.

4.1.2 Combustion products

Starting from equivalence ratios above 1.0, complete combustion cannot be achieved due to the low oxygen content of the mixture. The numerical (lines) and experimental (symbols) results for concentrations of major combustion products (CO, H₂, CO₂, CH₄) are presented in Fig. 3.

The numerically predicted trends show good agreement with the experimental results. In particular, the concentration of hydrogen, carbon monoxide and methane are increased with equivalence ratio and

concentration of CO₂ is reduced. The concentrations of H₂ and CO are underpredicted by the model especially on the boundary of the rich flammability limit ($\phi \approx 1.4$). The predicted concentrations of CO₂ agree well with the experiment. The leftover CH₄ is over predicted in comparison with the experimental data. The improvement of model accuracy for prediction of chemical products is closely related to improvement chemical kinetic mechanism describing combustion in these rich and ultrarich conditions.

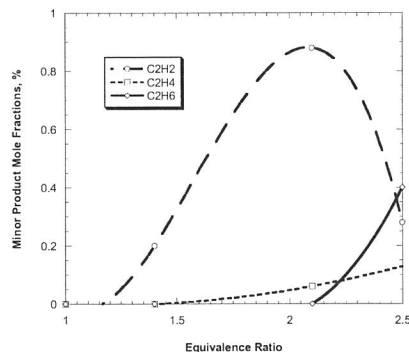


Figure 4: Experimental measured of minor methane-air combustion products.

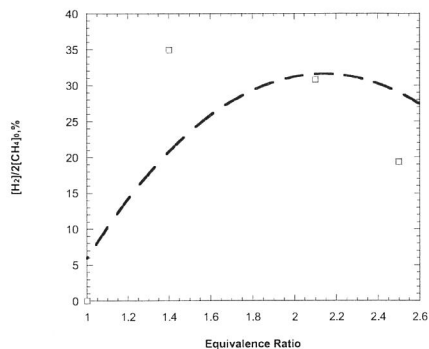


Figure 5: Degree of methane conversion to hydrogen for rich and ultra-rich waves.

Significant concentrations of C₂ hydrocarbons appear in the exhaust gases (Fig. 4). Ethylene and acetylene appears in the exhaust gases at equivalence ratio above 1.7. In fact, the ultra-rich superadiabatic

wave is capable of inducing chemical transformation of methane in the mixtures with very small oxygen concentrations. Thus, the process could be characterized as fuel reformation or modification rather than combustion. For example, Fig. 5 shows that the degree of methane conversion to hydrogen could be as high as 32% for highest equivalence ratios studied.

4.2 Hydrogen production from propane combustion

4.2.1 Combustion wave temperature and propagation rate

Combustion temperatures of propane (Fig. 6) display similar behaviour to methane combustion in that the demarcation point for under and superadiabatic sections falls in same neighbourhood, $\phi \approx 2.2$. Starting at 1282 K at $\phi = 1.0$ (1000 K less than the adiabatic temperature), a maximum of 1530 K occurs at equivalence ratio of 1.6. From there on, combustion temperature practically remains constant independent of the propane content. The results of the numerical model for combustion temperatures show good agreement with the experimental data.

The experimental wave propagation rate shows a maximum absolute value of 0.0098 cm/s in the limit of LVR in the direction opposite to the gas flow at $\phi = 1.0$, relative concurrent value (0.0019 cm/s) at $\phi = 2.5$. A rich standing wave is observed for $\phi \approx 2.0$ and downstream propagation occurs in the ultrarich region, where the speed increases with propane content. The satisfactory agreement in predicting wave velocities is obtained for propane in the ultrarich regions. The difference in the numerical and experimental results is observed near the stoichiometry. Near the experimental propagation velocities are essentially higher (by ~ 2 times). The observed discrepancy is clearly attributed to the change of the propagation mechanism in the limit of LVR. These differences can be attributed to two factors: (i) the low value of the volumetric

convective heat transfer coefficient used in the numerical simulation, (ii) the limited applicability of the GRI 3.0 Mech.

