FEASIBILITY ANALYSIS OF METHANOL FUELLED
SOFC SYSTEMS FOR REMOTE DISTRIBUTED
POWER APPLICATIONS

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ABSTRACT

This paper analyzes the feasibility of converting a 5 kW natural gas SOFC
power generator system designed to operate on natural gas to be fuelled by
methanol. The analysis included laboratory methanol fuel processing
experimentation, methanol reformate SOFC cell testing, and SOFC system
mass and energy balance modelling. Methanol fuel processing
experimentation indicated that theoretical reformate compositions can be
achieved for high temperature (600-900°C) methanol steam reforming. A
6% open circuit voltage decrease and a 10% peak power current density
decrease between cell operation on humidified hydrogen and methanol
reformate was observed. SOFC system mass and energy balance
modelling indicated that a natural gas SOFC system can be converted to
operate on methanol fuel with minimal (1%) efficiency impact; however,
the systems’ thermal integration can be impacted.

INTRODUCTION

Fuel flexibility is a critical facet, and benefit, of solid oxide fuel cell technology. For
distributed power generation solid oxide fuel cell (SOFC) applications not located on the
natural gas grid, there is a requirement for an alternative fuel that can be easily
transported and stored to feed the SOFC system. Methanol is the ideal alternative fuel for
this remote SOFC distributed power generation market for the following reasons: (a)
methanol is readily available in liquid form, and therefore can be easily transported and
stored via current infrastructure; (b) methanol has negligible sulphur content, and
therefore the desulphurization component necessary for other hydrocarbon fuels can be
removed from the SOFC system; and (c) methanol, like natural gas, is a single carbon
hydrocarbon fuel, and can be considered a clean fuel alternative to gasoline and diesel.

Methanol fuel processing has been demonstrated in a variety of fuel cell applications
(1,2). However, research and development is needed to fully understand the operating
envelope differences between methanol and natural gas fuelling as well as the overall
impact of the changes on the SOFC generator system. This paper will analyze the
feasibility of converting a 5 kW natural gas SOFC power generator system to be fuelled by methanol. The analysis included laboratory methanol fuel processing experimentation, methanol reformate SOFC cell testing, and SOFC system mass and energy balance modeling in AspenTech HYSYS software.

The objective of the methanol fuel processing experimental research was to determine the lowest practical steam-to-carbon ratio to operate a methanol reformer at. Steam-to-carbon ratio, defined as n:m from the following reaction (3-10): \( m\text{CH}_3\text{OH} + n\text{H}_2\text{O} \rightarrow x\text{H}_2 + y\text{CO} + z\text{CO}_2 + w\text{H}_2\text{O} \), determines the volume of water required for addition to the methanol fuel stream. The ideal condition for methanol fuel processing for use in solid oxide fuel cell operation is a steam-to-carbon ratio of 0:1, zero water addition, which would yield the following reaction: \( 1\text{ CH}_3\text{OH} + 0\text{ H}_2\text{O} \rightarrow 2\text{ H}_2 + 1\text{ CO} \). However, practical operation at this steam-to-carbon value would lead to coke (carbon) formation in the reformer, as steam is also a strong coke formation inhibitor. Furthermore, much research was done into the temperature of reforming the methanol fuel. As natural gas is reformed at temperatures in the 600-900°C range, the ideal methanol fuel processor could function over the same catalyst at similar temperatures so that the possibility of a fuel-flexible, methanol/natural gas operation could be achieved.

The objective of the SOFC cell testing was to determine the practical operating variance in performance of operating a SOFC cell on methanol reformate versus standard humidified hydrogen. Research was performed to determine the open circuit voltage (OCV) and polarization curve (IV curve) effects. The SOFC cells that were under test were planar Ni-YSZ anode supported, YSZ electrolyte, and LSM cathode cells from IndEC® in Holland. The SOFC cell testing was performed at 750°C. The composition of the reformate at the fuel cell inlet and outlet was monitored as a function of time by the use of a gas chromatograph. Carbon deposition was based on visual analysis.

