

# Novel catalytic reactor for oxidative reforming of methanol

Maxim Lyubovsky\*, Subir Roychoudhury

*Precision Combustion, Inc., 410 Sackett Point Road, North Haven, CT 06473, USA*

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## Abstract

Oxidative steam reforming (OSR) of methanol is shown to produce extremely high hydrogen yield. Specific hydrogen production rates as high as 425 kW<sub>l</sub> per liter of reactor volume were demonstrated in a novel Microlith<sup>®</sup>-based catalytic reactor. At reduced space velocities hydrogen concentration in the reformate stream was as high as 50%, while CO concentration was as low as 1.2%. The thermal efficiency of the OSR process is greater than 80%.

It is shown that the autothermal OSR process consists of three reactions – methanol oxidation, methanol decomposition and water gas shift. These reactions have different kinetic rates and progress in an overlapping sequence along the catalyst bed. A radial flow catalyst configuration enables varying gas flow velocity to accommodate the different kinetic rates and heat release characteristics of these reactions. This allows a flat temperature profile and approach to equilibrium product composition to be achieved in a single catalyst bed.

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## 1. Introduction

Methanol is a readily available fuel for fuel cell powered electronic and transportation applications. Although, the energy density of methanol is about half that for gasoline or diesel fuels, methanol is more reactive and can be used in direct methanol fuel cells (DMFCs) or can be reformed to hydrogen in a relatively low-temperature process for use with proton exchange membrane (PEM) fuel cells. DMFCs are very attractive for low-power applications, such as miniature power sources for electronic devices. However, the power density of such cells remains significantly lower than for hydrogen PEM cells. Therefore, for higher power applications, where the size of DMFC systems becomes too large, use of PEM systems is preferred. DMFCs also require dilute aqueous methanol feeds that result in additional weight penalties, and also currently suffer from membrane permeability and durability concerns. If small and efficient reformers were available to convert methanol into hydrogen for PEM cells, the reformer/PEM cell combination may be preferred over

the DMFC approach when both size and weight are prime considerations.

Much effort has been directed towards development of efficient methanol steam reforming micro-reactors with improved heat exchange properties. Literature suggests that in the steam-reforming reaction Cu-based catalysts provide high selectivity towards CO<sub>2</sub> versus undesirable CO [1,2]. This is attributed to a reaction pathway, where adsorbed intermediate HCHO (formaldehyde) species react with water to directly produce H<sub>2</sub> and CO<sub>2</sub> without forming a CO intermediate. This results in a product mixture with CO concentrations below the equilibrium value. This is unlike the water-gas shift (WGS) pathway characteristic for Group VIII metal catalysts, where CH<sub>3</sub>OH is decomposed into CO and H<sub>2</sub> and CO is reacted with water to produce H<sub>2</sub>, and CO<sub>2</sub> in the WGS reaction. In this case the reaction yields CO concentrations equal to or greater than the equilibrium value.

While Cu-based catalysts are used in industrial WGS reactors, several factors limit application of Cu to small-scale fuel-reforming systems. For example, Cu catalysts have to be activated through a controlled process prior to operation, dispersed Cu catalysts can violently oxidize if exposed to ambient air, and the ability of Cu catalysts to retain activity over the multiple start/stop cycles has not been demonstrated. Because of these limitations application of more sta-

\* Corresponding author. Tel.: +1-203-287-3700;  
fax: +1-203-287-3710.

*E-mail address:* [mlyubovsky@precision-combustion.com](mailto:mlyubovsky@precision-combustion.com)  
(M. Lyubovsky).

ble precious metal catalysts to methanol reforming appears attractive. Takezawa and Iwasa [1] found that a catalyst comprised of Pd supported on ZnO demonstrated high reaction selectivity to CO<sub>2</sub> similar to that of Cu catalysts, while providing high activity comparable to the activity of precious metals. Metal–support interaction was a critical factor for this performance, as Pd supported on all other transition metal oxide supports tested in their work demonstrated the usual, non-selective behavior.

An alternative approach to methanol reforming is oxidative steam reforming (OSR). In this method a small amount of air is added to the methanol/steam mixture, such that oxidation and reforming reactions occur in the same reactor thermally balancing each other. This eliminates the need to transfer heat across a heat-conducting boundary and allows the reaction to proceed at much higher rates in a smaller reactor volume. While addition of nitrogen to the reformat stream dilutes the reformat mixture, in the case of methanol reforming only small amounts of air are required for the process, such that the negative effect can be minimized. Fierro and co-workers [3,4] studied the OSR of methanol over Cu and Pd catalysts supported over ZnO and Zn–Al. They found that oxygen concentration in the gas phase is the main parameter determining the reactor performance and suggested an oxidation/decomposition followed by reforming scheme for the process.

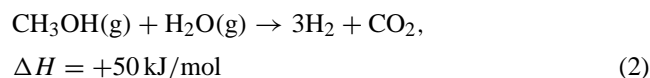
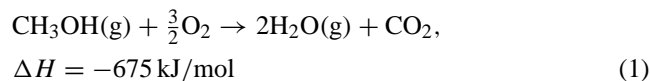
Zum Mallen and Schmidt [5] investigated partial oxidation of methanol over bulk Pt and Rh catalysts. They found that Rh and Pt, while having generally similar characteristics, showed significant differences in the mechanism of the methanol oxidation process. On Pt catalyst, decomposition behavior is dominated by breaking of the methanol C–O bond and formation of carbon on the surface at low temperatures. This had an overall effect of suppressing catalyst activity below ~500 °C. The addition of oxygen served to reduce surface carbon level and to increase catalytic activity. In contrast, on Rh catalyst, the methanol C–O bond remains non-dissociative and the activity loss due to surface carbon formation was never noted. The authors observed that Rh generally favored H<sub>2</sub> desorption, while Pt favored formation of H<sub>2</sub>O.

In this work we experimentally studied the OSR of methanol over catalysts with enhanced heat and mass transfer characteristics. Two different reactor configurations were tested under autothermal conditions, one with extremely high space velocity and short contact time, and the other with larger overall volume and varying flow rate along the reactor. The results are discussed in terms of the reaction mechanism and preferred reactor designs and characteristics.

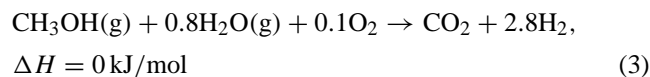
### 1.1. Thermodynamic analysis of the oxidative steam-reforming concept

The oxidative steam-reforming approach to methanol reforming combines the exothermic oxidation (1) and en-

dothermic steam reforming (2) reactions into a single process. Note that the enthalpies for both reactions are given for all gaseous components assuming pre-vaporization of methanol and water before entering the reforming reactor:

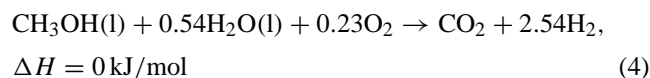


The ultimate goal of methanol reforming for PEMFC is to convert the fuel into H<sub>2</sub> and CO<sub>2</sub> by reacting it with water and oxygen through a combination of reactions (1) and (2). Any CO formed in the primary reformer should be converted into CO<sub>2</sub> in the downstream WGS and PROX reactors, or through some other cleanup process. Maximizing H<sub>2</sub> yield is the goal for increasing the efficiency of the process. Obviously, with higher amount of oxygen added to the reactant mixture more methanol is combusted in reaction (1), such that the overall process becomes more exothermic. With higher amount of water more methanol is reformed in reaction (2) consuming more heat. Combining Eqs. (1) and (2) an overall equation for the process can be written, where H<sub>2</sub> and CO<sub>2</sub> are the only products. Furthermore, the coefficients in this equation can be balanced to make the overall OSR process thermally neutral (enthalpy change equals zero) as shown by Eq. (3). Eq. (3), therefore, represents an ideal reforming process, where methanol is completely converted to hydrogen and no heat is lost.



