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A compact CO selective oxidation reactor for solid polymer fuel cell powered vehicle application

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Abstract

Solid polymer fuel cells (SPFCs) are attractive as electrical power plants for vehicle applications since they offer the advantages of high efficiency, zero emissions, and mechanical robustness. Hydrogen is the ideal fuel, but is currently disadvantaged for automotive applications by the lack of refuelling infrastructure, bulky on-board storage, and safety concerns. On-board methanol reforming offers an attractive alternative due to its increased energy storage density. Since CO is always present as a by-product during the reforming reaction, it must be reduced to a level less than 20 ppm in order to avoid rapid deactivation of the platinum electro-catalyst in the fuel cells. In this paper, a compact CO selective oxidation unit based upon two coated aluminium heat exchangers, developed at Loughborough University, is reported. The geometric size of the whole unit is 4 litre and experimental results show that the selective oxidation unit can reduce the CO from up to 2% to less than 15 ppm and is suitable for a vehicle fuel cell power plant of 20 kW$_e$. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Due to the ever increasing concerns regarding emissions from the internal combustion engine, fuel cell technology is now emerging as a serious "clean" alternative for automotive propulsion. For automotive applications, the solid polymer fuel cell (SPFC) is currently the most favoured technology by the majority of the automotive companies due to its high power densities, mechanical robustness and fast start-up and dynamic response characteristics. A combination of technological advances over the last decade and the environmentally driven regulatory pressure has resulted in virtually all of the major automotive manufacturers becoming involved in programmes to assess the ultimate suitability of SPFC technology. Daimler-Chrysler [1,2], Ford [1], General Motors [1], Honda [3], and Nissan [4] have all stated that they expect to have launched SPFC vehicles by the year 2004 [5].

A critical issue in the continued development of SPFC vehicles is that of fuel choice. In addition to the associated infrastructure issues, the choice of fuel has serious implications on both design of the SPFC vehicle and the re-fuelling mechanism required. Each of the fuels under consideration, i.e. hydrogen, methanol and gasoline, has its own inherent advantages and disadvantages for SPFC automotive application. No particular fuel is yet universally favoured and this is reflected by the stance of "fuel neutrality" currently being adopted by DaimlerChrysler, GM and Ford [1]. Hydrogen is the ideal fuel for the SPFC vehicle since it offers the advantages of simple system integration, maximum efficiency and truly zero emissions. Poor volumetric density of currently available on-board gaseous storage and the lack of an adequate supply infrastructure are presently seen as major disadvantages.

Alternatively, the reforming of hydrocarbons is now becoming an increasingly attractive proposition, since the hydrogen can be chemically stored at significantly increased energy densities. While gasoline is viewed by many as the ideal fuel for reforming, significant advances in its reforming technology have still to be made. Factors such as the impurity levels in the pre- and post-reformed fuel are of concern if the reformer and fuel cell are to be maintained at an acceptable level of operating efficiency.

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Consequently, methanol is now gaining much favour as the initial hydrocarbon of choice for on-board reforming. In particular, methanol offers the advantages of being a cheap, mass producible commodity chemical, and easily reformed. Initial development of the re-fuelling infra-structure has been reported as being less expensive for methanol compared to hydrogen (although an increase may be anticipated once a new methanol production capacity is required) [6,7]. At present, DaimlerChrysler (NECARs 3 and 5) [1], GM (EV1 type and Opel Zafira) [1], Honda (EV Plus type) [5] Nissan (R'nessa type) [2], Toyota (RAV4) [8], and VW (Golf type) [9] all have SPFC vehicles operating on reformed methanol in various stages of development.