**EXPERIMENTAL**

**Methanol Fuel Processing**

MeOH reforming/decomposition catalyzed by a Ni-based industrial catalyst (Haldor Topsoe R-67R-7H, 12-15% NiO, 25-30% MgO, 60-65% Al₂O₃) was investigated in the 600-900°C temperature range at different S/C (steam-to-carbon) ratios. Figure 1 below is a schematic of the experimental apparatus used for research on methanol fuel processing.

![Figure 1. Schematic representation of the methanol reformer test apparatus.](image)
Methanol Reformate SOFC Cell Testing

The following is a brief discussion of the relationship between methanol and how it can be used as a fuel for solid oxide fuel cells. The medium to high operating temperatures of the solid oxide fuel cell allows carbon monoxide, as well as hydrogen, to be used as anode fuel reactants. The fuel cell reactions for a SOFC are as follows:

\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \]  
Carbon monoxide Fuel Cell Reaction

\[ 2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O} \]  
Hydrogen Fuel Cell Reaction

Because the products of reaction for methanol and natural gas are not equivalent in yield rates, a methanol-fuelled system may need to be operated at a different pressure than a natural gas system to achieve a constant power output. The effect of operational changes on fuel cell performance will be assessed based on open circuit voltage (OCV) and polarization (IV) curves. Figure 2 below is a schematic of the experimental apparatus used for research of methanol reformate SOFC cell testing.

Figure 2. Schematic diagram of the methanol solid oxide fuel cell test apparatus.

Steady State SOFC System Modelling

The objective of the steady state systems modelling was to determine the holistic impacts of a complete solid oxide fuel cell system operating on methanol fuel versus natural gas. Research was completed utilizing Aspentech HYSYS® software to model the various heat exchanger, reformer, SOFC stack, and balance of plant components that make up a 5 kW SOFC system. HYSYS® is used to accurately model the mass and energy balance of
a complete chemical process. Figure 3 below shows a picture of the computer model programmed in HYSYS® to research the operating envelope differences between a methanol system and a natural gas system. Figures 4, 5, and 6 are the HYSYS® models for the heat exchanger, reformer, and SOFC stack sub-systems respectively.

![Figure 3. Aspentech HYSYS® model of a 5 kW SOFC system.](image)

![Figure 4. Heat exchanger sub-system of the 5 kW SOFC system model.](image)
RESULTS AND DISCUSSION

Methanol Fuel Processing

The aim of this initial study was to determine the lowest possible S/C at which to successfully convert MeOH (methanol) into the desired H2- and CO-rich gaseous mixture without incurring in C-deposition problems, caused by a series of possible parasitic processes (eqs. 1-3) that could in turn lead to catalyst deactivation.
2 CO $\rightarrow$ C + CO$_2$ \hspace{1cm} (1) Boudouard reaction

CO + H$_2$ $\rightarrow$ C + H$_2$O \hspace{1cm} (2)

CH$_4$ $\rightarrow$ C + 2 H$_2$ \hspace{1cm} (3)

Prevention of coking can be achieved by the addition of controlled amounts of H$_2$O to the MeOH feed and the consequent water gas-shift (WGS) and gasification reactions (eqs. 4, 5).

CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$ \hspace{1cm} (4)

C + H$_2$O $\rightarrow$ CO + H$_2$ \hspace{1cm} (5)

While the Boudouard reaction is thermodynamically unfavourable at higher temperatures (3-10) ($K_{eq} \sim 0$ at $T > 800^\circ$C), CH$_4$ decomposition (eq. 3) is likely the major reaction pathway leading to the observed C-deposition, as also indicated by the disappearance of the GC (gas chromatograph) signal corresponding to CH$_4$ at $T > 800^\circ$C (detected, although as a minor product, in the 600-800°C range). The low selectivity of the MeOH reforming/decomposition toward the production of CH$_4$, on the other hand, may account for the relatively limited C-deposition observed after the tests at $T > 800^\circ$C.