Coefficients in Eq. (3) show the maximum amount of hydrogen, which can be obtained in a reforming process. For pre-vaporized reactants this amounts to 2.8 mol of H<sub>2</sub> per mole of methanol, which represents ~2.0 standard liters H<sub>2</sub> per gram of methanol. This maximum value is independent of the reforming strategy (unless heat import from an external source is available) and provides means for comparing different reforming systems on the basis of hydrogen output per unit of reformed fuel. Eq. (3), therefore, provides a measure of a thermal efficiency of an OSR reactor with 100% efficiency equating to the maximum hydrogen yield allowed by the reaction stoichiometry.

Since Eq. (3) assumes steam and pre-vaporized methanol in the feed stream it corresponds only to a single reforming reactor with pre-vaporized and pre-mixed inlet gas stream. An overall reforming system, where both methanol and water are in the liquid state, can be represented by Eq. (4). This would account for heat required for vaporization of these two components and more accurately describe an overall reforming process.



Because a certain amount of heat now has to be spent on vaporization of reactants the maximum hydrogen yield decreases to 2.5 mol of H<sub>2</sub> per mole of methanol, or about 1.8 standard liters per gram of methanol. Coefficients in Eq. (4) indicate the ideal amounts of water and oxygen required for reforming methanol. These are the overall amounts, i.e. combined at all consecutive stages of the process. For example, these would include water added before a WGS reactor, oxygen added to a PROX reactor and oxygen consumed in the combustion side of a steam reforming reactor. Thus, Eq. (4) provides a measure for efficiency of the overall reforming process.

A more common definition used for measuring efficiency of a reforming process is based on comparing the lower heating values (LHVs) of the products and the fuel, Eq. (5) [6]:

$$\eta = 100\% \times \frac{\text{LHV (products)}}{\text{LHV (fuel)}} \quad (5)$$

One can easily see that this amounts to the same value as the efficiency of an OSR reactor measured on the basis of Eq. (3), where LHV of 2.8 mol of H<sub>2</sub> equal to LHV of 1 mol of methanol vapor. On the other hand, for an overall reforming process, where liquid fuel and water are used, Eq. (5) predicts lower efficiency than Eq. (4). This is due to the fact that LHV of fuel assumes steam as the combustion product and, therefore, does not account for water vaporization, as does Eq. (4). Because of this discrepancy maximum achievable thermal efficiency of the thermally neutral reforming process (4) calculated by definition (5) is only 90.7%.

The analysis presented above corresponds to an ideal, lumped reforming process in which H<sub>2</sub> and CO<sub>2</sub> are the only products. However, in an actual OSR process CO will be formed in addition to CO<sub>2</sub>. Also methanol, oxygen and water may not be fully consumed in the reactor, and methane

and other components may form as by-products. To estimate achievable conversion levels and hydrogen yields for an oxidative steam reforming reactor, a thermodynamic analysis was performed using standard STANJAN software [7]. This software allows calculating the thermodynamic equilibrium conditions (temperature, pressure and equilibrium mixture composition) for mixtures with given initial parameters. The results of these calculations are presented in Fig. 1. Mixtures of methanol, steam and air at 227 °C with a constant methanol-to-steam ratio of 1:1 and varying amounts of air were used as the initial mixture (representing the compositions/concentrations of the inlet stream). Calculations were performed under constant enthalpy and pressure constraints, simulating an adiabatic reactor. CH<sub>3</sub>OH, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub> and H<sub>2</sub> were allowed as the reaction products.

The results of thermodynamic analysis suggest that the process becomes exothermic at O<sub>2</sub>-to-methanol ratios above 0.12. Under all conditions shown in the plot, conversion of methanol and oxygen at equilibrium was above 99.9%. With more air added to the mixture the equilibrium temperature rapidly increases leading to a decrease in hydrogen yield and an increase in the amount of unwanted CO in the product mixture. This suggests that the process has to be operated at the lowest possible amount of air in the mixture.

Fig. 1 shows that with small amounts of air added to the fuel, hydrogen concentration in the product stream can be as high as 60%. The relatively low air addition required in oxidative reforming of methanol allows higher efficiency and smaller size and weight of the cell stack, or if a membrane is used to separate hydrogen, it allows for a smaller membrane size and lower pressure drop. This is an advantage of methanol reforming over hydrocarbon reforming, where higher oxygen to carbon ratios are required in order to achieve conversion of the fuel, which leads to lower hydrogen concentration in the reformate.

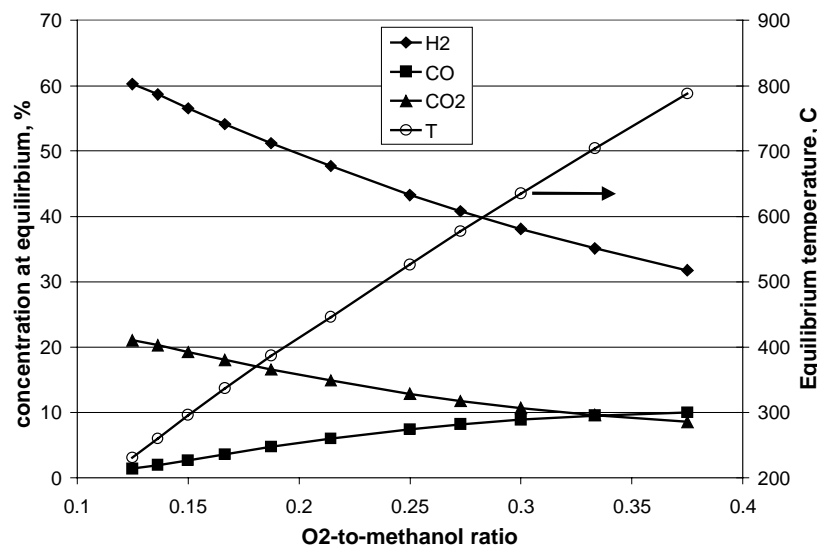


Fig. 1. Temperature and composition of the equilibrium mixture for oxidative steam reforming of methanol as a function of added air. Methanol-to-steam molar ratio equals 1:1. Inlet temperature = 227 °C, pressure = 1 atm.

Another advantage of the methanol reforming is the ability to produce reformat with low concentrations of CO. Fig. 1 shows that CO concentration is small at low O<sub>2</sub>-to-methanol ratios. Under thermally neutral conditions (O<sub>2</sub>-to-methanol equal to 0.12) CO concentration at equilibrium can be as low as 1.4%. Increasing the amount of steam in the mixture above 1:1 used in our calculations can lead to further decrease in CO concentration. However, additional steam, which is not converted in the reforming reactions, would further dilute the gas mixture. Furthermore, additional heat would be required to vaporize the unutilized water, which would lead to irreversible heat losses and decrease the overall system efficiency. Therefore, increasing the amount of steam input far beyond that required by the process stoichiometry may not be desirable. Lower CO concentrations can also be achieved if the reaction can be carried out at lower inlet temperatures.

