

HYDROGEN PRODUCTION FROM FOSSIL AND BIOMASS FUELS: CATALYST DEVELOPMENT, KINETICS, AND REACTOR MODELING

Ahmed Aboudheir and Raphael Idem⁺

HTC Pureenergy, Regina, SK, S4P 0S4, Canada;

⁺Faculty of Engineering, University of Regina, Regina, SK, S4S 0A2, Canada

Introduction

Fossil and biomass fuels could be made to be a clean and/or alternative energy source if the energy is obtained in an environmentally sustainable manner. This could be achieved through the use of hydrogen energy derived from fossil and biomass sources with carbon capture. This paper will demonstrate new and innovative ways to produce hydrogen in an environmentally sustainable manner from natural gas and from crude ethanol as examples of the two fuel sources.

In the first technology, a unique two-stage process of producing hydrogen by the reforming of natural gas has been developed. This process, called “the dry reforming process”, consists of a two-stage reformer. In the first reformer (dry reformer), methane or natural gas reacts with CO₂ to produce H₂ and CO while in the second reformer (water gas shift reformer), CO reacts with steam to produce additional H₂ and CO₂ as the end products; the CO₂ is separated and partly recycled to the first reformer with the balance being captured. The proposed hydrogen reformation technology is highly scalable from appliance size to industrial scale plants. As a result, this technology can be deployed to produce hydrogen ‘on-site’ for use as a fuel and/or industrial gas for local and/or widely dispersed consumption. This ‘on-site’ production capability overcomes one of the main barriers to the widespread adoption of hydrogen as an industrial and consumer end-use fuel or industrial gas, i.e. the difficulty in storage and transportation of H₂ due to metal embrittlement, leakage, and the high cost of compressing H₂ for transport. Because of its scalability capability, the technology can be applied to produce hydrogen from methane obtained from biogas, and low quality natural gas (both consisting of a large fraction of CO₂ in the produced gas). In the latter case, the typical practice is to remove the CO₂ from the natural gas in order to produce a saleable natural gas. The dry reforming technology actually takes advantage of the presence of the CO₂ in the gas as this mixture can provide the direct feed with minimal augmented CO₂ for the process, and obviates the need and cost associated with CO₂ removal.

In the second technology, a new method for hydrogen production from crude ethanol has been developed. The crude ethanol term is used in this paper to represent filtered but not distilled fermentation broth containing water, ethanol and other oxygenated hydrocarbons such as glycerol, lactic acid and maltose. By producing hydrogen from crude ethanol, the plant operators have the option to sell the hydrogen as a

commodity or use this lower cost secure supply of energy within the ethanol plant. Because the crude ethanol is composed of a wide range of oxygenated hydrocarbons, it means the HTC reformer process can use a wide range of renewable bio-feedstocks including crude ethanol, glycerol, cellulose and hemi-cellulose based feedstocks, methanol and higher order alcohols like propanol, butanol and pentanol, and organic acids (i.e. essentially any liquid oxygenated hydrocarbon materials containing carbon, hydrogen and oxygen in their molecules).

Catalysts engineering, kinetic studies and reactor modeling for these processes as well as their application in a multi-feed hydrogen production demonstration will be presented.

Catalyst Development

The developed catalysts for dry reforming and water gas processes as well as for crude ethanol reforming are very robust and the same catalyst could be used for all the oxygenated hydrocarbons reactions, and for the dry reforming process with little or no modification. The catalysts are based on a generic synthetic approach which makes them to be constituent members of the same family of catalysts. The supports of these catalysts are composed essentially of CeO₂ and/or ZrO₂ and/or La₂O₃ and/or Al₂O₃ and are prepared via a surfactant-assisted method. This approach imparts to the catalysts nano-crystallinity and high surface area resulting in a high dispersion of the impregnated active non-noble metal (Ni and/or Cu) on the catalyst. The presence of CeO₂ in the support leads to a high oxygen storage capacity in the catalyst, which together with nano-crystallinity and high metal dispersion, lead to the avoidance of carbon deposition (or coking) during reaction. As a result, our catalysts are inherently stable. Consequently, these processes require minimal replacements of the catalysts unlike what is commonplace in the literature if nickel is used. For example, a long-term (more than 200 hours) stability tests were conducted to evaluate the durability of the developed catalyst for the reaction with the highest carbon density, the dry reforming reaction as shown in Figure 1. During catalyst development, activity screening tests are carried out alongside an extensive characterization of the catalysts using a wide array of characterization tools. The results are used to establish catalyst activity – property relationships, which are then used to fine-tune the catalyst design in order to produce the improved catalysts. The details of the catalyst development and characterization are documented elsewhere [1-3].