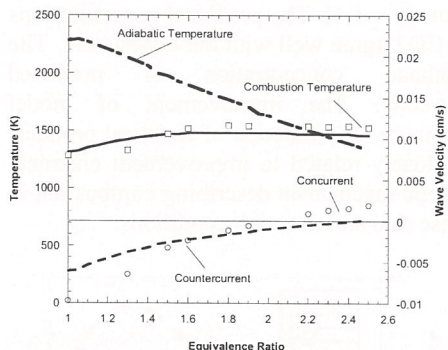


Figure 6: Combustion temperature and wave velocity of propane-air mixture.

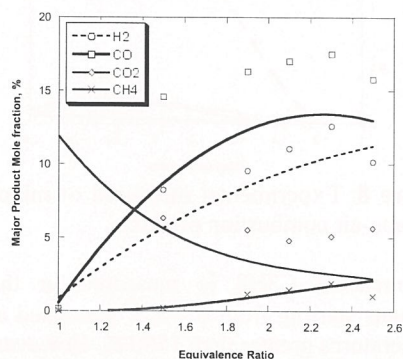


Figure 7: Concentration of the major products of rich and ultra-rich propane/air combustion in a packed bed.

4.2.2 Combustion products

Concentrations of CO_2 and H_2O decrease and partial oxidation products such as H_2 , CO (Fig. 7) and significant concentrations of C_2 hydrocarbons (Fig. 8) appear in the exhaust gases. H_2 and CO become dominant products for superadiabatic combustion waves at $\phi > 2.0$. The numerical results for concentrations of major combustion products (CO , H_2 , CO_2 , CH_4) show good agreement with the experimental results. In particular, the concentration of hydrogen, carbon monoxide and methane are increased with

equivalence ratio and concentration of CO_2 is reduced. The concentration of H_2 and CO are underpredicted by the model especially on the boundary of the rich flammability limit ($\phi \approx 1.4$). The predicted concentrations of CO_2 agree well with the experiment. The methane concentration is predicted correctly. The improvement of model accuracy for prediction of chemical products is closely related to improvement chemical kinetic mechanism describing combustion in these rich and ultrarich conditions.

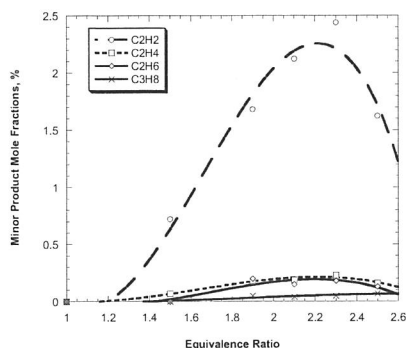


Figure 8: Experimental measured of minor propane-air combustion products.

Unreacted C_3H_8 is measured in the products starting from $\phi = 1.5$, generated at temperatures greater than 1500 K. However, during these tests the products temperature remained considerably above this critical temperature. Hence, the significant amounts of CH_4 and C_2H_2 species measured are due to finite rate kinetic effects, rather than the reverse steam reforming reaction. The measured concentrations of C_2H_4 and C_2H_6 could be as high as 0.2%. In fact, the ultra-rich superadiabatic wave is capable of inducing chemical transformation of propane in the mixtures with very small oxygen concentration. Thus, the process could be characterized as fuel reformation or modification rather than combustion. For example, Fig. 9 shows that the degree of propane conversion to hydrogen could be as high as 36% at the range of equivalence ratios studied.

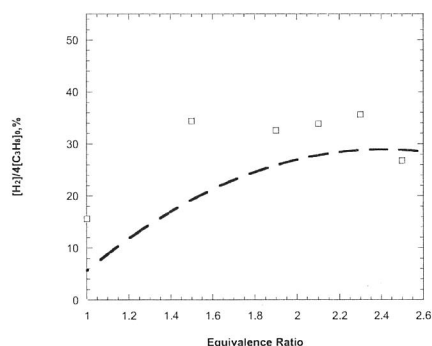


Figure 9: Degree of ethane conversion to hydrogen for rich and ultra-rich waves.

5. CONCLUSION

The concept for hydrogen production using filtration combustion waves in an inert porous media are studied experimentally and numerically for methane/air and propane/air mixtures at the equivalence ratio range from stoichiometry ($\phi = 1.0$) to $\phi = 2.5$. The studied range covers the superadiabatic and underadiabatic combustion waves formed in the rich region.