Thermodynamic analysis of the OSR process suggests that operating at a low inlet temperature and low oxygen-to-methanol ratio would allow complete conversion of methanol to hydrogen with high concentration of hydrogen and low concentration of CO in the product stream. This concept was experimentally tested to study how the space velocity or contact time, and transport properties of the reactor affect the ability of the OSR process to reach the thermodynamically predicted equilibrium state.

## 2. Experimental

The catalysts used in these experiments were based on series of discrete, ultra-short-channel length metallic monoliths substrates (trademarked by Precision Combustion, Inc., as Microlith<sup>®</sup>) coated with high surface area ceramic washcoats and precious metal-based active component. Such designs dramatically increase the heat and mass transfer coefficients in the catalytic reactor, greatly enhancing the rates of mass transfer limited catalytic combustion and partial oxidation reactions. A detailed description of the properties of the Microlith-based catalytic systems can be found elsewhere [8,9].

In this work testing of the OSR process was performed using two different types of Microlith-based reactors. The

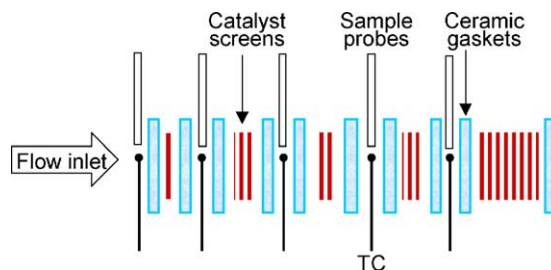


Fig. 2. Schematic diagram of the short contact time linear flow Microlith reactor used to test feasibility of OSR approach to methanol reforming into hydrogen. Ceramic gaskets were placed to hold instrumentation between the screens.

first type was a 6 mm long linear flow cylindrical reactor with a diameter equal to 4.1 cm (cross-sectional area  $A = 13 \text{ cm}^2$ ), as shown in a diagram in Fig. 2. The reactor volume was  $\sim 8 \text{ cm}^3$ . Gas sample probes and thermocouples were inserted between the catalytic screens along the axis of the reactor as shown in the diagram. Note that reactor length and volume do not include additional space required for instrumentation. More probes were installed at the front end of the reactor where higher temperature and composition gradients were expected. This reactor was tested at a methanol feed rate of 16 g/min, oxygen-to-methanol ratio between 0.05 and 0.4 and water-to-methanol ratio between 0 and 2. These test conditions correspond to a thermal load of about  $5.6 \text{ kW}_t$  (power density  $\sim 700 \text{ kW}_t/\text{l}$ ), space velocity of about  $400,000 \text{ h}^{-1}$ , or a contact time of about 3.5 ms. In all tests reported in this paper water and methanol were premixed as liquids in the required molar ratio and the solution was then vaporized in an electrically heated stainless steel coil, mixed with air and fed into the reactor.

Subsequently, a larger reactor was made of a Microlith screen wound in a cylindrical coil through which gas was passed in a radial direction from the inside out. A picture and a diagram of the radial flow reactor used in the tests and a diagram showing the gas flow direction and approximate positions of the thermocouples and the sampling probes inside the coil are shown in Fig. 3. The catalyst coil was 5 cm long with 5 cm OD, which corresponds to a volume of about  $100 \text{ cm}^3$ . Diameter of the inlet section of the radial flow

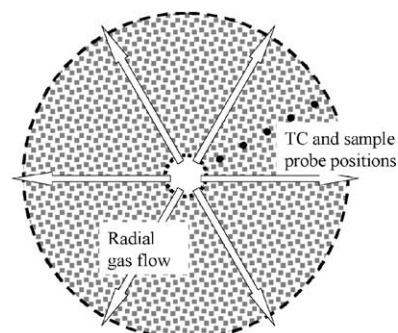


Fig. 3. Radial flow Microlith reactor for oxidative steam reforming of methanol.

reactor was 0.35 cm, such that the effective cross-sectional area of the catalyst bed increased from 5.5 to 79 cm<sup>2</sup> along the gas flow lines. The Microlith coil was held between two flanges with ceramic paste placed on the edges of the coil to ensure a good seal and eliminate bypass flow of the reformate mixture. The inlet mixture containing methanol, oxygen and steam was introduced through a narrow tube into the central part of the coil and the exit gas was collected into a plenum around the catalyst coil. This reactor was tested under the same range of methanol, water and air feed rates as the linear flow reactor. Because of larger reactor volume the space velocity decreased to  $\sim 30,000 \text{ h}^{-1}$ .

Both linear and radial flow Microlith reactors were tested under autothermal conditions, i.e. no external heat was provided to the catalyst. Pre-vaporized methanol and steam mixture was added to the pre-heated air stream and fed into the catalytic reactor. The temperature of the inlet mixture was between 100 and 200 °C. The catalyst bed temperature increased from the inlet temperature to the operating temperature as soon as methanol and steam were added to the air flowing through the reactor. Such rapid temperature rise is characteristic of “light off” in the catalytic combustion reactions. Following the initial “light off” the catalyst temperature remained steady and only depended on the composition of the inlet gas mixture.

Gas sampling probes were installed throughout the catalyst bed and at the reactor exit. Gas samples were passed through a chiller to remove water and any unconverted methanol. Composition of the gas samples was further analyzed by a gas chromatograph for H<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> content. Knowing the amount of air added to the mixture at the reactor inlet and assuming that nitrogen remains inert at the reactor temperature, nitrogen was used as an internal standard to convert percentages of each component in the gas sample into the molar flow units. Methanol conversion was then determined as a ratio of the sum of CO,

CO<sub>2</sub> and CH<sub>4</sub> to the molar methanol input to the reactor as determined by the liquid pump rate. Efficiency of the process was determined as the molar amount of H<sub>2</sub> and CO produced in the reactor per mole of inlet methanol divided by 2.8, which is the maximum amount determined by Eq. (3). Note that this definition implies 100% conversion of CO into hydrogen in a downstream WGS reactor.

### 3. Experimental results

#### 3.1. Linear flow catalyst results

Fig. 4 shows the temperature and the species concentration profiles along the linear flow reactor. Methanol feed rate in this test was 16 g/min, steam-to-methanol ratio of 2:1, oxygen-to-methanol of 0.29 (all molar ratios), inlet temperature of  $\sim 100 \text{ °C}$  (just sufficient to vaporize the methanol/water mixture). The data shows that all oxygen present in the inlet mixture is consumed on the very front of the catalyst bed. This leads to rapid oxidation of methanol, high heat release, rapid temperature rise and to a very high rate of H<sub>2</sub> and CO production at the inlet section of the catalyst bed. Temperature reaches the highest value at the 1 mm position and slowly decreases after that. At the point where all the oxygen is consumed, which is less than 2 mm into the catalyst bed (which corresponds to a space velocity of about 1 million h<sup>-1</sup> and to a residence time of 1 ms) H<sub>2</sub> concentration in the mixture is already 42%, while CO concentration is 20% and CO<sub>2</sub> concentration is 7%. Note that at the first sample probe position (0.2 mm) CO<sub>2</sub> is predominantly formed in the reaction, while after 1 mm into the reactor there is more CO than CO<sub>2</sub>. After all the oxygen is consumed H<sub>2</sub> concentration further increases at a much slower rate, while CO and CO<sub>2</sub> concentrations remain almost constant. At the reactor exit near-complete