Kinetics Studies

For each reaction process, the kinetics experiments were carried out at atmospheric pressure in a packed bed tubular reactor. The experiments to collect the intrinsic kinetic data were performed at various reaction temperatures and ratios of weight of catalyst to mass flow rate of main reactant (W/F_{A0}). The reaction temperature for dry reforming, water gas, and

crude ethanol were ranged within 700-850 °C, 400-600 °C, and 320-520 °C, respectively. Certain criteria for packed-bed reactors were observed, according to Froment and Bischoff, to ensure that flow conditions in the reactor were close to plug flow in order to obtain isothermal reactor operation, eliminate back mixing and minimize channeling. These are: (a) ratio of catalyst bed height to catalyst particle size (L/D_p) > 50, and (b) ratio of internal diameter of the reactor to the catalyst particle size (D/D_p) > 10. These conditions were considered in all kinetic experiments in order to ensure plug flow behavior in the reactor. Several reaction mechanisms, new and/or reported were used to interpret the collected experimental kinetics data. For example, Eley Rideal assumptions where the surface reaction involved an adsorbed species and a free gaseous species were used to develop the reaction mechanism and four models were proposed based on this mechanism, from which a new kinetic model based on the dissociation of adsorbed crude ethanol as the rate-determining step was developed for this novel catalytic process. The obtained experimental rates for the production of hydrogen by the reforming of crude ethanol were compared with those predicted by the new developed mechanistic rate model. The results are shown in the parity chart of Figure 2. This figure shows excellent predictive ability of the model with an average absolute deviation of 6.0%. This shows that the assumptions made in terms of rate determining step for this Eley Rideal mechanism based new developed model and neglecting the effects of the products for deriving the model were justified as documented elsewhere [2].

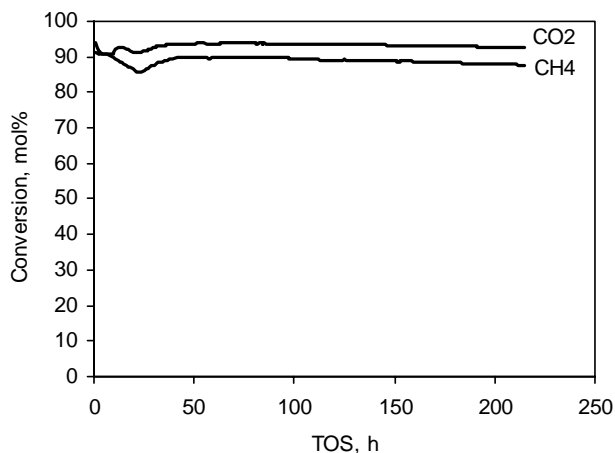


Figure 1. Long-term stability test for dry reforming in terms of conversion of CH₄ and CO₂ versus time on stream

Membrane Reactor for hydrogen separation

At the bench scale level, a membrane reactor is used for the water gas shift reaction and the crude ethanol reforming to separate hydrogen from the reformat gas. Commercial membrane tubes were used, which are located inside the membrane reactor. These membrane tubes can handle the temperature and the pressure required for the hydrogen separation, which are in the range 400 - 600 °C and 20 - 40

bar, respectively. Our laboratory scale membrane reactor has been characterized and used for running the water gas shift reaction. The model used for evaluating the membrane reactor is presented in Equation 1.

