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Technical Notes

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Hydrogen from Steam Reforming of Coal-Derived Methanol

Hyung Chul Yoon* and Paul Anders Erickson†
University of California, Davis, Davis, California 95616

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Nomenclature

k = chemical kinetic reaction rate
Q = liquid methanol input flow rate, m^3/h
V = catalyst packing volume, m^3

I. Introduction

CLEAN coal technology research was begun in 1985 to determine the commercial feasibility of converting coal syngas into methanol. Coal-derived methanol can be purified to be compatible with current chemical-grade standards, theoretically making it possible for coal-derived methanol to be used as a hydrogen feedstock for fuel cells. Indeed, hydrogen production via coal-derived methanol was suggested in the initial technical report for the methanol production plant [1]. Initial research using a low-grade coal-derived methanol to produce hydrogen was previously performed [2] and the results were compared to chemical-grade methanol. Because of high concentrations of impurities, the low-grade coal-derived methanol was determined to be incompatible with steam-reformation processes. Since this previous study, the provider (Eastman Chemicals) has further improved the coal-based methanol production process and removed most of the problematic compounds. This study is the first to evaluate the further refined coal-derived methanol for use in the steam-reformation process.

Methanol steam reformation is one of the well-known hydrogen production technologies for fuel cell applications [3–13]. As seen in Eq. (1) for methanol and stoichiometric steam, a 75% hydrogen concentration can be produced based on 100% carbon dioxide selectivity. In practice, H_2 outlet concentration is less than 75% and the fuel conversion is strongly dependent on reactor size as well as fuel flow rate due to heat and mass transfer limitations.

$$CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2(\Delta h = +49\ \mathrm{kJ/kmol_{CH3OH}}) \quad (1)$$

$$CH_3OH \leftrightarrow CO + 2H_2(\Delta h = +90.1\ \mathrm{kJ/kmol_{CH3OH}}) \quad (2)$$

$$CO + H_2O \leftrightarrow H_2 + CO_2(\Delta h = -41.2\ \mathrm{kJ/kmol}) \quad (3)$$

As seen in Eqs. (2) and (3), steam reforming of methanol includes both methanol decomposition [Eq. (2)] and the water–gas–shift reaction [Eq. (3)]. To prevent carbon formation, excess steam (1.3–1.5 steam:carbon ratio) is added [14]. The reaction pathway of the overall steam-reforming methanol is much more complex than Eq. (1). The exact mechanism and pathway is still debated [10,11]. As seen in Eq. (2), methanol decomposition is shown as an endothermic reaction. Because of the endothermicity, the methanol decomposition reaction rate is smaller than the water–gas–shift reaction rate as evidenced by CO concentration far below the thermodynamic equilibrium calculation [10,11,15]. As seen in Eq. (3), the water-–gas–shift reaction yields more hydrogen created by the reaction of carbon monoxide with water. This reaction is vital because it reduces carbon monoxide poisoning with the fuel cell catalyst anode in both proton exchange membrane (PEM) and phosphoric acid (PA) fuel cell applications. The water–gas–shift reaction yields low CO levels at low temperatures (200–280°C), with even faster kinetics at higher temperature [16].

Carbon monoxide formation with copper-based catalysts is being debated. In the literature, there are two suggestions associated with the reaction pathway for methanol steam reforming and carbon monoxide formation. One suggested pathway is that CO is the primary product from methanol decomposition and water–gas–shift reaction follows to control the concentration of CO [5,13,17]. Another suggested pathway is that CO is a secondary product produced through a reverse water–gas–shift reaction [7,12,18]. These two pathways start from two observations. First, the concentration of CO is below the thermodynamic equilibrium. Second, the copper-based catalyst is typically preferable for the water–gas–shift reaction. In the first suggestion, CO is produced directly through methanol decomposition and then CO is converted into CO_2 by the water–gas–shift reaction as shown in Eq. (3). The formation of CO from methanol decomposition is noticeably small, so that concentration of CO is lower than the equilibrium calculation [9–11,15]. The other suggestion in the literature proposes that CO cannot be produced as a primary product of methanol decomposition because CO production decreases as contact times decrease even though a copper catalyst had been used [18]. Therefore, it can be thought of as a secondary product through a reverse water–gas–shift reaction as seen in Eq. (3) [7,12,18]. Peppley et al. [10,11] suggest that methanol decomposition, the water–gas–shift and steam-reforming reactions should be thought of as a combined reaction network because a small amount of CO can be poisons for the proton exchange membrane fuel cell (PEMFC).