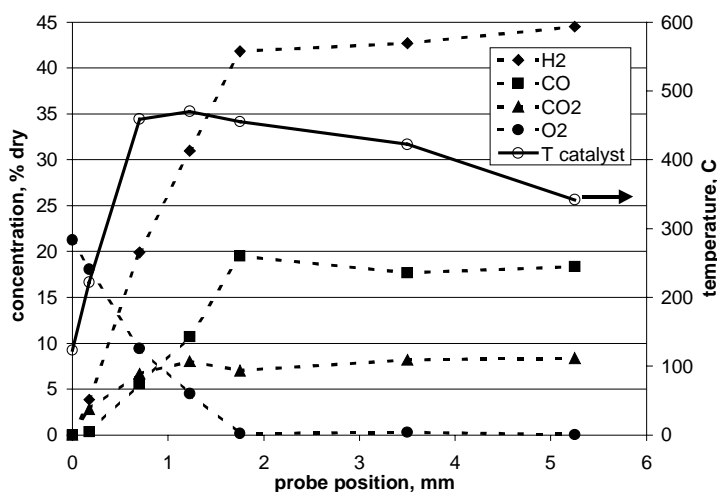


Fig. 4. Temperature and gas species profile along the linear flow Microlith microreformer. CH<sub>3</sub>OH feed rate – 16 g/min;  $T \sim 100 \text{ °C}$ ; H<sub>2</sub>O-to-CH<sub>3</sub>OH = 2:1; O<sub>2</sub>-to-CH<sub>3</sub>OH = 0.29 molar ratios.

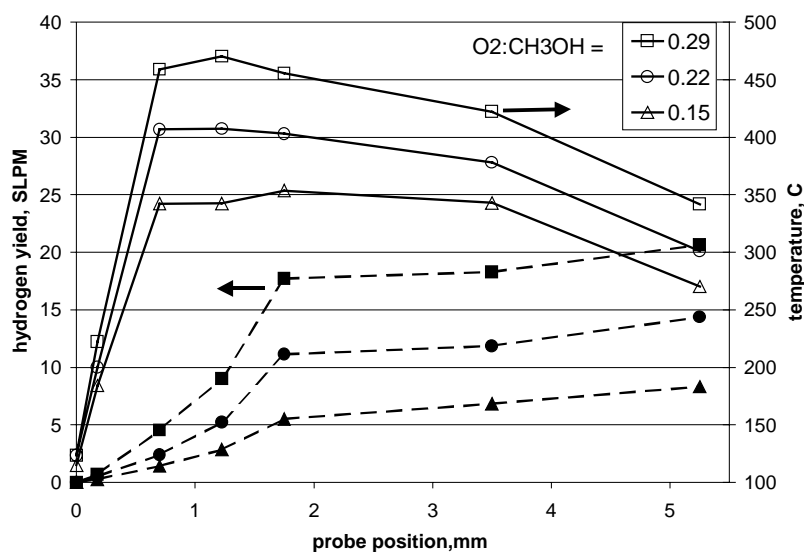


Fig. 5. Temperature and hydrogen production profiles along the OSR reactor. Steam to methanol molar ratio is 2:1. Oxygen to methanol molar ratio was varied between 0.15 and 0.29.

conversion of methanol was achieved with H<sub>2</sub> and CO concentrations in the reformat stream at 45 and 20%, respectively.

Thermodynamic analysis of the process suggested that operating the OSR reactor at lower oxygen to methanol ratio is desirable. Therefore, experiments similar to that shown in Fig. 4 were repeated with different amounts of air added to the mixture at a constant methanol/water feed rate. Fig. 5 shows the hydrogen yield and temperature profiles along the linear flow OSR reactor at varied O<sub>2</sub> to CH<sub>3</sub>OH ratios. The data show that increasing the amount of oxygen significantly raises both the catalyst temperature and the hydrogen production rates. Note that in spite of the difference in the magnitude, the temperature and the hydrogen yield profiles are similar. Under all tested conditions the maximum temperature is reached at about 1 mm into the catalyst bed. The complete consumption of oxygen occurs at a point about 1.8 mm into the catalyst bed and is followed by the pronounced decrease in the rate of hydrogen production. Hydrogen yield increases near linearly from 7.7 to 21 SLPM (130–340 cm<sup>3</sup>/s) with increasing O<sub>2</sub> to CH<sub>3</sub>OH ratio, which corresponds to a linear increase in methanol conversion. Concentration of the species in the reformat (on a dry basis), though, remains nearly constant under these conditions. Table 1 summarizes the data obtained in these tests.

### 3.2. Effect of catalyst formulation

Literature data suggest that in steam reforming of methanol Pd supported on ZnO can provide high activity for hydrogen production combined with very low CO yield [2]. In the initial tests we investigated application of a similar catalytic system for the OSR process. Two catalyst samples

were prepared by sequential and co-impregnation of alumina washcoat with Zn and Pd precursors followed by calcination in air at high temperature to convert precursors into the oxides and then by hydrogen reduction to reduce PdO to the metal state. Performance of these catalysts was tested in the linear flow Microlith reactor under conditions similar to that described above. Water-to-methanol ratio was 2:1 and the oxygen-to-methanol ratio was varied between 0.05 and 0.3. It was found that at low O<sub>2</sub>:CH<sub>3</sub>OH ratios the catalyst did not light off at inlet temperature up to 150 °C (catalyst temperature remained below the inlet gas temperature), reaction rate was very slow (methanol conversion of only few percent was measured) and only CO<sub>2</sub> and H<sub>2</sub>O were the reaction products. As the amount of air was increased, the reactor lit off, at which point the surface temperature jumped to about 350 °C. This led to a significant increase in the reaction rate and methanol conversion, but also led to the production of a large amount of CO. Yield of CO was about equal to that of H<sub>2</sub> under these conditions. Therefore, it was concluded that in the OSR process Pd supported on ZnO does not support the selective reforming of methanol with low CO yield as it does in steam reforming.

Fig. 6 shows the results of comparative testing of Pt, Rh and Pd catalysts for the OSR process. For all samples the

Table 1  
Effect of increasing oxygen-to-methanol ratio on methanol reformer performance

O <sub>2</sub> :CH <sub>3</sub> OH (molar)	Peak T (°C)	H <sub>2</sub> yield (cm <sup>3</sup> /s)	Conversion (%)	CO (%)
0.15	350	140	40	13.7
0.22	407	240	70	17.3
0.29	470	340	100	18.4

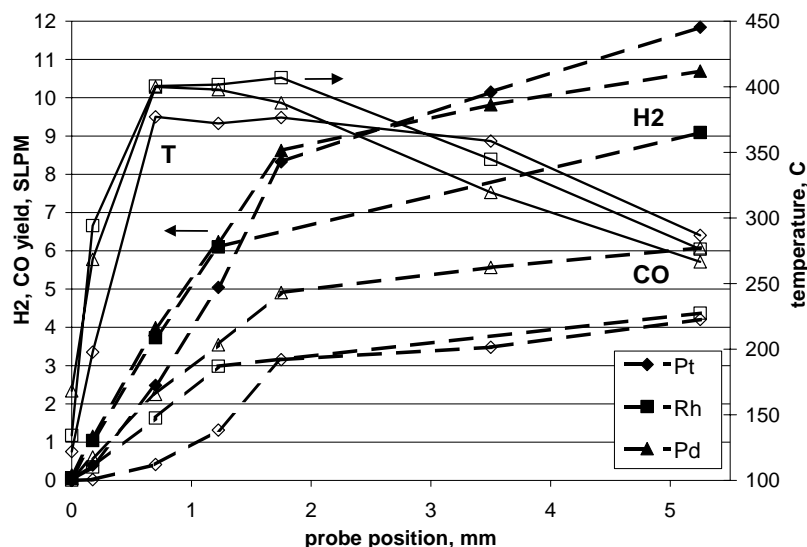


Fig. 6. Temperature profiles and hydrogen and CO yield from the linear flow reactor for Pt, Rh and Pd catalysts supported on stabilized alumina.  $\text{CH}_3\text{OH}$  feed rate – 16 g/min;  $T \sim 100^\circ\text{C}$ ;  $\text{H}_2\text{O}$ -to- $\text{CH}_3\text{OH} = 2:1$ ;  $\text{O}_2$ -to  $\text{CH}_3\text{OH} = 0.22$ .

