THERMODYNAMIC ANALYSIS OF DIESEL REFORMING OPTIONS FOR SOFC SYSTEMS

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ABSTRACT

Development of a diesel reformer for solid oxide fuel cells widens the application of the SOFC system by making it more fuel-flexible. While technologies for conversion of fuels containing these hydrocarbons are commercially available, the industrial scale processes and the composition of the reformed gas are not ideally suited to SOFC systems. The work is extremely challenging and will require some novel approaches to solving some of the technical problems. A key step in fuel processing is reforming of the fuel to a mixture containing hydrogen and methane. There are three routes for this conversion: steam reforming, autothermal reforming and partial oxidation. In this work we carried out a thermodynamic analysis of the three reforming routes. Minimum steam-to-carbon ratios for steam reforming and for autothermal reforming and minimum oxygen-to-carbon ratios for autothermal reforming and partial oxidation and their corresponding temperatures required for carbon-free operation were identified. Fuel processor efficiencies and reformer heat requirements were computed to identify practical operating conditions. SOFC stack efficiencies for 85% fuel utilisation were computed to identify the commercially viable options for the system.

INTRODUCTION

Pipeline natural gas is the fuel of choice for solid oxide fuel cell systems. There are several reasons for this. Foremost among them are the abundance, supply infrastructure and current and foreseeable future prices of natural gas. This choice is supported by the fact that with a small fuel-processor upstream of the fuel cell stack, for pre-reforming the relatively small amounts of higher hydrocarbons in natural gas, this type of fuel cells can be operated on partially pre-reformed gas converting the higher hydrocarbons present in natural gas in the pre-reformer, with internal reforming of methane occurring on the SOFC anode. However, there is significant interest in developing the capability of using other hydrocarbon-based fuels like LPG, gasoline and diesel for solid oxide fuel cells if the hydrocarbons in these fuels can be converted to a mixture of gases that is suitable for SOFC applications. Amongst these, interest in processing of diesel for SOFC-based APU applications has grown rapidly over the last few years. Ceramic Fuel Cells Ltd. have initiated a fuel processing technology development program, which is aimed at optimizing the operating conditions of selected commercial catalysts for delivering a suitable gas mixture to SOFC stacks by processing a range of utility fuels. Work on LPG...
has been demonstrated in a 1-5 kWe size fuel processor by utilizing the steam reforming technology. The fuel-processing project has now been extended to processing of diesel by using steam reforming, partial oxidation or autothermal reforming.

Each reforming route has its own advantages and disadvantages. Partial oxidation is a fast exothermic reaction with rapid start-up and dynamic response features. Moreover, the process is more tolerant to contaminants like sulfur as a direct consequence of the presence of oxygen in the reaction mixture, which converts the catalyst contaminating sulfur compounds to the innocuous sulfur dioxide. However, carbon formation risk is high for this reaction and that could lead to fouling of the reactor and/or deactivation of the catalyst. Moreover, it dilutes the fuel supply to the fuel cell stack and generates a lot of waste heat, thereby lowering the overall system efficiency. Steam reforming is endothermic requiring additional energy input and suffers from slow start-up and long response times. If the energy requirement can be met by waste heat from other parts of the system e.g. by heat exchange with the anode off-gas stream, the steam-reforming route can provide very high overall system efficiencies. However, no sulfur tolerant steam reforming catalysts have been developed yet, resulting in the need for a very efficient sulfur removal unit upstream of the reformer. The autothermal reforming route combines the features of partial oxidation and steam reforming. It has rapid start-up and dynamic response features like partial oxidation and depending on the reforming conditions can have high efficiencies. With respect to sulfur removal, the presence of steam in the reaction mixture reduces the effectiveness of converting sulfur compounds to sulfur dioxide resulting in the formation of hydrogen sulfide instead. However, if the fuel does not contain very high levels of organic sulfur compounds, the levels of H2S formed may be tolerated by the catalyst with little or no poisoning. This will also depend on the type of material used in the catalyst. For fuel-cell systems for vehicular auxiliary power units fast response and start-up times may not be as critical as in the case of automotive propulsion fuel cells as the APU can run on the prime mover while the fuel-cell system is started up. The final choice will depend on among other things the efficiency of the overall system.