Initial research using low-grade coal-derived methanol, also known as stabilized methanol from the first distillation column, to produce hydrogen in a steam-reformation process was tested at both 255 and 400°C and compared with chemical-grade methanol [2]. The stabilized methanol had 97% methanol purity with a small concentration of hydrocarbon and water impurities. Sulfur and chlorine poisons had not been considered due to negligible concentrations. Severe deactivation of the copper-based catalyst

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*Researcher, Mechanical and Aeronautical Engineering Department, MAE University of California, One Shields Avenue, Davis, CA 95616-5294.

†Assistant Professor, Mechanical and Aeronautical Engineering Department, MAE University of California, One Shields Avenue, Davis, CA 95616-5294.

occurred due to physical deposition of mineral oil on the catalyst surface at lower temperatures (255°C). However, the vapor form of mineral oil at higher temperature (~400°C) did not coat the catalyst surface so that minimal catalyst degradation was observed. To investigate the effect of higher hydrocarbon impurities, mineral oil or kerosene was added to fuel cell grade methanol and degradation rates were compared. The catalyst degradation rate with kerosene was smaller than that with mineral oil added. In the case of catalyst durability, even small differences in the degradation rate could be important for fuel cell applications. This past study concluded that stabilized methanol was not a suitable fuel for use with a low temperature steam-reformer system used to supply a phosphoric acid fuel cell. However, higher reformer catalyst temperatures (>400°C) can use stabilized coal-derived methanol and achieve acceptable catalyst degradation rates. This study evaluates a higher grade of coal-derived methanol for potential use with PEM fuel cells.

II. Experimental Approach and Facility

The experimental facility as seen in Fig. 1 can be used for both autothermal reformation and steam reformation. Moreover, it has the versatility of using different fuels such as natural gas, gasoline, ethanol, etc.

The process of steam reformation starts from a water–methanol mixture (premix) in the reservoir. Premix consists of deionized water and methanol mixed with 1.5:1 molar ratio (0.9075–0.9085 kg/cm^3 at 24°C). The scale was used for measuring the amount of premix used during a certain time. Premix was pumped into the vaporizer through the gear pump. Three-stage vaporizers help the premix fuel to obtain a gas phase. As the temperature of the premix gases is not stable, the superheater is used to ensure a constant gas temperature into the catalyst bed or catalyst bed housings. Various types of reactors can be adapted and interchanged after the superheater. Using valves, the flow of gas after the catalyst bed is routed to a condenser. Condensed liquid (e.g., liquid water and unconverted methanol) is collected in the condensate trap. After the trap, dry gas is directed into the gas analyzer. When using a copper catalyst, the reformer should be sealed off from oxygen by means of purging the reactor with carbon dioxide.

In Fig. 2, two different reactors are shown. Reactor A was constructed from a 61 cm (24 in.) stainless-steel pipe (nominal 3/4 in diameter, schedule 40) threaded at both ends. In the case of reactor A, eight nozzle band heaters [2.5 cm (1 in.) inner diameter (ID), 5.1 cm (2 in.) width], with a 120 V, 275 W rating were used as the external heat source. To evenly supply heat and increase thermal distribution into the reactor, aluminum tape was wrapped around the exterior of the housing. The reactor was controlled by 25 0.159 cm (0.0625 in.) diam stainless-steel-sheathed, ungrounded K-type thermocouples. Seventeen 0.32 cm (0.125 in.) male national pipe threads (MNPT) to 0.32 cm (0.125 in.) pipe fittings welded on the housing were used to hold thermocouples. Left-side thermocouples were located at the centerline of the reactor. The right-side thermocouples were situated inside at the wall surface of the reactor. Temperatures of the gas flow were controlled from both measured temperature of the gas at the centerline and inside surface in real time. The eight external band heaters were also controlled by eight 0.025 cm (0.010 in.) diameter ungrounded K-type thermocouples placed between the band heater and a reactor wall. The wall interior was maintained at a temperature of 250°C.