metal was supported on stabilized alumina washcoat with a BET surface area of about  $130\text{ m}^2/\text{g}$  providing metal dispersion of about 40%. The catalysts were tested in the linear flow reactor configuration at water-to-methanol ratio of 2:1 and oxygen-to-methanol ratio between 0.17 and 0.33. The data for the case of  $\text{O}_2:\text{CH}_3\text{OH} = 0.22$  is shown in Fig. 6, which is representative of the relative catalyst behavior under other tested conditions. These data suggest that all precious metal catalysts demonstrate similar behavior in the methanol-reforming process. For all tested catalysts high selectivity to  $\text{CO}_2$  could be achieved only at very low catalyst temperatures where methanol conversion and hydrogen production rates were prohibitively low. When the OSR process was performed at temperatures between 300 and  $500^\circ\text{C}$ , conditions where high yield of hydrogen could be achieved, CO was also produced, such that the  $\text{H}_2$  to CO ratio was near 2. This suggests that for all tested catalysts the process goes through the water-gas shift mechanism.

The results obtained for the OSR of methanol over linear flow reactors show that, while very high hydrogen yield can be achieved in a very small volume, this always coincides with a proportionally high CO yield. This is in contradiction with the thermodynamic analysis above, suggesting that the space velocity in these experiments was too high for the mixture to reach the equilibrium state. Therefore, a larger radial flow reactor was designed, allowing more than a ten-fold increase in the overall residence time under the same experimental conditions. Furthermore, by passing the inlet stream through the small cross-sectional area of the internal section of the radial flow reactor same high gas flow velocity can be preserved in the front of the coiled catalyst bed, as that in the linear flow reactor. This allows preserving the reaction behavior observed in the linear flow experiments, as discussed below.

### 3.3. Radial flow reactor performance results

Fig. 7 shows the temperature and species concentration profiles along the radial flow Microlith reactor. Platinum supported on high surface area alumina washcoat was used as a catalyst in this test. Catalyst loading and operating conditions in this test were similar to those used in the test shown in Fig. 4. The methanol feed rate was 16 g/min (equivalent to a thermal input of about 5.6 kW or power density of  $56\text{ kW}_t/\text{l}$ ). Methanol was mixed with water in a 1:2 molar ratio in the fuel tank.

The first vertical broken line in Fig. 7 ( $r = 1.7\text{ mm}$ ) shows the radial position of the inlet of the catalyst relative to the central axis of the coil ( $r = 0$ ). The second vertical broken line shows the position within the radial flow reactor where the space velocity is equal to that at the exit of the linear flow reactor. No data was available from the first few millimeters of the radial flow catalyst bed because unlike the linear flow reactor, the first TC and gas sample probe could only be installed at the 3 mm position. Data in Fig. 7 suggests that as expected the behavior of the OSR process at the front of the radial flow reactor was similar to that observed for the linear flow reactor. It was found that oxygen was completely consumed by the second sample probe at 7 mm radial position (though comparison with data in Fig. 4 suggests that oxygen is actually consumed before this point). Rapid consumption of oxygen was again accompanied by fast rate of methanol conversion and a very high rate of hydrogen and CO production. Hydrogen concentration exceeded 40% and CO concentration approached 20% by the time all the oxygen was consumed. Similar to the linear flow reactor the catalyst temperature rapidly increased from the inlet temperature of  $200\text{--}450^\circ\text{C}$  on the very front of the catalyst bed (even before the first TC position).

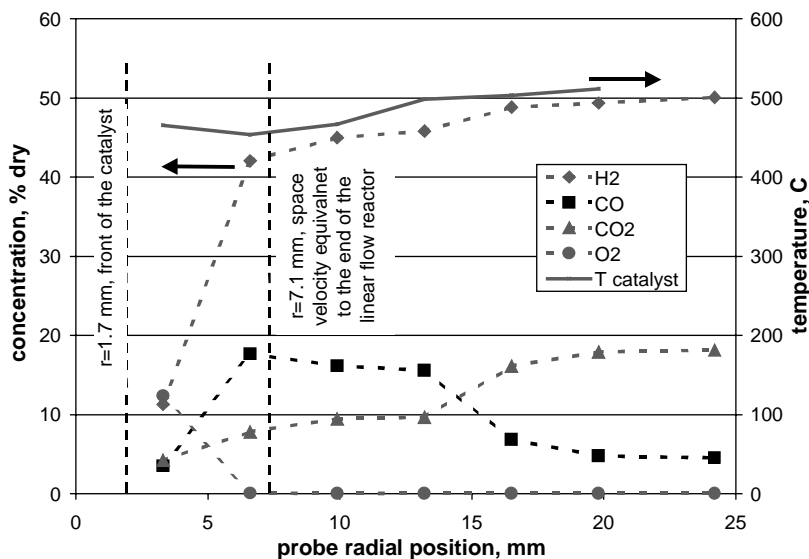


Fig. 7. Temperature and species concentration profiles along the radial flow Microlith reactor in OSR of methanol. CH<sub>3</sub>OH feed rate – 16 g/min;  $T \sim 200$  °C; H<sub>2</sub>O-to-CH<sub>3</sub>OH = 2:1; O<sub>2</sub>-to-CH<sub>3</sub>OH = 0.27.

The reaction behavior at the downstream part of the radial flow catalyst bed suggests that increased contact time led to continuation of the reactions within the catalytic bed. The temperature profile across the bed remained flat and the temperature even increased slightly towards the exit of the reactor. Hydrogen concentration increased steadily throughout the reactor and reached 50% at the reactor exit. At the flow conditions used in this experiment this concentration corresponded to a hydrogen production rate of 450 cm<sup>3</sup>/s, or about 4.5 kW<sub>t</sub>. Comparing the hydrogen yield observed in this test with that for the ideal reactor given by Eq. (3) above (2 standard liter H<sub>2</sub> per gram of CH<sub>3</sub>OH) we obtained an efficiency of the reformer of about 81%. (This is assuming no further conversion of CO into H<sub>2</sub> in a low-temperature water gas shift reactor.)