Presently, reformer technology for SPFC automotive applications is predominantly based upon steam reforming [8,10,11], partial oxidation [12–14] or a combination of both, i.e. autothermal reforming [15,16], of the hydrocarbon fuel. While the exothermicity of the partial oxidation reaction facilitates fast start-up, increased hydrogen yields and potentially improved system efficiency are possible via steam reforming [17]. Common to all the methods of hydrocarbon reforming is the production of carbon monoxide as a by-product. At typical SPFC operating temperatures of $< 85°C$, CO will rapidly and strongly adsorb onto the platinum electro-catalyst, resulting in a substantial decrease in cell performance [18]. Although advances are being made to increase the electro-catalyst's CO tolerance [19–22], a stage of CO removal between the reformer and the fuel cell is still presently a necessity. Methods for CO removal are generally based either upon physical separation (e.g. palladium based diffusion membranes [11,17,23]) or via catalytic selective oxidation [8,10,12,15,24–28].

2. Development of compact CO oxidation reactor

Research at Loughborough University has sought to minimise the size and weight of the CO oxidation reactor through the direct application of the CO oxidation catalyst onto a suitable compact heat transfer structure. For such an application, the heat transfer technology should, therefore, fulfil the following criteria:
· High surface area to volume ratio.
· Suitability for catalyst application.
· Lightweight.

2.1. Heat transfer technologies

Potential heat transfer technologies were identified and a comparative overview of the technologies assessed is presented in Table 1.

Table 1
Survey of heat transfer technologies

	Plate and gasket	Shell and tube	Compact fin
Cost	Mass produced and commercially available. Typically $< £200$.	Mass produced and commercially available. Typically $< £1000$.	£2-5K depending upon fabrication metal. Cost reductions with volume production, e.g., automotive radiator technology.
Surface/volume ratio	Typically 200 m^2/m^3.	740 m^2/m^3	Exceptionally high 800–1500 m^2/m^3.
Ease of catalyst application	Simple. Unit can be disassembled for coating.	Direct coating of tubes or introduction of catalyst support material into tubes.	Catalyst coating after metal bonding. Difficult to assess uniformity of washcoat application.
Material aspects	Gasketing material (nitrile, neoprene and viton) can limit operating temperature.	All metal structure and bonding avoids potential gasketing problems.	All metal structure and bonding avoids potential gasketing problems.
Temperature range	Dependent upon gasketing material. Typically $< 200°C$.	All metal construction. Typically $< 650°C$.	$< 400°C$ (aluminium). $< 1200°C$ (stainless steel).
Pressure range	Typically up to 20 bar.	Typically up to 20 bar.	Typically up to 20 bar.
Design flexibility	Expense of re-tooling limits designs commercially available	Large range of sizes commercially available	Not ''off the shelf technology''. Aerospace and high performance automotive applications.
Reactant mixing	Platelet surface patterns promote turbulence and efficient mixing.	Reduced cf. plate and gasket and compact fin.	Fin design should facilitate excellent gas mixing

Plate and gasket heat transfer technology was not pursued for reactor applications due to the temperature limitations of the available gasketing material and the limited specific surface area available for heat transfer. Although, not ideal for GCU: gas clean-up applications, the use of shell and tube heat exchangers offered particular advantages regarding the thermal management of the exothermic oxidation reaction during the screening of multiple catalyst samples. Since the catalysts would be prepared in micro-sphere form, then easy catalyst charging of the heat exchanger, and insertion of both control and monitoring thermocouples would be possible. Additionally, the coating of expensive heat exchange substrates with catalyst formulations that may ultimately not provide the required degree of activity would be avoided.

Compact fin heat transfer technology offered many potential advantages as a heat transfer substrate for catalyst coating, for both GCU and reformer applications, i.e. compactness, high surface area, all metal bonding and excellent heat transfer efficiency. Due to the relative expense of the technology, catalyst washcoating would only be carried out once the final selection of the most suitable oxidation catalyst had been made. The heat transfer technology would be manufactured from aluminium in order to minimise the reactor weight.