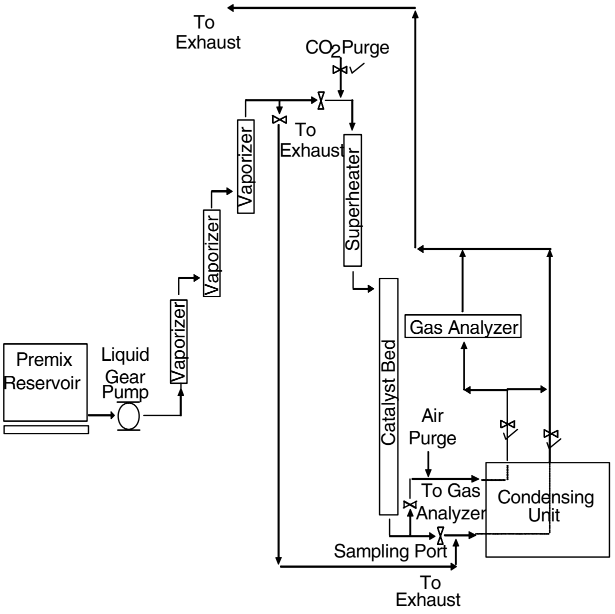
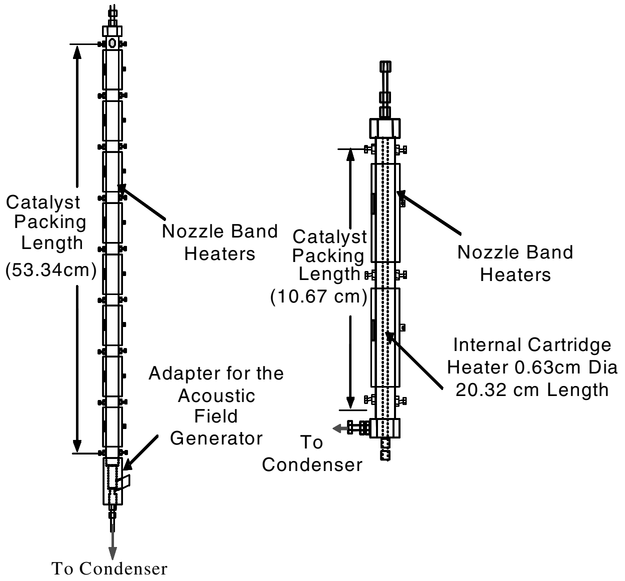


Fig. 1 Simplified drawing of the steam reformer.



a) Reactor A **b) Reactor B**

Fig. 2 Schematic of reactors.

Reactor B was constructed from a 12.7 cm (5 in.) stainless-steel pipe (nominal 3/4 in diameter, schedule 40) threaded at both ends. In reactor B, two nozzle band heaters (2.5 cm (1 in.) ID, 5.1 cm (2 in.) width), each with a 120 V, 275 W rating were adapted for external heating. Furthermore, one internal cartridge heater [0.635 cm (0.25 in.) diam 20.32 cm (8 in.) length], with a 120 V, 600 W rating was also applied to this reactor through the bottom cap. The reactor surface was wrapped with aluminum tape to increase heat transfer from the band heaters. The reactor was controlled by six 0.159 cm (0.0625 in.) diam stainless-steel sheathed, ungrounded K-type thermocouples inside the flow. Six 0.32 cm (0.125 in.) MNPT to 0.32 cm (0.125 in.) pipe fittings welded on the surface of the housing were used to hold thermocouples at each zone. Left-side thermocouples were located at the surface of the internal cartridge heater near the centerline. The right-side thermocouples were situated inside at the surface wall of the reactor. Temperature of the gas flow was controlled from both the measured temperature of the internal cartridge heater and the inside surface wall in real time. In addition, three 0.0508 cm (0.020 in.) diameter ungrounded K-type thermocouples were used for controlling reactor exterior surface temperature between the nozzle heater band and the exterior wall of the reactor. Reactors A and B were insulated by a 3-in. thick calcium silicate material with temperature tolerance of 649°C (1200°F). The wall interior was maintained at a temperature of 250°C.