The most prominent deviation from the linear flow reactor performance appeared in the CO and CO<sub>2</sub> profiles. In the entry region of the catalyst bed CO and CO<sub>2</sub> profiles were similar to that in the flat catalyst bed, i.e. CO<sub>2</sub> is formed at a higher rate along the first few millimeters of the catalyst bed, while CO production rate increases and becomes faster than that for CO<sub>2</sub> after the 3 mm sample port. Both the CO and CO<sub>2</sub> concentrations remain near constant between 7 and 13 mm sample probes along the radial direction of the bed, but then CO concentration rapidly drops, while the CO<sub>2</sub> concentration increases. Carbon monoxide concentration at the exit of the radial flow Microlith reactor in this test was only 4.5%, while CO<sub>2</sub> concentration was 18%. Thermodynamic equilibrium composition under the conditions of this experiment at the reactor exit temperature  $T = 510$  °C predicts

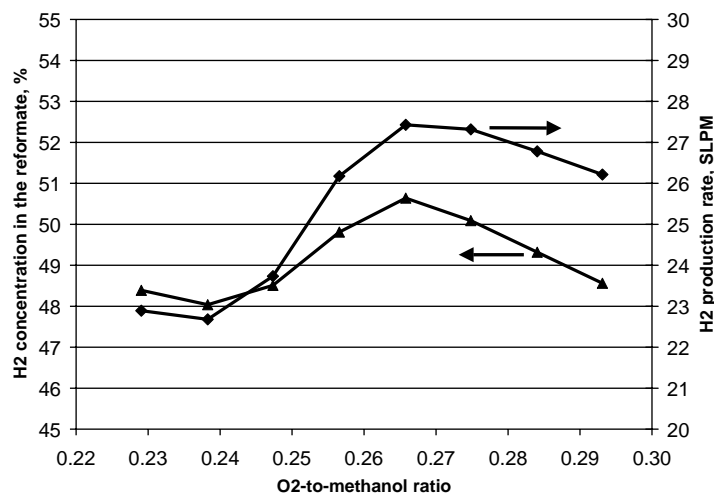


Fig. 8. Hydrogen production rate and concentration in the product mixture in the radial flow Microlith reactor for OSR of methanol. CH<sub>3</sub>OH feed rate – 16 g/min; H<sub>2</sub>O-to-CH<sub>3</sub>OH = 2:1.

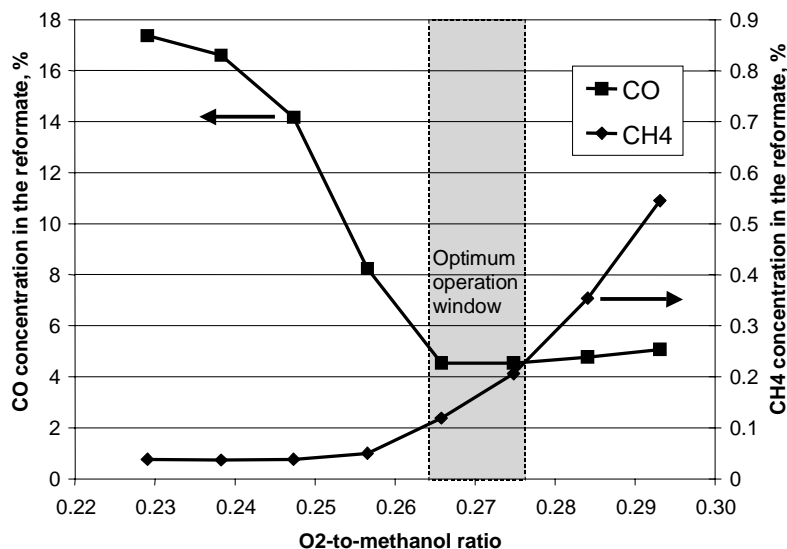


Fig. 9. CO and CH<sub>4</sub> concentration in the product mixture in radial flow Microlith reactor for OSR of methanol. CH<sub>3</sub>OH feed rate – 16 g/min; H<sub>2</sub>O:C = 2:1.

CO concentration (on the dry basis, same as that measured by the GC) of 4.6%, and is in good agreement with the experimental value. This suggests that for a larger radial flow reactor the reacting mixture reaches equilibrium.

In the next test the dependence of the radial flow reactor performance on O<sub>2</sub>:CH<sub>3</sub>OH ratio by increasing the amount of air flow added to the inlet mixture at a constant flow of the methanol/water mixture was studied. Fig. 8 shows hydrogen concentration in the exit gas (on a dry basis) and the rate of hydrogen production as a function of O<sub>2</sub>:CH<sub>3</sub>OH ratio. Fig. 9 shows corresponding CO and CH<sub>4</sub> concentrations in the exit gas. It was found that with low amounts of air, hence low catalyst temperatures, CO concentration, after the rapid increase on the front of the reactor did not decrease towards the back of the catalyst as was observed in the test shown in Fig. 7. At low O<sub>2</sub>:CH<sub>3</sub>OH ratios CO concentration profile remained nearly flat and the exit concentration was near 18%. As the amount of air was increased, leading to higher catalyst temperature, CO concentration in the exit gas decreased to a minimum value of 4.5% at O<sub>2</sub>:CH<sub>3</sub>OH molar ratio of 0.27 and started to increase gradually at higher O<sub>2</sub>:CH<sub>3</sub>OH values. This observation is contrary to the thermodynamic predictions, which suggested that lower CO concentrations should be observed at lower O<sub>2</sub>:CH<sub>3</sub>OH ratios and lower catalyst temperatures. This also suggests that below a critical value of O<sub>2</sub>:CH<sub>3</sub>OH of ~0.27 kinetic limitations of the reaction prevented attaining thermodynamic equilibrium. Methane formation was negligible at low O<sub>2</sub>:CH<sub>3</sub>OH ratios, but started to increase rapidly above O<sub>2</sub>:CH<sub>3</sub>OH = 0.26. However, concentration of methane observed even at O<sub>2</sub>:CH<sub>3</sub>OH = 0.29 was much lower than that allowed by thermodynamics suggesting that methane formation was limited by the kinetics of the reaction.

### 3.4. Varying space velocity

It was found that lowering the feed rate to the radial flow reactor resulted in lower CO concentration in the reformate stream. The test shown in Fig. 9 was repeated at a methanol flow rate of 8 and 1.6 g/min. An aqueous methanol solution with H<sub>2</sub>O:C = 2:1 was used in all tests. The airflow rate was varied for each fuel feed rate and the minimum CO concentration was determined. With decreasing feed rate the minimum in CO concentration decreased to 3.7% at 8 g/min and 1.2% at 1.6 g/min (Fig. 10). Therefore, by decreasing the space velocity by a factor of 10, the minimum CO concentration decreased by a factor of 4.

### 3.5. Long-term steady-state performance

Continuous performance of the radial flow reactor was tested for 50 h under the conditions of the previous test with

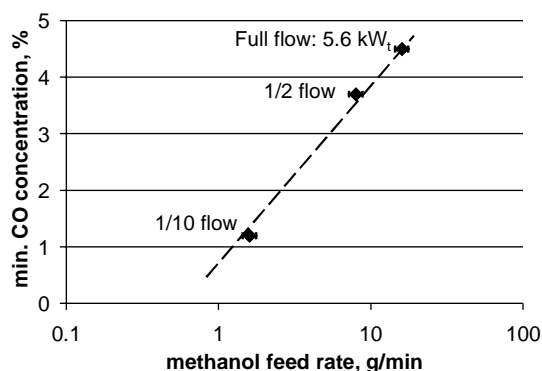


Fig. 10. Minimum CO concentration in the product mixture of the radial flow Microlith reactor achievable for different methanol feed rates. H<sub>2</sub>O-to-CH<sub>3</sub>OH = 2:1.