Figures 7-11 compare the theoretical dry ((H$_2$O content normalized out) equilibrium conversion values with that of the experimental results at steam-to-carbon ratios of 1:1, 0.75:1, 0.5:1, 0.25:1, and 0:1, respectively. For 1:1, 0.75:1, and 0.5:1 molar steam-to-carbon ratios, good overlap between theoretical and experimental gas compositions was achieved, and therefore it can be concluded that at a steam-to-carbon ratio of 1:1 and a space velocity less than 1,500 hr$^{-1}$ nearly equilibrium conversions can be achieved. No carbon was qualitatively detected under these test conditions. For the 0.25:1 molar steam-to-carbon ratios, good overlap between theoretical and experimental gas compositions was achieved; however, carbon was qualitatively detected under these test conditions. At 0:0 molar steam to carbon ratio, carbon was qualitatively detected under these test conditions. Coke formation posed too much risk for our test apparatus, so the tests were halted after 600°C. Until coke inhibiting methanol thermal decomposition catalyst is developed, it is not advisable to operate under these conditions. The catalyst utilized in these experiments was a standard methane steam reforming nickel-based catalyst from Haldor-Topsoe. The catalyst was pre-treated with 5%H$_2$/N$_2$ at 250°C for a period of two hours prior to all testing.

\[ \text{Figure 7. Theoretical to experimental dry equilibrium composition comparison for} \]
\[ S/C = 1 \text{ mol/mol at 0.058 mL/min (liq.) and N}_2 \text{ at 13 mL/min (GHSV } \sim 875 \text{ hr}^{-1}). \]
Figure 8. Theoretical to experimental dry equilibrium composition comparison for 
S/C = 0.75 mol/mol at 0.045 mL/min (liq.) and N₂ at 13 mL/min (GHSV~1660 h⁻¹).

Figure 9. Theoretical to experimental dry equilibrium composition comparison for 
S/C = 0.5 mol/mol at 0.045 mL/min (liq.) and N₂ at 13 mL/min (GHSV~1594 h⁻¹).

Figure 10. Theoretical to experimental dry equilibrium composition comparison for 
S/C = 0.25 mol/mol (3.20 g Ni catalyst loading) at 0.071 mL/min (liq.) and N₂ at 13 
ml/min (GHSV ~ 1061 h⁻¹).
Figure 11. Theoretical to experimental dry equilibrium composition comparison for S/C = 0 (GHSV=750 h⁻¹).

Methanol Reformate SOFC Cell Testing

Figure 12 shows a graph of the performance variance test results obtained in the methanol SOFC tests. From the graph one can observe the 6% reduction in OCV (zero load) and 10% reduction in current density at 3.25 A/0.65 V full load based on operation of methanol reformate versus humidified hydrogen.

For the steam-to-carbon ratios of 1:1, 0.75:1, and 0.5:1, the results for post-reformer / pre-SOFC cell gas compositions are shown in Table 1, which is a comparison between...
theoretical and experimental in the Methanol Fuel Processing tests discussed above, and experimental in the methanol solid oxide fuel cell tests. Reformer conditions throughout the methanol SOFC tests were operational temperature of 900°C, space velocity of 1,500 hr⁻¹, and over the Haldor Topsoe 15% Ni, 25% Mg, and 60% Al₂O₃. Table 2 is a comparison between gas samples taken at no load and at peak power load. The no load condition is the open circuit voltage (OCV) and the peak power load was 3.25 A and 0.65 V.

Table 1. Theoretical and Experimental Gas Composition Analysis for Methanol Reformate at Steam-to-Carbon Ratios of 1:1, 0.75:1, and 0.5:1.

| Analysis                        | Products (mole %) |
|---------------------------------|-------------------|
|                                 | H₂    | CO    | CO₂   | CH₄   | Total |
| Theoretical 1:1 Dry             | 68.9  | 24.3  | 6.8   | 0.0   | 100   |
| Experimental MeOH Ref Tests 1:1| 68.1  | 25.1  | 6.8   | 0.0   | 100   |
| Experimental MeOH SOFC Tests 1:1| 67.0  | 21.3  | 10.2  | 0.5   | 99    |
| Theoretical 0.75:1 Dry          | 68.5  | 26.0  | 5.5   | 0.0   | 100   |
| Experimental MeOH Ref Tests 0.75:1| 69.1  | 26.3  | 4.5   | 0.0   | 100   |
| Experimental MeOH SOFC Tests 0.75:1| 66.2  | 23.4  | 8.7   | 1.0   | 99    |
| Theoretical 0.5:1 Dry           | 68.0  | 28.0  | 4.0   | 0.0   | 100   |
| Experimental MeOH Ref Tests 0.5:1| 68.4  | 27.7  | 4.1   | 0.0   | 100   |
| Experimental MeOH SOFC Tests 0.5:1| 65.3  | 24.5  | 7.1   | 2.0   | 99    |