Conversion is defined as the difference of the amount of fuel consumed in the reactor in relation to the fuel input to the reactor as shown in Eq. (4).

$$\text{Conversion}\ (\%) = \frac{MeOH_{\text{in}} - MeOH_{\text{out}}}{MeOH_{\text{in}}} \times 100 \tag{4}$$

Both the volumetric flow rate through the reactor and the effective catalyst packing volume can be expressed as "space velocity" as shown in Eq. (5).

$$\mathrm{LHSV\text{-}M} = \left(\frac{Q}{V}\right) \tag{5}$$

Space velocity gives a general guideline to account for different conversions at different flow rates. Different space velocities were selected from 1 up to 4 liquid hourly space velocities of methanol (LHSV-M). 2.5 LHSV-M was used in the degradation test.

III. Results and Discussion

A. Steam Reforming of Coal-Derived Methanol and Chemical-Grade Methanol

Coal-derived methanol was compared to a chemical-grade methanol which has been used for fuel cell applications. This test was performed at different liquid hourly space velocities of methanol from 1 to 4 during a steady-state operation. Other dependent variables (e.g., the amount of loaded catalyst, inlet temperature of premix, set point of reactor temperature controller) were held constant so that only the fuel quality would be compared.

Figure 3 shows the fuel conversion of both coal-derived and chemical-grade methanol using reactor A with a pelletized catalyst. Three replications at each space velocity were obtained in random order. A new catalyst was used for each fuel dataset. As shown in Fig. 3, the average conversions and the corresponding error bars demonstrate that the conversions of the two methanols at different space velocities are similar.

B. Catalyst Degradation Test for Both Coal-Derived and Chemical-Grade Methanol

Catalyst degradation experiments were performed with both coal-derived and chemical-grade methanol using reactor B which has the internal cartridge heater. Care was taken to reduce the thermal gradients by using this reactor. Much attention was paid to each degradation test to prevent bias of conversion for each of the continuous 70 h tests. In this experiment, there is only one independent value which is the fuel type. Other variables were kept identical for each separate test. The reactor inlet temperature was 250–253°C (482–487.4°F), and a space velocity of 2.5 LHSV-M was adopted for this experiment. A crushed catalyst of 39 g was used for these tests and the catalyst was replaced and reduced before each run.

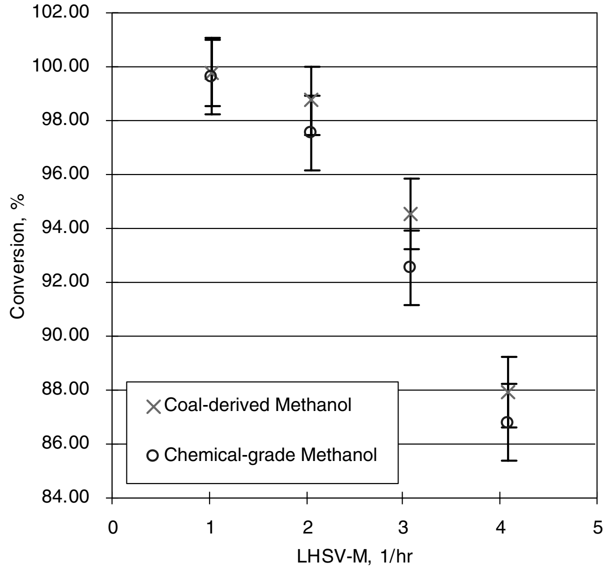


Fig. 3 Conversion of coal-derived and chemical-grade methanol.