Downstream (superadiabatic) wave propagation was observed for ultrarich ($\phi > 1.5$) methane-air mixtures. Upstream (underadiabatic) propagation corresponds to the range of equivalence ratios from 1.0 to 1.5. LVR of filtration gas combustion is observed for $(\text{CH}_4)/\text{air}$ mixtures for all the range of ϕ .

For propane-air mixtures, a maximum absolute value of velocity (~ 0.01 m/s) is observed at the limit of LVR at $\phi = 1.0$. The maximum combustion temperature corresponding to the ultrarich mixtures ($\phi \geq 1.6$) where it is practically independent of the propane content.

In rich and ultra-rich mixtures complete combustion could not be achieved due to the low oxygen content in the mixture. This resulted in formation of partial oxidation products such as H_2 , CO , and C_2 hydrocarbons. The maximum generated mole fraction of hydrogen was 13% for

propane and 11% for methane flames stabilized inside the porous burner. This corresponds to a conversion to CO and H₂ of 55%, and 60% respectively. Considerable amounts of CH₄, C₂H₂ and C₂H₄ were measured in the combustion products of methane and propane at higher equivalence ratios due to finite chemical reaction rates. These results show that steady rich combustion inside a porous medium can be used to reform gaseous fuels into hydrogen and syngas.

A variety of hydrocarbon fuels can be presently used in practical combustion applications for the ultra-rich cases. For example, natural gas compositions typically contain various concentrations of C1-C3 hydrocarbons. This suggests that further experimental and numerical studies of porous combustion of C1-C3 hydrocarbons and their mixtures are practically important. The further extension of this work will be experimental studies on porous combustion of characteristic hydrocarbon mixtures typical for various sources such as gasification, biogasification, natural gas suppliers and refineries. The numerical model describing the porous combustion of C1-C3 hydrocarbons and their mixtures will be further developed using comprehensive chemical mechanisms and validated in comparison with experimental data.

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REFERENCES

[1] Babkin, V. 1993. Filtration combustion of gases, present state of affairs and prospects. *Pure and Applied Chemistry*. Vol. 65. pp335-344. USA.

[2] Kennedy, L, Bingue, J, Saveliev, A, Fridman, A, Foutko, S. 2000. Chemical structures of methane-air filtration combustion waves for fuel-lean and fuel-

rich conditions. *Proc. of the Combustion Institute*. Vol. 28. pp1431-1438. USA.

[3] Toledo, M, Bubnovich, V, Saveliev, A, Kennedy, L. 2006. Comparative study of lean and rich filtration combustion of methane/air, ethane/air, and propane/air mixtures, *Proc. of the 4th Wseas Int. Conf. on Heat Trans. Thermal Eng. and Environment*. 21th-23th August. Greece.

[4] Drayton, M, Saveliev, A, Kennedy, L, Fridman, A, Li, Y. 1998. Syngas production using superadiabatic combustion of ultra-rich methane-air mixtures. *Proc. of the Combustion Institute*. Vol. 26. pp1361-1367. USA.

[5] Bingue, J, Saveliev, A, Fridman, A, Kennedy, L. 2002. Hydrogen production in ultra-rich filtration combustion of methane and hydrogen sulphide. *Int. Journal of Heat and Mass Transfer*. Vol. 27. pp643-649. England.

[6] Kaviany, M. 1991. *Principles of Heat Transfer in Porous Media*. Springer-Verlag. USA.

[7] Henneke, M, Ellzey, J. 1999. Modeling of filtration combustion in a packed bed. *Combustion and Flame*. Vol. 117. pp832-840. USA.

[8] Wakao, N, Kaguei, S. 1982. *Heat and Mass Transfer in Packed Beds*. Gordon and Breach Science Publications. USA.

[9] Touloukian, Y, Ho, C. 1972. *Eds. Thermophysical Properties of Matter*. Vol. 2. USA.

[10] Smith, G, Golden, D, Frenklach, M, Moriarty, N, Eiteneer, B, Goldenberg, M, Bowman, C, Hanson, R, Song, S, Gardiner, W, Lissianski, V, Qin, Z. http://www.me.berkeley.edu/gri_mech/.

[11] Kee, R, Rupley, F, Miller, J. 1989. Report No. SAND89-8009B UC-706. Sandia National Laboratories.

[12] Kee, R, Grcar, J, Smooke, M, Miller, J. 1985. Report No. SAND85-8240 UC-401. Sandia National Laboratories.