A range of non-precious metal and precious metal activated metal oxides suitable for selective CO oxidation in the presence of H_2 within the temperature range of 130–200°C were identified [25]. The catalysts were evaluated in micro-sphere form, using a shell and tube heat exchanger-based reactor design. Controlled isothermal operation of the reaction could thus be effected. Of the catalysts screened, a Pt–Ru formulation was found to exhibit the best levels of activity and selectivity towards CO oxidation. Of the other catalysts appraised, although the Pd samples exhibited high levels of CO oxidation activity during micro-reactor analysis, the activity of the formulation using synthesised methanol reformate was considerably reduced. The reduced level of CO oxidation was compromised by the high activity of the Pd formulation towards H_2 oxidation. Initial high levels of CO oxidation were also achieved using a Cu-based formulation, however, continued and irreversible chemical reduction of the metal oxide lattice resulted in a substantial and unacceptable level of catalyst de-activation.

2.2. One litre prototype reactor

Characterisation of the two 0.5-litre reactors in terms of optimum operating temperature indicated that maximum levels of CO removal could be achieved at 160–170°C and 145–160°C for two dissimilar platinum and ruthenium washcoated heat exchangers [29]. Based upon recorded CO and O_2 output concentrations w.r.t. temperature, it was found that below these temperature ranges the catalysts exhibited significantly reduced activity, while above these, the catalyst selectivity for CO oxidation in the presence of the large H_2 excess was reduced. Operation of the individual reactors over a range of CO input concentrations (500–10,000 ppm), and with a range of air flow rates revealed that CO exit concentrations of ≤ 20 ppm were not achievable for SPFC equivalent fuel flow rates of > 5 kW_e. Further investigation of the reactors with fixed CO input (7000 ppm) at SPFC equivalent fuel flow rates of
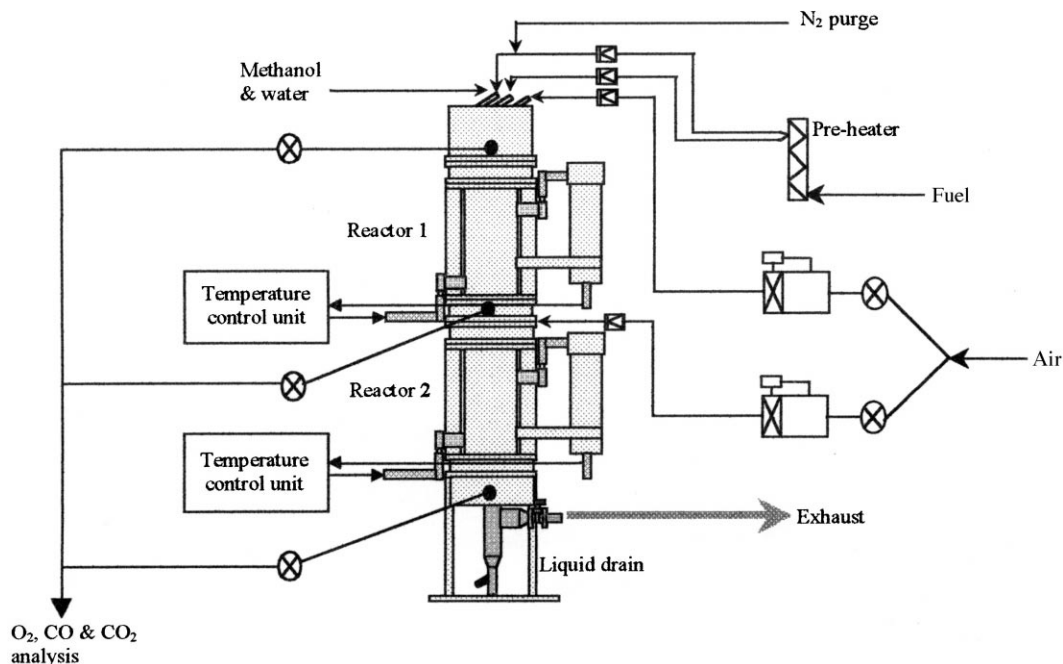

Fig. 1. Schematic of 4-litre dual stage reactor test assembly.