Diesel is a blend of different kinds of petroleum-derived compounds such as paraffins, cyclic hydrocarbons, olefins, aromatics, naphthenes, oxygenates, and the carbon chain and ring structures which makes it difficult to convert it to desirable products i.e. methane, hydrogen and carbon monoxide. Because of the high boiling point interval of the fuel, diesel evaporation requires high temperatures. Such high temperatures can lead to cracking of some of the fuel components leading to carbon formation on the surface of the catalyst. The problem of carbon deposition on the catalyst can be avoided by using a high steam/hydrocarbon ratio in the steam reforming route. However, such high steam ratios lead to fuel dilution resulting in lower electrical efficiency in the fuel cell. Partial oxidation route suffers from fuel dilution by nitrogen in the air. Autothermal reforming may be the most attractive route as it offers the prospect of using lower steam and air contents than the other two routes and can be thermally self-sustaining. None of the routes is proven for diesel reforming particularly for solid oxide fuel cell application. Development of a diesel reformer for solid oxide fuel cells widens the application of the SOFC system by making it more fuel-flexible. As a first step, a thermodynamic analysis needs to be carried out for the three routes to determine conditions for carbon-free operation and high fuel cell system efficiencies and that is the objective of this work.
In this work we have arbitrarily chosen Diesel Grade-2 for carrying out a thermodynamic analysis of its use in a SOFC system using the three different routes for reforming. The composition of Diesel Grade 2 (B.P. 343°C, Mol. Wt. 179.8, H/C=1.88) is shown in Table 1.

Table 1. Composition of Diesel Grade-2 (mass fractions).

|                |               |                   |
|----------------|---------------|-------------------|
| n-Nonane       | 0.0122        | n-Pentylbenzene   | 0.0027 |
| n-Decane       | 0.0243        | n-Hexylbenzene    | 0.0041 |
| n-C11          | 0.0517        | n-Heptylbenzene   | 0.0055 |
| n-C12          | 0.0912        | n-Octylbenzene    | 0.0058 |
| n-C13          | 0.2007        | n-Nonylbenzene    | 0.0059 |
| n-C14          | 0.1959        | n-Decylbenzene    | 0.0065 |
| n-C15          | 0.0980        | n-C11benzene      | 0.0030 |
| n-C16          | 0.0490        | n-C12benzene      | 0.0020 |
| n-C17          | 0.0245        | Naphthalene       | 0.0302 |
| n-C18          | 0.0122        | 1-Methylnaphthalene | 0.0654 |
| n-C19          | 0.0061        | 1-Ethynaphthalene | 0.0453 |
| n-C20          | 0.0031        | 1-Propynaphthalene | 0.0322 |
|                |               | 1-Butynaphthalene | 0.0215 |

THERMODYNAMIC ANALYSIS

The thermodynamic analysis was performed using HSC Chemistry (2), which is based on minimisation of Gibbs free energy. The possible species that might be found in the final product were assumed to be C, CO, CO2, H2, O2, N2, H2O, CH4, C2H6, C3H8, C4H10, C5H12, C6H14, C7H16, C8H18, C2H2, C2H4, C3H4, C3H6, C4H6, C6H8, C7H10, C8H12 and C9H16. The product yields are normalised on the basis of one mole of diesel grade-2 fed to the reformer. The following operating parameters were included in the analysis: Steam-to-Carbon (S/C) ratio for steam reforming and autothermal reforming, Oxygen-to-Carbon (O2/C) ratio for autothermal reforming and partial oxidation. Pressure was kept constant at atmospheric value consistent with operation of most SOFC systems. For a range of S/C and O2/C values, the equilibrium compositions have been calculated in the temperature range 300 to 800°C, as this is the range where most catalysts will be active for these reactions without the risk of thermal degradation.