$$N_{H_2} = \frac{P_m e^{(-E_a/RT)}}{\delta_{H_2}} (\sqrt{P_{H_2}^{high}} - \sqrt{P_{H_2}^{low}}) F^n \quad (1)$$

where N_{H_2} is the H₂ permeation rate through the membrane [mol/(m²s)], P_m is the pre-exponential factor of the membrane [mol m/(s m² bar^{0.5})], E_a is the apparent activation energy of the membrane [J/mol], R is the gas constant [J/(mol K)], T is the absolute temperature [K], δ_{H_2} is the thickness of the membrane layer [m], $P_{H_2}^{high}$ is the partial pressure of H₂ in the reaction side [bar], $P_{H_2}^{low}$ is the partial pressure of H₂ in the non-reaction side [bar], ΔP is the total pressure difference between the reactor side and the permeate side of the membrane (psig), F is the total flow rate [mL/min], and n is the “reaction” order with respect to the flow rate.

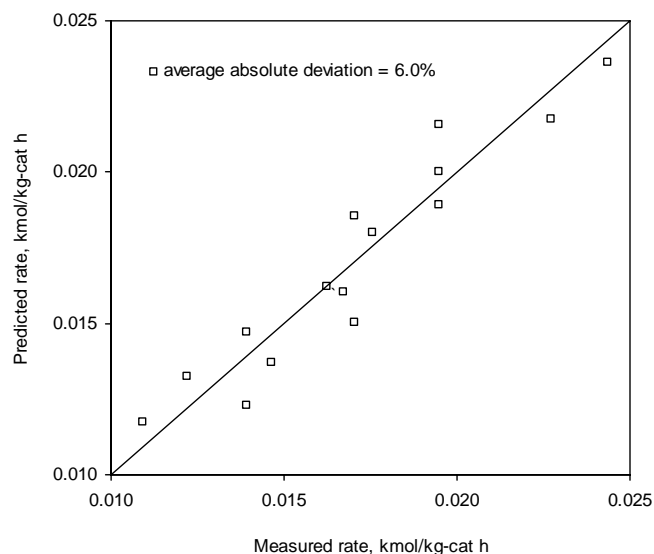


Figure 2. Comparison of measured and predicted rates of reaction for crude ethanol reforming within the temperature range 320 - 520 °C and WHSV range 1.9 - 4.6 h⁻¹.

Reactor Modeling

A rigorous numerical model was developed to design and simulate the production of hydrogen from dry reforming of methane/water gas shift reaction and the reforming of oxygenated hydrocarbons such as crude ethanol. The model was based on the coupling of mass and energy balance equations as well as the new kinetic models developed for each process (i.e. dry reforming, water gas shift reaction, and reforming of crude ethanol). The general mass, energy, and momentum balance equations used in our model are presented in Equations 2 to 4.

$$\frac{\partial C_i}{\partial t} + v_z \frac{\partial C_i}{\partial z} = D \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} + \frac{\partial^2 C_i}{\partial z^2} \right) + \rho_B r_j \quad (2)$$

$$\rho_g C_p \left(\frac{\partial T}{\partial t} + v_z \frac{\partial T}{\partial z} \right) = \lambda \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} \right) + \rho_B \left[\sum -\Delta H_j r_j \right] \quad (3)$$

$$\rho_g \left(\frac{\partial v_z}{\partial t} + v_z \frac{\partial v_z}{\partial z} \right) = -\frac{\partial P}{\partial z} + \mu \left[\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r} \frac{\partial v_z}{\partial r} + \frac{\partial^2 v_z}{\partial z^2} \right] + \rho_g g_z \quad (4)$$

where D denotes effective diffusivity, v denotes velocity, C_i denotes concentration of each chemical species, ρ_B denotes the catalyst bulk density, r_j denotes reaction rate (if the diffusant is being consumed by the reaction, r_j will be negative in these equations), t denotes time, ρ_g denotes gas density, C_p denotes heat capacity, λ denotes effective thermal conductivity, T denotes temperature, ΔH denotes heat of reaction, g_z denotes acceleration gravity, and P denotes pressure. The pressure drop in packed bed can be calculated from Ergun's formula of Equation 5 as recommended by Froment and Bischoff, 1990.