Table 2. Gas Composition Analysis for Methanol Reformate At No Load and Peak Power Load for Steam-to-Carbon Ratios of 1:1, 0.75:1, and 0.5:1.

| OCV vs Load Analysis          | Products (mole %) |
|-------------------------------|-------------------|
|                               | H₂    | CO    | CO₂   | CH₄   | Total |
| 1:1 MeOH SOFC OCV             | 67.0  | 21.3  | 10.2  | 0.5   | 99    |
| 1:1 MeOH SOFC 3.25A/0.65V Load| 64.9  | 20.1  | 14.4  | 0.5   | 100   |
| 0.75:1 MeOH SOFC OCV          | 66.2  | 23.4  | 8.7   | 1.0   | 99    |
| 0.75:1 MeOH SOFC 3.25A/0.65V Load| 64.6  | 21.5  | 12.3  | 0.5   | 99    |
| 0.5:1 MeOH SOFC OCV           | 65.3  | 24.5  | 7.1   | 2.0   | 99    |
| 0.5:1 MeOH SOFC 3.25A/0.65V Load| 63.6  | 24.2  | 10.1  | 1.0   | 99    |

The results for the theoretical versus experimental gas composition analysis, shown in Table 1, were quite comparable, however it should be noted that in all three methanol solid oxide fuel cell tests (MeOH SOFC) hydrogen and carbon monoxide are slightly lower than expected and carbon dioxide and methane are higher than expected. The variance from expectations is within experimental tolerance; however the trends lead towards electrochemical reactions taking place even at zero applied load.
The results for the no load versus peak power load gas composition analysis, shown in Table 2, displayed the SOFC electrochemical reactions quite well. Results are not dramatic due to the low (15%) fuel utilization used for these tests; however the trends are quite evident. Upon an applied load to the SOFC cell, a change in the fuel gas composition is in principle to be expected. Hydrogen and carbon monoxide shall decrease as these species are consumed in the electrochemical fuel cell reactions, and carbon dioxide and steam shall increase. As gas chromatograph analysis requires a dry gas sample, steam content from the methanol reformate must be condensed out prior to sampling. From Table 2, one can observe the trend of decreasing hydrogen and carbon monoxide, and increasing carbon dioxide.

One final important addition to note is that coke formation was noticed at 0.5:1 steam-to-carbon ratio testing. This was not observed in the previous methanol reforming tests, possibly because run times and flow rates were too low to visually see the carbon formation. No carbon was detected at 1:1 or 0.75:1.

**Steady State SOFC System Modelling**

The following Table 3 draws conclusions and comparisons to the 5 kW SOFC system operating on natural gas and that on methanol.

| SYSTEM MODEL PARAMETER | NATURAL GAS | METHANOL |
|------------------------|-------------|----------|
| Overall Electrical Efficiency (%) | 40.5% | 39.8% |
| Reformer Heat Duty (kW) | 3.9 kW | 3.2 kW |
| Actual Fuel Flowrate | 18.7 slpm | 48 ml/min |
| Gross Power Output (kW) | 5.95 kW | 5.95 kW |
| Recirculation Fuel % | 67% | 43% |
| Exhaust-Fuel Heat Exchanger Duty (kW) | 0.18 kW | 1.11 kW |
| Exhaust-Air Heat Exchanger Duty (kW) | 6.6 kW | 5.8 kW |
| Stack Radiation Heat to Air Available (kW) | 2.26 kW | 3.00 kW |
| Recovery Water Heat Exchanger Cogen Available (kW) | 5.3 kW | 5.1 kW |
| Reformate Composition after Pre-Reformer | | |
| Carbon monoxide, CO | 23.6% | 23.8% |
| Hydrogen, H₂ | 39.1% | 40.9% |
| Steam, H₂O | 27.0% | 25.8% |
| Carbon dioxide, CO₂ | 10.3% | 9.5% |
The background and assumptions used in this model for both the natural gas and methanol models are as follows:

- 6 kW gross DC power out of the SOFC stack
- Oxygen-to-Carbon ratio for recirculation maintained at > 2.1
- System heat loss is 500 W
- Fuel utilization maintained at 83%
- Air utilization maintained at 40%

The steady state model showed an expected natural gas system efficiency of 40.5% and a methanol system efficiency of 39.8% for the two systems; however the realization of these numbers is based on the other parameters operating as specified in this table. Other results of interest are the 18% reduction in reformer heat duty between the natural gas system (3.9 kW) and the methanol system (3.2 kW); the lower methanol system reformer duty is beneficial to the overall system operation. Recirculation percentage is another notable result. The methanol system requires 35% less recirculation versus the natural gas system, 67% recycle in the natural gas system and 43% in the methanol system. Note that a fixed point ejector would not work for dual fuel operation.

The most notable results are for the system heat exchange performance. The exhaust-to-fuel heat exchange for the natural gas system is 180 W versus 1.11 kW for the methanol system; it should be noted that these heat exchange duties are very low and quite easily designed. The exhaust-to-air heat exchange performance is quite different, the duty required by the natural gas system is 6.6 kW and for the methanol system 5.8 kW. These duties are very high and could raise problems in system operation. Recovery water heat exchange available is roughly 5 kW in both systems.

The reformate composition in the natural gas system is quite comparable to the methanol system. From these results one can expect that stack and cell performance should not vary too much between operation on methanol and operation on natural gas.

A point to make clear is that high temperature methanol reforming requires over 40% steam addition (on a molar basis) to prevent coke formation through the vaporization regime of the methanol (equivalent to a Steam-to-Carbon ratio of 0.75:1). This steam addition is depleting the fuel value, and thus impacting the overall system operation performance. The effect of the depleted fuel value on the SOFC system can be seen from the methanol decomposition and steam reformation reactions shown below:

\[
\text{Methanol Decomposition:} \quad \text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2
\]

\[
\text{Methanol Steam Reforming:} \quad \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2
\]

From these reactions conclusions can be drawn to the effects of adding water content to the methanol in an attempt to eliminate the carbon formation issue. In both reactions three moles of SOFC fuel (hydrogen and/or carbon monoxide) products are generated, however in the decomposition reaction only one mole of reactant methanol is required versus two moles of reactants in the steam reforming reaction (one mole of methanol and one mole of water). Therefore, in order to get the same power output, a greater
volumetric flow rate of methanol/water input fuel must be used, and the increased flow will have an impact to the thermal operation of the system; particularly, how and where the required heat duty to vaporize the increased fuel flow is taken from. Furthermore, there is the logistics of having a higher volume of fuel storage required.

CONCLUSIONS

In regards to the methanol fuel processing test activity three conclusions can be drawn. Firstly, methanol vaporization in copper coils showed to be inactive catalytically through the temperature range of 100-300°C. Secondly, the addition of steam can move the decomposition temperature regime of methanol from 400°C to > 800°C. Thirdly, for methanol reforming at high temperatures (600-900°C), the recommended minimum steam-to-carbon ratio before coke formation occurs is 0.75:1.

In regards to the methanol reformate SOFC cell testing four conclusions can be drawn. Firstly, gas composition differences between the three steam-to-carbon ratios tested (1, ¼, and ½) were insignificant to SOFC cell performance results. Secondly, no SOFC cell degradation was observed due to operation on methanol reformate. Thirdly, a consistent 6% reduction in SOFC cell open circuit voltage (OCV) and 10% reduction in cell peak power current density was observed when run on methanol reformate versus humidified (3%) hydrogen. Fourthly, gas composition changes from samples taken at zero load versus at 3.25A/0.65V full load showed an increase in carbon dioxide, indicating that SOFC conversion reactions were taking place and can be quantified with our approach.

In regards to the steady state modelling activity three conclusions can be drawn. Firstly, it is possible for a natural gas SOFC system design to be converted to run on methanol with minor engineering modifications. Secondly, a negligible efficiency loss of roughly one percent (1%) can be expected in operating the natural gas system design on methanol fuel. Thirdly, the biggest impact in design for an internally reformed or integrated stack/reformer is a reduction of approximately twenty percent (20%) in reformer heat duty operating the natural gas system design on methanol fuel.

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