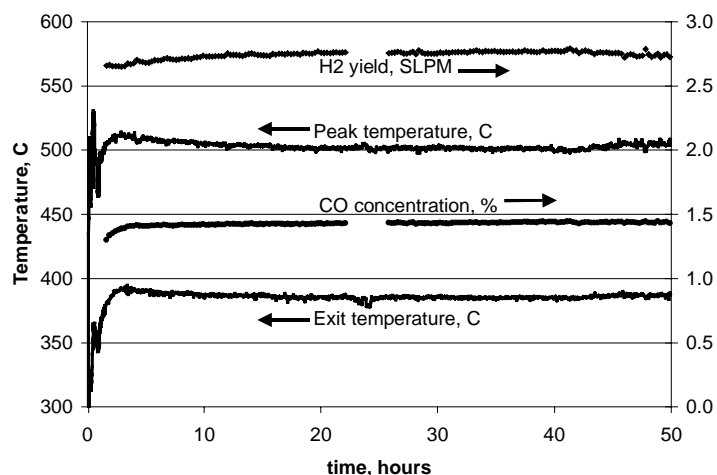


Fig. 11. 50-h durability test results.  $\text{CH}_3\text{OH}$  feed rate – 1.6 g/min;  $T \sim 100^\circ\text{C}$ ;  $\text{H}_2\text{O}$ -to- $\text{CH}_3\text{OH} = 2:1$ ;  $\text{O}_2$ -to- $\text{CH}_3\text{OH} = 0.30$ .

low methanol feed rate of 1.6 g/min – a point where low CO output in the mixture was detected. The results of this test are shown in Fig. 11. The inlet temperature was about  $100^\circ\text{C}$  to ensure pre-vaporization of the methanol/water mixture. Peak temperature in the bed and exit gas temperature were continuously recorded by a data acquisition system. Gas mixture composition at the exit of the reactor was sampled and analyzed by a gas chromatograph every 15 min and also recorded by the data acquisition system. The test showed that after the initial break-in period, during which the catalyst temperature and CO concentration increased slightly, the reactor performance remained steady. No deactivation of the catalyst was observed over 50 h.

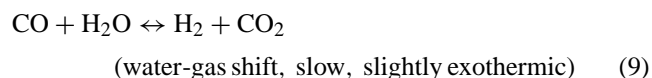
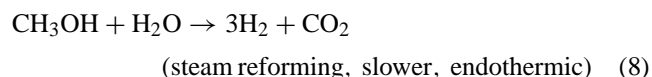
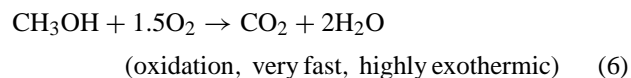
#### 4. Discussion

Extremely high rates of hydrogen production were observed in the oxidative steam reforming of methanol. In the linear flow reactor with a volume of only  $8\text{ cm}^3$ , a hydrogen yield of  $340\text{ cm}^3/\text{s}$  was achieved with complete conversion of methanol as shown in Fig. 4. This amounts to a power density equivalent of  $425\text{ kW}_t/\text{l}$ . The reformat from this reactor has high levels of CO. For the larger radial flow reactor a hydrogen yield of  $450\text{ cm}^3/\text{s}$  was demonstrated with lowered CO concentration in the reformat stream. This hydrogen yield amounts to power density of  $45\text{ kW}_t/\text{l}$ . At low fuel feed rate, where the CO concentration in the reformat stream decreased to 1.2% (a level at which further clean up could be achieved by a preferential CO oxidation reactor), hydrogen yield of  $46\text{ cm}^3/\text{s}$  was achieved, which corresponds to a power density of  $4.6\text{ kW}_t/\text{l}$ . These power densities are substantially larger than those obtained in the steam reforming of methanol, although a reformat with slightly lower CO concentration can be achieved through steam reforming. For example, de Wild and Verhaak [10] reported  $600\text{ l/h}$  ( $170\text{ cm}^3/\text{s}$ ) hydrogen yield from a coated heat exchanger-based steam-reforming reactor with a volume of

$\sim 460\text{ ml}$ . This amounts to a power density of  $3.7\text{ kW}_t/\text{l}$ . Concentration of CO in the product under the conditions of this experiment was 0.8%.

Apparently, the higher rate of hydrogen production in the OSR is due to the autothermal nature of this process. In the endothermic steam-reforming process heat is transferred across a heat-conducting boundary to support the reforming reaction between methanol and water. The rate of the process is usually limited by the rate of heat transfer across the boundary. Therefore, improvements to steam reforming are generally sought in designing reactors having low heat resistance and intimate contact between the reforming and the heating zones, such as microchannel technology. On the other hand, in the OSR process heat release is part of the overall reforming process, such that the heat transfer limitation is removed allowing for a many-fold increase in the reaction rate.

Species concentration and temperature profiles observed in our experiments suggest that the OSR process does not occur in a single reaction between methanol, steam and oxygen, as was assumed by the initial thermodynamic analysis. The actual process instead consists of several overlapping reaction steps with significantly different rates and heat release characteristics:



Reaction (6) is an oxidation reaction, which takes place on the front of the catalyst bed. High reaction rate and high heat release in this reaction lead to a rapid increase in the catalyst temperature observed in the experiments. The results of the short linear flow reactor testing shown in Fig. 4, where CO<sub>2</sub> was mostly detected as a product at the location of the first gas sample port, with very little amount of CO, suggest that complete oxidation products predominantly form in the beginning of the process. As temperature increases and oxygen is consumed along the catalyst bed the amount of partial oxidation products increases, suggesting an increasing rate of decomposition reaction (7). Note that in the case of methanol reforming partial oxidation can be viewed as a linear combination of complete oxidation (6) and decomposition (7) reactions.

The fast rate of methanol oxidation and decomposition reactions is accompanied by a rapid increase in CO concentration in the gas mixture. This suggests a standard WGS mechanism for the OSR process, unlike an alternative aldehyde mechanism proposed for the steam reforming of methanol over the Cu and Pd/ZnO catalysts [2]. In our experiments high rate of CO production was observed for all tested catalysts, including Pd/ZnO. Apparently, the aldehyde mechanism can only be achieved in steam reforming of methanol, where the process occurs at lower temperatures and at much lower rates than in the OSR. Our results show that in the OSR process, where complete conversion of methanol may be achieved at space velocity as high as 1 million h<sup>-1</sup>, methanol decomposition leads to a high rate of CO production and to CO being an intermediate step of the process.

The species composition profiles shown in Figs. 4 and 7 demonstrate that oxygen is consumed much faster than methanol. This is consistent with reaction (6) being much faster than the other steps of the OSR process (reactions (7)–(9)). Note that, in fact, the steam-reforming reaction (8) may be represented as a combination of methanol decomposition reaction (7) and water-gas shift reaction (9), and therefore, may not be considered as a separate reaction step. Only reactions (6), (7) and (9) can be considered in order to describe and model the OSR process.

After all the oxygen is consumed from the mixture, the OSR process continues through slower reactions ((7) and (9)). Both reactions lead to the production of hydrogen, while carbon monoxide is produced in reaction (7) and is consumed in reaction (9). These result in gradual increase in hydrogen concentration and near-constant CO concentration in the middle part of the reactor (Fig. 7). After methanol is consumed from the mixture, WGS reaction leads to a rapid decrease in CO concentration producing more H<sub>2</sub> and CO<sub>2</sub>. While the WGS step was not observed in the linear flow reactor experiments, it is clearly seen over the larger radial flow bed, where CO concentration rapidly decreases from 16 to 7% between the probes positioned at 13 and 17 mm and then gradually decreases to 4.5% at the exit from the

catalyst bed. Similar results were reported recently by Deluga et al. for oxidative reforming of ethanol into hydrogen [11]. It was found that for a linear flow catalytic reactor used in that work a two-stage design (partial oxidation stage followed by a 4.5 times larger WGS stage) was required to reach low CO output. Furthermore, stream temperature had to be adjusted between the stages. Our results and the results of [11] indicate that even at high temperatures at the front of the OSR reactor the rate of the WGS reaction is insufficient to reach equilibrium at the short contact time characteristic for a linear flow reactor.