$$-\frac{dP}{dz} = \frac{\rho_g v_z^2}{d_p} \frac{1 - \varepsilon}{\varepsilon^3} \left[1.75 + \frac{150(1 - \varepsilon)}{Re} \right] \quad (5)$$

where

$$\varepsilon = 0.38 + 0.073 \left[1 + \frac{(d_i/d_p - 2)^2}{(d_i/d_p)^2} \right]$$

$$Re = \frac{d_p \rho_g v_z}{\mu}, \quad d_p \text{ denotes particle diameter, } d_i$$

denotes internal tube diameter, ε denotes void fraction of packing, Re denotes Reynolds number, and μ denotes dynamic viscosity. Diffusion is the only transport mechanism in the membrane phase (a vertical cylindrical membrane). Thus, the unsteady state mass balance in cylindrical coordinate for the permeable gases through the inert membrane can be represented as in Equation 6.

$$\frac{\partial C_i}{\partial t} = D_m \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) \quad (6)$$

where D_m denotes effective diffusivity in the membrane.

These equations for the model were solved subject to the initial and boundary conditions for each process in order to design or simulate the behavior of the reactors. For example, the simulation results for crude ethanol conversion were found to be in accordance with our experimental data as shown in Table 1. A further validation of our model was obtained by

using the model to simulate a well-documented reaction process in the literature [4] as shown in Figure 3. This confirmed the validity of the numerical model to design pilot and commercial plants as reported elsewhere [5].

Multi-feedstock Hydrogen Production demonstration plant

Based on our successful lab scale results demonstrated in the previous sections, a multi-feedstock demonstration plant was designed to produce 1.0 kg/h of hydrogen. A schematic diagram of the hydrogen production demonstration plant is shown in Figure 4. The pilot plant will be used for dry reforming/water gas shift process (operation mode # 1) or steam reforming of oxygenated hydrocarbons (operation mode # 2).

Table 1. Outlet Concentration Profiles Of The Reactor At Feed Temperature Of 320 °C And W/F_{A0} Of 2016 Kg-Cat S/Kg-Crude

Fluid	Measured mol%	Predicted mol%	AD%
Crude ethanol	2.9	2.8	3.45
Water	80.5	82.2	2.11
CO ₂ , CO, CH ₄ , etc.	4.3	3.9	9.30
Hydrogen	12.3	11.1	9.76
Average absolute deviation, AAD%			6.15

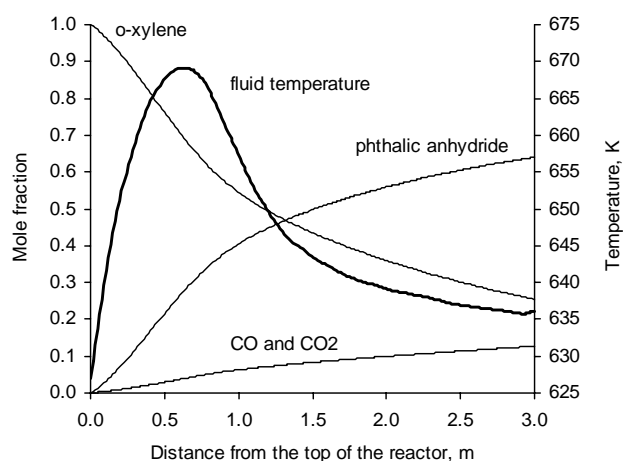


Figure 3. Center line axial concentration and temperature profiles in multi-tubular *o*-xylene oxidation reactor, industrial scale.

In operation Mode # 1, Dry reforming process and water gas shift reaction, the natural gas and carbon dioxide is the feed stream comprising of 50% methane and 50% CO₂. This stream is delivered at about 2 bar to the desulphurization unit and then to the multi-tubular dry reforming reactor. The

required reaction temperature is in the range 700-850 °C with the endothermic heat obtained via a natural gas/molten salt furnace. The reformat gas product stream is cooled to about 60 °C and then compressed to about 20-40 bar. The reformat gas and steam are then heated and delivered to the multi-tubular membrane reactor at about 400-600°C. The water gas shift reaction and the separation of hydrogen will be carried out simultaneously in this membrane reactor. The residue (raffinate) from the membrane reactor returns to the furnace and combusted for additional heating to the reformer. Another option to explore is to add a membrane filter at the end of the raffinate stream to further remove additional hydrogen from the raffinate according to Equation 1. The resulting raffinate could be recycled to the dry reformer. In this case, there will be a purge stream downstream of the membrane filter in order to keep the CO₂ levels in the various streams in the process fixed. The pure hydrogen stream will be cooled, compressed and stored after cooling at about 400 bar for utilization.

