Microstructured reactors on the 5 kW scale for the water gas shift and preferential oxidation reactions using surrogate diesel reformate

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Summary

5 kW$_{el}$ One-Stage Water Gas Shift (WGS) and Preferential Oxidation (PROx) reactors were designed and evaluated for the clean-up of surrogate diesel reformate. For the WGS reactor, CO conversions of up to 95% were attained using typical surrogate synthetic diesel reformate. The PROx reactor was capable of converting a feed concentration of 1.0 mol% CO to 20 ppm. The two reactors were then integrated for the purposes of reducing the carbon monoxide levels in a reformate exit stream to levels below 100 ppm.

Keywords

Microreactors, fuel cells, surrogate diesel

Introduction

For small to medium sized applications in the portable and transportation power areas, it is generally believed that proton-exchange membrane (PEM) fuel cells are the most promising due to their low temperature operation and high power density. However, as dictated by the poisoning limit of the Pt catalyst in a conventional low temperature PEM fuel cell, CO levels must be decreased to levels lower than 10 ppm. Generally speaking, the H_2 rich gas produced after reforming contains 6-12 vol% CO depending on the type of reforming and the corresponding reaction parameters. Usually (except for methanol reformers), this CO is sent to a high temperature (375°C-450°C) and low temperature water gas shift stage (200°C-300°C) which is capable of reducing the CO concentration to under 1 vol%. In this contribution, 5 kW$_{el}$ One-Stage Water Gas Shift (WGS) and Preferential Oxidation (PROx) reactors were designed and evaluated for the clean-up of surrogate diesel reformate. Both partial load operation and load changes for both reactors could be carried out without significant overshoots of carbon monoxide. The reactors were then integrated and evaluated. Herein, the evaluation of these integrated WGS and PROx reactors are also reported. Experiments were performed at S/C ratios of 3.2 and 3.8. Careful control of the system was necessary so as to achieve CO concentrations of less than 100 ppm at the exit of the PROx reactor.

Results and Discussion

For all testing, reformate surrogate was generated by dosing and mixing separately nitrogen, carbon dioxide, carbon monoxide and hydrogen and then pre-heating in an electrical gas heater. Water was dosed separately, evaporated in a dedicated evaporator, super-heated in a separate electrical gas-heater and added to the feed flow. The measurements of all gas compositions was performed with micro-GC and downstream the PrOx reactor with an IR-sensor for CO after water removal. In some cases additional analyses was performed with conventional GC. Because most data came from the Micro GC and the IR sensor they are referred to on a dry basis (d.b.).

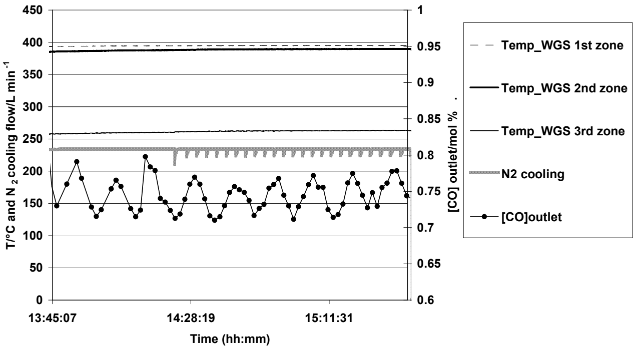

Figure 1: Typical steady state operation of the OS-WGS, with fresh catalyst, at 100% LL

Figure 1 shows a typical steady state operation of the WGS reactor at 100% load level. The minor fluctuations of the GC analysis are regarded as an irregularity of the sampling procedure. The temperature zones in the figure refer to the inlet, the body and the outlet of the reactor. The carbon monoxide content in the outlet stream of 0.75 mol% was still satisfactory when one considers that levels of up to 1% are acceptable as input to a PROX reactor in a fuel processor unit, depending of course on the reformer feedstock. Figure 2 shows an example of 2.5 hours stable operation of the reactor at 100% load. Having started with CO content in the feed of 1.0 vol%, the carbon monoxide content was reduced to well below 50 ppm, the lowest value being 23 ppm. Also in the graph(s) are the results obtained with the IR sensor which agree well with the GC analyses. These may be regarded as more reliable,

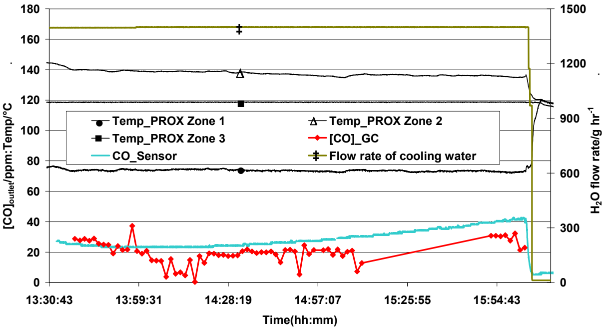

Fig 2: Typical steady state operation of the PROx reactor at 100% LL

especially for the dynamic measurements as the GC measurements always showed a certain time delay owing to the sampling procedure. At the end of the experimental run shown in Figure 2, the reactor was shut down. It is visible, that the reactor achieves isothermal conditions very quickly once the cooling water and reformate flow are stopped.