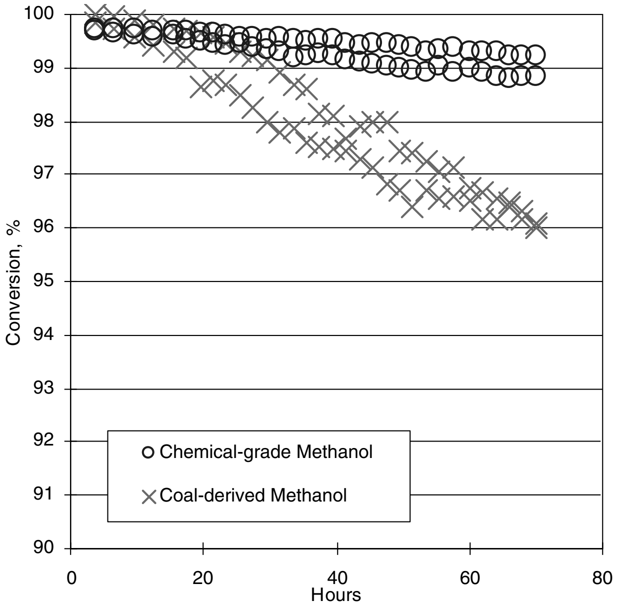


Fig. 4 Degradation test for coal-derived methanol and chemical-grade methanol for 70 h.

Figure 4 represents the results of catalyst degradation tests using both methanol types. This figure shows the fuel conversion vs time for four separate 70 h continuous tests. Two tests were run with coal-derived methanol and two tests were run with chemical-grade methanol. The rate of performance degradation for the coal-derived methanol is greater than that of the chemical-grade methanol. Through preliminary internal and external chemical analysis we saw that the coal-derived methanol has more hydrocarbon compounds than does the chemical-grade methanol. Even though these trace impurities are at seemingly negligible amounts, the cumulative effect is seen in the conversion data.

Higher hydrocarbons should cause poisoning as well as fouling by the chemical reaction with the copper and physical blocking of the catalyst pores. Relative hydrocarbon levels are shown through an external analysis of coal-derived (17 mg/l) and chemical-grade (5.9 mg/l) methanol.

Preliminary tests of the fuel purity show that trace levels of higher hydrocarbons are still seen in coal-derived methanol in spite of further refinement as seen in Fig. 5.

In Fig. 6 the hydrocarbon concentrations of the output gas are shown during the 70 h degradation tests. The higher levels of output gas hydrocarbons with the coal-derived methanol indicate that upstream hydrocarbons are passing through unreacted or partially reacted. As shown in Fig. 6, for the first 12 h, hydrocarbon gas concentration of coal-derived methanol is nearly equal to that of chemical-grade methanol. However, after around 12 h, hydrocarbon dry gas concentration of coal-derived methanol increases faster than that of chemical-grade methanol. It seems that the catalyst degradation is evidenced in the reactor at this point. This is most likely due to fouling and poisoning from the trace hydrocarbons. It seems that the catalyst does absorb some of the hydrocarbons early in the tests. As the catalyst degradation continues, the excess hydrocarbons pass through or partially react in the catalyst bed.

Figures 7 and 8 represent CO_2 selectivity and CO selectivity. In general, at low temperatures of 220–280°C (428–536°F), reduced copper has another role which is to facilitate the water–gas–shift reaction while the steam-reforming reaction is occurring. Inside the reactor, there may be no specific area for the water–gas–shift reaction nor a separate area for the steam-reforming reaction. In other words, the reduced copper sites might be shared for both reactions. Under this assumption, both reactions should be degraded at the same rate and at the same time even though the water–gas–shift reaction is an exothermic reaction as opposed to the steam-reforming reaction which is endothermic. Therefore, the concentration of CO_2 produced by the water–gas–shift reaction should decrease due to a deactivated catalyst. However, in Fig. 7 we see that the CO_2 selectivity keeps increasing slowly even though catalyst degradation is taking place.