In operation Mode # 2 for oxygenated hydrocarbon reforming, only the multi-tubular membrane reactor and the second will be utilized. The biomass feed (i.e. oxygenated hydrocarbons such as crude ethanol) will be heated and delivered to the membrane reactor at 400-550 °C and 20-40 bar using a liquid pump prior to the heating furnace that uses natural gas/raffinate as a fuel to maintain the temperature of the reactor that is immersed in molten salt. The residue (raffinate) from the membrane reactor is returned to the furnace and combusted for additional heating required by the reactor. Also, another option to explore is to add a membrane filter at the end of the raffinate stream to further remove additional hydrogen from the raffinate. The pure hydrogen stream will be cooled, compressed and stored after cooling at about 400 bar for utilization.

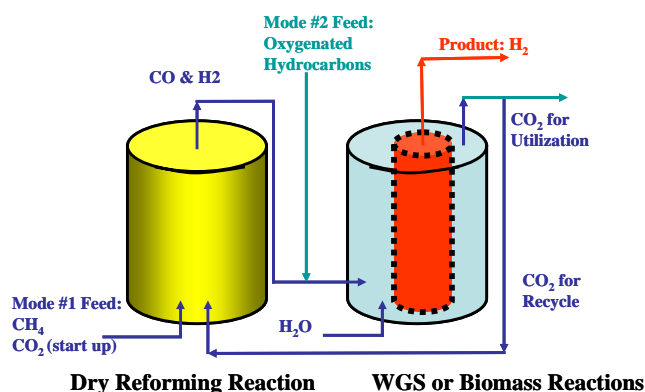


Figure 4. A schematic diagram of Hydrogen Production Demonstration Plant: Mode # 1, Dry Reforming of Methane followed by the Water Gas Shift Reaction for hydrogen production or Mode # 2, Liquid Oxygenated Hydrocarbons (Biomass) Reforming

Conclusions and Recommendations

New stable catalysts and new kinetics models were developed for dry reforming of natural gas and water gas shift reaction as well as for crude ethanol reforming. These catalysts are very robust and the same catalyst could be used for any oxygenated hydrocarbons reactions, and for the dry reforming process with little or no modification.

In addition, a comprehensive model for the design and simulation of these hydrogen production processes was developed. On both laboratory and industrial scales, the developed mathematical model is capable of accurately predicting the concentration profiles of all the chemical species and the temperature profiles of the fluid in both axial and radial directions. The simulation results on the laboratory scale was able to demonstrate that plug flow and isothermal behaviors could not always be guaranteed even by following well-known operating criteria. As a result, it is recommended to use a comprehensive model to verify whether or not plug flow behavior is attained for each kinetic experimental condition. Utilizing the experimental and modeling findings, a demonstration plant is designed to produce 1 kg/h of hydrogen by dry reforming natural gas and oxygenated hydrocarbons. It is recommended to implement this demonstration plant in order to optimize the design configuration and all the operating parameters, as well as to validate the integration between the unit operations before moving to a commercial scale.

References

- (1) Idem, R.O., Kumar, P.; Sun, Y.; Catalysts for Hydrogen Production, *US Patent, Application Number: 2006/0216227*, Publication date September 28, 2006.
- (2) Akande A.J.; Idem, R.O.; Dalai, A.K.; *Applied Catalysis A: General*, **2005**, 287, 159–175.
- (3) Kumar, P.; Sun, Y.; Ibrahim, H.H.; Akpan, E.R.; Aboudheir, A.; Idem, R. O.; *Appl. Catal.*, submitted, 2006.
- (4) Froment G.F.; Bischoff K.B.; *Chemical reactor analysis and design*. 2nd ed., New York: Wiley; 1990.
- (5) Aboudheir, A.; Akande, A.J.; Idem, R.O.; Dalai, A.K.; *International Journal of Hydrogen Energy*, **2006**, 31, 752–761.