There is a large mismatch between the rates of the reactions constituting the OSR process. While the oxidation reaction (6) usually occurs at space velocities of several millions per hour, the consecutive methanol decomposition (7), steam reforming (8) and WGS (9) reactions occur at space velocities on the order of 100,000 or even 10,000 h<sup>-1</sup>, i.e. 10–100 times slower. Carrying out all the reactions with such a large variation in the reaction rate over one catalyst bed sets a number of challenges. On the one hand, even at very high inlet flow rate the oxidation reaction is completed within a very short distance at the entrance to the catalyst bed, leading to temperature peaking at near 500 °C (Figs. 4 and 7). If the flow rate was to decrease to accommodate for the longer residence time required for decomposition and WGS reactions, all oxygen would be consumed on contact with the catalyst. More complete oxidation products (CO<sub>2</sub> and H<sub>2</sub>O) would form under these conditions, releasing more heat in a much smaller volume of the catalyst bed. This would create much larger temperature gradients and higher peak temperatures leading to higher heat loss from the front of the catalyst, the loss of process efficiency and higher rate of undesired methanation reaction. On the other hand, to complete the OSR process over a catalyst bed with a uniform cross-sectional area at the high flow rate needed by the selective oxidation reaction, would require an extremely long catalyst bed leading to high pressure drop.

A coiled cylindrical reactor with a radial flow pattern allows for effective combination of fast oxidation reactions on the front of the catalyst bed with slower reforming reactions at the back. For a radial flow reactor, linear flow velocity across the catalyst screens is very fast at the inlet section of the catalyst bed where oxidation reactions take place but decreases towards the reactor outlet where the slower decomposition and shift reactions occur. Therefore, long overall residence time can be combined with short contact time required by the oxidation reactions. Varying flow rate also allows for better thermal balance between exothermic oxidation and WGS reactions and endothermic decomposition reaction leading to a flat temperature profile along the reactor. Note that while for both flat and radial flow reactors the peak temperatures at the front were ~470 °C (Figs. 4 and 7), for the linear flow reactor this is followed by a rapid temperature decrease (Fig. 4), essentially shutting off the WGS reaction on the back of the reactor. On the contrary, for the

radial flow reactor, a nearly flat temperature profile along the catalyst bed was observed with a slight temperature rise towards the back, due to moderate heat release in the WGS reaction.

Thermodynamic equilibrium analysis of the OSR process shown in Fig. 1 suggests that CO concentration in the product mixture should decrease steadily as the oxygen to methanol ratio in the inlet mixture is decreased. The actual experimental data presented in Fig. 9, though, shows the opposite effect of decreasing CO concentration in the reformate mixture at increasing  $O_2:CH_3OH$  ratio (Fig. 9). This discrepancy can also be explained in terms of sequential reactions of the OSR process and kinetic limitation of WGS reaction. For the linear flow reactor the temperature rise on the front of the reactor was proportional to  $O_2:CH_3OH$  ratio (Fig. 5). Similar dependence was observed for the radial flow reactor, though, because the first TC was installed much further downstream, the exact temperature gradient on the front of the reactor could not be measured. Therefore, at low  $O_2:CH_3OH$  ratio the rate of the WGS reaction is too low to approach equilibrium even at the longer residence time provided by the radial flow reactor. In this case a sharp increase in CO concentration on the front of the catalyst bed caused by the oxidation and decomposition reactions is followed by an essentially flat CO profile, such that the CO concentration at the reactor exit remained at 18%. This is also consistent with the results reported in [11] where high process selectivity towards CO at low catalyst temperatures was observed even at longer residence times. As the  $O_2:CH_3OH$  ratio and the reactor temperature increase, the rate of the WGS reaction increases, such that the mixture composition can reach equilibrium while passing through the catalyst bed. Note that the decrease in CO concentration correlates with a sharp increase in  $H_2$  yield (Fig. 8), which is also consistent with a “light off” of a WGS reaction under these conditions. Further increases in  $O_2:CH_3OH$  ratio leads to a gradual increase in CO concentration which is due to WGS equilibrium favoring CO at higher temperatures.

It was also observed that when the catalyst temperature increased above  $450^\circ C$ , significant amounts of methane started to form in the mixture due to the methanation reactions between CO,  $CO_2$  and  $H_2$ . Unlike CO, which can be converted to hydrogen in a downstream low-temperature WGS reactor, methane, once formed, cannot be converted to hydrogen at the temperatures available anywhere in the methanol reformer and will pass through the system as an inert gas leading to lowering the overall efficiency. Methane formation, therefore, is highly undesirable. Optimum oxygen to methanol ratio for the reformer operation is at the point where CO has just reached the equilibrium value and methane production rate is still relatively low. Application of a more active WGS catalyst at the downstream region of the catalyst bed would allow reaching equilibrium at lower temperatures and, therefore, shift the operational window towards lower amounts of air. This would further decrease

the amount of methane produced in the reactor and increase the overall efficiency of the system.

Similar effects may be achieved by lowering the space velocity. Data in Fig. 10 show that by reducing the flow rate at the inlet to the radial flow reactor by a factor of 10, minimum CO concentration in the exit stream was lowered from 4.5 to 1.2%. Apparently this is due to a combination of longer residence time of the gas mixture in the catalytic reactor and a reduced  $O_2:CH_3OH$  ratio at which the reactor can be operated. This is an important finding because when CO concentration in the reformate is near 1% it can be further reduced to below 10 ppm (level tolerated by PEM fuel cells) in a preferential CO oxidation (PROX) reactor. This allows designing an integrated methanol-reforming system for PEM fuel cells without an additional WGS reactor, which translates into significant overall size and complexity reduction.

Steady operation of the radial flow reactor over 50 h suggests that no deactivation of the catalyst occurs under the reaction conditions of the OSR of methanol. A longer durability study was recently reported for a similar Microlith-based catalytic system applied to catalytic partial oxidation of natural gas [9]. In that work steady catalyst performance was observed for 500 h. While in OSR of methanol the peak catalyst temperature reached  $500^\circ C$ , catalyst temperatures in excess of  $1000^\circ C$  were observed in CPOX of methane. Long-term degradation of the catalyst performance in these processes would be primarily due to sintering and volatilization of the active metal phase and to sintering and spallation of the washcoat from the Microlith substrate. All these mechanisms would be accelerated at high operating temperatures and, therefore, longer durability should be expected in the low-temperature methanol reforming than in high-temperature partial oxidation of methane.

## 5. Summary

Oxidative steam reforming of methanol is shown to provide effective conversion of methanol into hydrogen at specific hydrogen production rates as high as  $425 kW_t/l$ . At lower yields hydrogen concentration above 50% (on a dry basis) can be achieved in the reformate stream, while CO concentration can be as low as 1.2%. The thermal efficiency of the OSR process was above 80%.

The OSR process is an overlapping sequence of three reactions – methanol oxidation, methanol decomposition and water-gas shift. A novel radial flow Microlith-based reactor configuration enables varying the gas flow velocity along the catalyst bed to accommodate for the difference in the kinetic rates and heat release of these reactions and provides essentially a flat temperature profile and near-equilibrium reformate composition in a single reactor.

The reactor temperature and performance is primarily determined by the oxygen to methanol ratio in the inlet mix-

ture. There is an optimum O<sub>2</sub>:CH<sub>3</sub>OH ratio at which the WGS thermodynamic equilibrium can be reached while, the methane production rate over the catalyst is low.

No apparent sign of reactor performance degradation was observed in over 50 h of testing.

### Acknowledgements

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