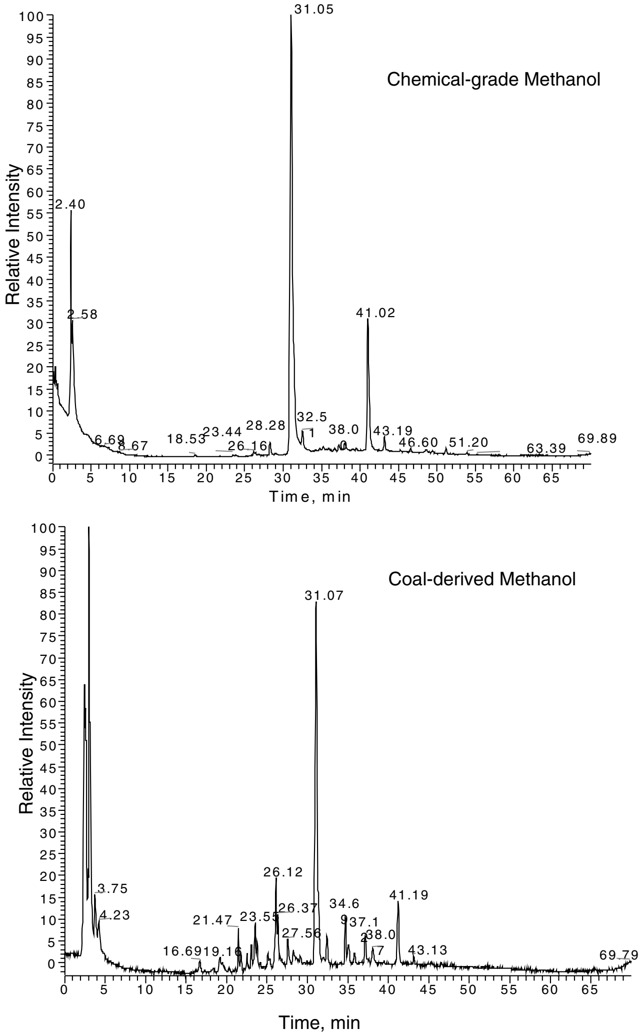


Fig. 5 Liquid chromatography for both chemical-grade and coal-derived methanol.

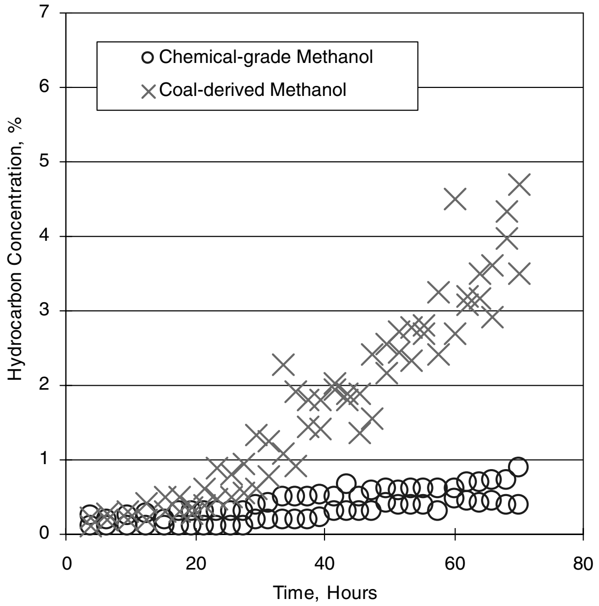


Fig. 6 Hydrocarbon concentration for both chemical-grade and coal-derived methanol actual data points.