Experiments were first run at S/C = 3.2, at partial loads from 20% to 80% LL. A typical steady state operation, performed at 80% LL is displayed in Figure 4. On closer inspection, it can be seen that the temperature at the outlet of the WGS reactor was stable at 250°C together with the inlet temperature of the PROx reactor which was maintained at an average of 90°C. These temperatures are vital for the overall thermal management and control of each reactor. During the run, the maximum CO concentration reached was 100 ppm with the lowest being 43 ppm. This was a good performance considering that the output from the shift reactor amounted to 1.18 vol% (d.b.).

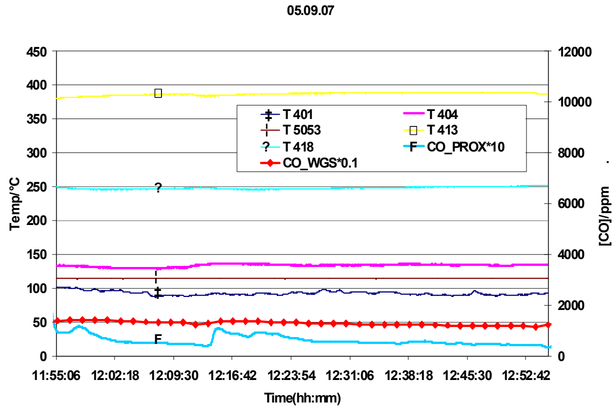

Figure 3: Steady state operation for the integrated system at 80% load level, S/C = 3.2

This amounted to 99.63% conversion for the PROx reactor.

The performance of the integrated system, at the other load levels in steady state conditions, in terms of both WGS and PROx output is summarised in Table 1. As one can see, [CO] concentrations downstream from the PROx reactor were always under 100 ppm at all levels up to and including 80% LL. However, at 100% LL such levels were never reached. This was primarily as a consequence of the relatively high amount of CO that was sent to the PROx reactor from the WGS reactor. This had the effect of increasing the temperature at the inlet of the PROx reactor to over 110°C and in the reactor body to over 160°C. From the individual component testing, it was realised that these temperatures were obliged to be at least 25°C lower for efficient operation of the PROx reactor and for the achievement of a CO conversion so that the target CO amounts were attained.

Taking this into consideration, the steam to carbon ratio was then raised to 3.8 and the runs at partial load were repeated. Better conversion levels for the shift were achieved (in analogous comparison with the lower S/C ratio) thus reducing the load for the PROx reactor. Values as low as 1.1% CO were measured at 80% LL compared to the higher levels observed at the lower S/C ratio. CO concentrations after the PROx were always below 100 ppm, occasionally reaching below 50 ppm. The improvements in results can be directly attributed to the performance of the shift reactor.

% LL	S/C	$[CO]_{OutletWGS}$ /vol%(d.b)	$[CO]_{OutletPROx}$ /ppm	% CO conversion (PROx reactor)
20	3.2	0.52	81	98.44
40	3.2	0.92	49	99.47
60	3.2	1.07	44	99.59
80	3.2	1.18	43	99.63
100	3.2	1.50	471	96.86
20	3.8	0.55	57	99.22
40	3.8	0.89	46	99.48
60	3.8	1.13	56	99.50
80 (run 1)	3.8	1.10	57	99.50
80 (run 2)	3.8	1.40	42	99.70

Table 1: A summary of the performance of the integrated WGS/PROx, at different load levels for both S/C = 3.2 and S/C = 3.8.

Load changes for both reactors could also be carried out without significant overshoots of carbon monoxide.

Conclusion

5 kW_{el} One-Stage Water Gas Shift (WGS) and Preferential Oxidation (PROx) reactors were evaluated for the clean-up of surrogate diesel reformate. For the WGS reactor, CO conversions of up to 95% were attained using typical surrogate synthetic diesel reformate. The PROx reactor was capable of converting a feed concentration of 1.0 mol% CO to 20 ppm. The reactors were then integrated and worked best at partial load levels.