RESULTS AND DISCUSSION

Conversion of diesel components was complete under all conditions in this study for all three reforming routes. Steam reforming computations were carried out at S/C values of 1.5, 1.8 and 2.0. At all S/C values, selectivity to H2 and CO increases with temperature and selectivity to CH4 decreases with temperature. The amount of unreacted steam also decreases with temperature. Both S/C and temperature significantly affects carbon formation. At S/C=1.5, significant carbon formation takes place until the temperature is raised to 700°C. In Fig.1, the amount of carbon formed decreases slightly with increase of temperature up to 400°C, then it increases slightly with increase of temperature up to
500°C. Finally, it decreases again with further increase of temperature until there is no carbon formation at 700°C. It can be postulated that the predominant carbon forming reaction is the Boudouard reaction which is favoured at lower temperatures. However, other carbon-forming reactions like cracking of diesel components and the reversible carbon gasification reaction along with the change in relative contents of the carbon-containing species and carbon-gasifying species have an effect of the same order as that of the Boudouard reaction in the temperature range 300 to 500°C. In particular, C₆H₆ and the unsaturated hydrocarbons like C₂H₂, C₂H₄, C₃H₄, C₃H₆, C₄H₆, C₄H₈, C₅H₁₀, C₆H₁₂ may be formed favourably under certain conditions and contribute to coking. These compounds contribute to coking unless they are converted to desirable products. In real systems, the selectivity and kinetics of these reactions on the chosen catalyst will determine the extent of carbon formation. The composition profiles at the other S/C values of 1.8 and 2.0 have the same trend with temperature with the notable exception that carbon-formation is completely eliminated thermodynamically in the entire temperature range with S/C=2. The results in Fig. 1 to 3 show that steam reforming of Diesel Grade-2 is thermodynamically feasible without carbon formation, at temperatures higher than 680°C with S/C=1.5, at temperatures higher than 580°C with S/C=1.8 and at all temperatures with S/C=2.

Autothermal reforming computations were carried out for the following four conditions: i) S/C=1.5, O₂/C=0.25, ii) S/C=1.8, O₂/C=0.25, iii) S/C=1.2, O₂/C=0.5 and iv) S/C=1.5, O₂/C=0.5. The results are shown in Fig. 4 to 7. Under condition (i), selectivity to H₂ increases with temperature up to 700°C and remains constant with further increase of temperature. At all other conditions, selectivity to H₂ increases up to 700°C and decreases thereafter. Selectivity to CH₄ decreases with temperature under all conditions. Compared to the steam reforming route, selectivity to methane is lower for all autothermal conditions; this is an important consideration for internal reforming and thermal management of solid-oxide fuel cell stacks. Under conditions (i) & (ii), the amount of steam in the product decreases up to 700°C and increases thereafter. For conditions (iii) & (iv), this reversal occurs at a lower temperature of 600°C. This is a reflection of the water-gas shift reaction equilibrium as shown by a concomitant increase in CO and decrease in CO₂.

No carbon formation is predicted for autothermal reforming at S/C=1.8, O₂/C=0.25 and at S/C=1.5, O₂/C=0.5. At the other two conditions, carbon formation is predicted up to 480°C and 580°C, respectively, for S/C=1.2, O₂/C=0.5 and S/C=1.5, O₂/C=0.25. Fig. 8 to 10 show that partial oxidation results in either very high N₂ levels in the product or with the risk of high levels of carbon formation depending on the temperature and O₂/C ratio. Carbon-formation can be avoided at T>750°C, with O₂/C=1 resulting in ~48% N₂ in product or at T>690°C with O₂/C=0.75, again with a significant level of N₂ dilution i.e. 37%. If the O₂/C ratio is lowered to 0.5 to reduce the extent of fuel dilution, the risk of carbon formation exists for the entire temperature range of 300-800°C, and is only avoided if T>800°C. Partial oxidation route at high temperatures to avoid carbon formation is unattractive as it generates a high degree of waste heat. With an exothermic fuel-cell stack in the system, there is little use for such waste heat.

Fig. 11 shows that auto thermal reforming at S/C=1.8, O₂/C=0.25 and at S/C=1.5, O₂/C=0.25 is thermoneutral at 500°C. Fuel-processor efficiencies for these cases, shown
in Fig. 12, are in the region of 90%. Autothermal reforming at S/C=1.5, O2/C=0.5 and S/C=1.2, O2/C=0.5 is thermoneutral at the high temperature of 700°C. Corresponding fuel processor efficiencies are around 85%. From these considerations along with considerations of carbon formation risk, autothermal reforming at S/C=1.8, O2/C=0.25 at 500°C, or at S/C=1.2, O2/C=0.5 are the most favourable autothermal reforming conditions. However, from a product composition consideration i.e. higher CH4 content and lower N2 content, autothermal reforming at S/C=1.8, O2/C=0.25 is more favourable.