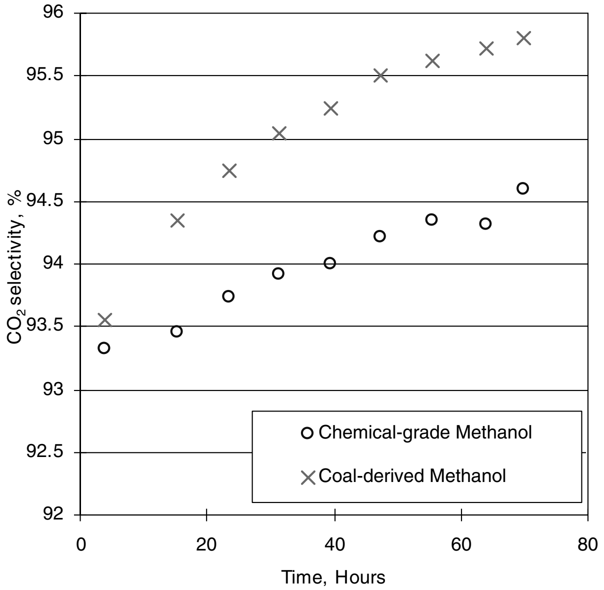


Fig. 7 CO_2 selectivity for both methanols.

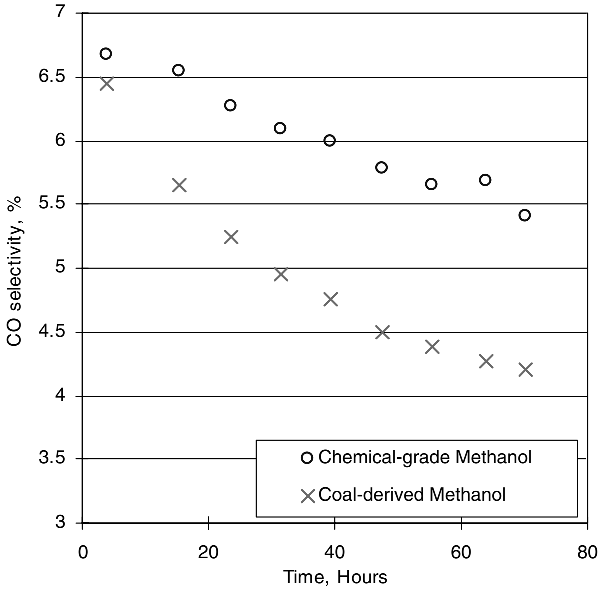


Fig. 8 CO selectivity for both methanols.

Conversely, CO selectivity keeps decreasing slowly as seen in Fig. 8. It seems that CO_2 cannot be produced by the water–gas–shift reaction even though copper has the ability to serve as a water–gas–shift catalyst. This might verify the above hypothesis that CO is a secondary product formed through a reverse water–gas–shift reaction instead of the forward water–gas–shift reaction. In comparing coal-derived methanol with chemical-grade methanol, CO concentrations from coal-derived methanol are lower than those produced from chemical-grade methanol. This seems to be because the reverse water–gas–shift reaction is deactivated more rapidly in the case of coal-derived methanol than in the case of chemical-grade methanol. This may be by means of fouling and poisoning of the catalyst by hydrocarbons.

Although higher degradation was observed with coal-derived methanol, there are indications that other factors such as reactor size also play a strong role in the degradation. Further work is continuing at the Hydrogen Production and Utilization Laboratory to establish the relative magnitude of geometry and fuel type in steam reformers with regards to catalyst degradation.

IV. Conclusions

The mechanisms of catalyst degradation and the relationship to steam reformation have been discussed. An experimental study of steam reforming with coal-derived methanol has taken place. A preliminary fuel analysis shows that coal-derived methanol has slightly more petroleum hydrocarbons than chemical-grade methanol typically used for fuel cell applications. With a fresh catalyst the reformation characteristics are very similar for a variety of space velocities. The conversion degradation rate with coal-derived methanol is slightly faster than with chemical-grade methanol for this specific steam reformer. As catalyst degradation goes on, CO selectivity decreases and CO_2 selectivity increases for both methanols. Even though the copper-based catalyst is generally well known for catalyzing the water–gas–shift reaction, the controlling reaction of the CO formation seems to be that of the reverse water–gas–shift reaction in steam reforming of methanol.

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T. Lieuwen
Associate Editor