Although very high fuel-processor efficiencies can be achieved for the steam-reforming route, the reaction is highly endothermic and as such will require significant heat input to the reformer depending on the reforming temperature. With 15% of the heating value of the fuel still available for target 85% fuel utilization and with further heat available from the heat released from fuel cell stack due to polarization and ohmic losses of the fuel cell, such heat input can be made available to the steam-reformer in a thermally integrated diesel reformer-SOFC stack unit. With such a thermally integrated unit, the steam reforming route is clearly the preferred route provided the high sulfur levels in diesel can be effectively and efficiently removed in the fuel-processing unit. With recent developments in deep desulfurisation along with the push for low-sulfur diesel, the latter becomes less of an issue making the steam reforming route by far the most preferable option.

From the consideration of thermoneutrality and fuel-processor efficiency, partial oxidation at O2/C=0.5 at 800°C is the only attractive one amongst the three partial oxidation conditions shown in this study. However, as discussed earlier, carbon formation risk and fuel dilution by N2 make it less attractive than the other reforming routes.

Fig. 13 shows SOFC efficiency is highest for the steam-reforming route with 57% at all temperatures for S/C=2 and 1.8 and at T>650°C for S/C=1.5. Autothermal reforming at S/C=1.8, O2/C=0.25 and at S/C=1.5, O2/C=0.25 have efficiencies around ~45% which would be acceptable for most target markets. Partial oxidation at O2/C=0.5 and at T>700°C has an efficiency of ~40% and may be acceptable from this consideration alone. However, from other considerations mentioned earlier it would not be practicable. Auto thermal reforming at the other two conditions have efficiencies lower than 40% and partial oxidation at the other two conditions have efficiencies less than 30%.

**CONCLUSIONS**

Low temperature steam reforming without the thermodynamic potential for carbon formation can be achieved by using a steam/carbon ratio, S/C=2. To use lower steam contents, the temperature must be raised to 580°C and 680°C for S/C=1.8 and 1.5 respectively. Higher methane content is desirable for internal reforming SOFCs and this is achieved by low temperature steam reforming. Thermodynamic potential for carbon formation is completely averted by autothermal reforming at S/C=1.8, O2/C=0.25. The same is achieved by autothermal reforming at S/C=1.5, O2/C=0.5 By comparison, steam reforming at S/C=2 achieves the same without the effect of fuel dilution by nitrogen. To lower the S/C ratio to 1.5 for autothermal reforming with O2/C=0.25, the temperature must be raised to 580°C. To lower the S/C ratio to 1.2 for autothermal reforming with
O₂/C=0.5, the temperature must be raised to 480°C. Carbon formation is avoided by partial oxidation at O₂/C=1 at T>580°C. To operate at O₂/C=0.75, the temperature must be raised to 690°C. To operate at O₂/C=0.5, the temperature must be raised to >800°C.

Considering all of the issues mentioned in this work i.e. SOFC efficiency, fuel processor efficiency, thermoneutrality and/or availability/utilisation of waste heat, carbon-formation risk and sulfur-removal ability, steam reforming at S/C=2 is the most attractive route for reforming of diesel for SOFC systems, followed by steam reforming at S/C=1.8 or autothermal reforming at S/C=1.8, O₂/C=0.25 or autothermal reforming at S/C=1.5, O₂/C=0.25 depending on the complexity of the fuel cleaning steps, the requirements of overall efficiency and the target market/product size. Although, specific cases of S/C and O₂/C values have been used in this work, the conclusions reached will be generally applicable over a wide range of conditions to allow reasonable conclusions to be made for values of S/C and O₂/C somewhat different from those used here. Furthermore, providing the hydrocarbon components in the fuel are similar, reasonable conclusions can be drawn for other grades of diesel fuel.

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Figure 2. Steam reforming of diesel at S/C=1.8

Figure 3. Steam reforming of diesel at S/C=2

Figure 4. Autothermal reforming of diesel at S/C=1.5, O₂/C=0.25
Figure 5. Autothermal reforming of diesel at S/C=1.8, O2/C=0.25

Figure 6. Autothermal reforming of diesel at S/C=1.2, O2/C=0.5

Figure 7. Autothermal reforming of diesel at S/C=1.5, O2/C=0.5
Figure 8. Partial oxidation of diesel at $O_2/C=1$

Figure 9. Partial oxidation of diesel at $O_2/C=0.75$

Figure 10. Partial oxidation of diesel at $O_2/C=0.5$
Figure 11. Reaction enthalpy for the various reforming options

Figure 12. Fuel processor efficiency for the various reforming options.

Figure 13. SOFC efficiency for the various reforming options.