3.75–7.5 kW$_e$, confirmed that the use of a single 0.5-litre reactor washcoated with either of the two formulations would be insufficient in reducing output CO concentrations to ≤ 20 ppm.

Operation of two 0.5-litre reactors in series, i.e., 1-litre dual stage reactor, proved successful in reducing inlet CO concentrations from 7000 ppm to ≤ 10 ppm. The combination of increased fuel residence time and optimised dual stage air injection, facilitated CO outputs of ≤ 10 ppm for SPFC equivalent fuel flow rates ≤ 7.5 kW$_e$. Steady state operation of the dual stage reactor for 40 h at SPFC fuel flow rate equivalent of 5 kW$_e$ has also demonstrated stable CO outputs of 10–12 ppm.

3. Development of the 20 kW$_e$ CO oxidation reactor

In order to achieve a flow rate sufficient for a 20 kW$_e$ fuel cell, a unit of 4 l (comprising of 2 l active reactor volume and 2 l coolant volume) was constructed. Catalyst washcoating of 2×2 l compact fin heat exchangers with a platinum and ruthenium formulation was carried out. The Pt–Ru formulation was selected in terms of its higher activity and higher selectivity toward CO oxidation [29].

3.1. Test assembly

A schematic of the test rig constructed for evaluation of the dual stage 4 l (2×2 l) washcoated heat exchangers is shown in Fig. 1.

Fuel mixtures typically produced by hydrocarbon reforming were synthesised in-house and supplied to the reactor via a series of automated mass flow controllers and liquid injection sub-system. The data acquisition system consists of an AT-MIO-16 data acquisition card and a SCXI (Signal Conditioning eXtension for Instrumentation) unit used in conjunction with National Instruments LabView (Ver. 4) software. A comprehensive description of the full test assembly has been detailed in Ref. [29].
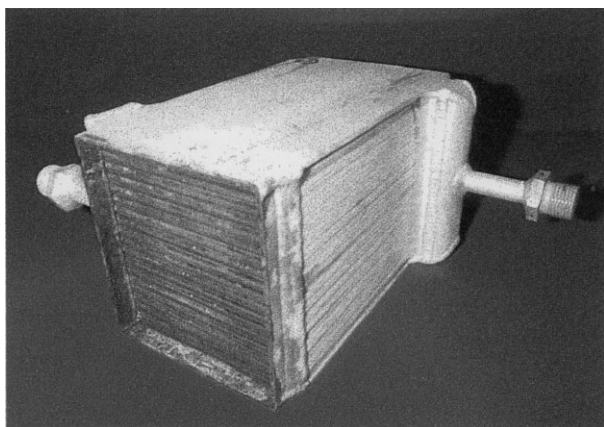
Table 2
Physical specifications of the 4-litre dual stage reactor

Specifications	Reactor 1 (Pt–Ru)	Reactor 2 (Pt–Ru)
Dimensions	100 mm (w) $\times$ 108 mm (h) $\times$ 171 mm (l)	100 mm (w) $\times$ 108 mm (h) $\times$ 171 mm (l)
Volume	1.85 l	1.85 l
Mass	2.464 kg	2.457 kg
Surface area	Gas stream tube plate 5277 cm^2	Gas stream tube plate 5277 cm^2
	Gas stream fins 15,162 cm^2	Gas stream fins 15,162 cm^2
	Oil stream tube plate 5258 cm^2	Oil stream tube plate 5258 cm^2
	Oil stream fins 15,097 cm^2	Oil stream fins 15,097 cm^2
Catalyst loading	8.54 g Pt–Ru	8.52 g Pt + Ru
Reactor material	Aluminium 1050A (99.5% pure)	Aluminium 1050A (99.5% pure)

The two reactors were operated in series with a regulated air feed supplied to each reactor. Each reactor had pre- and post-gas sampling. Six thermocouples were used in each reactor for thermal profiling. A further two thermocouples in each reactor allowed for the option of thermal control, from either the front or back face. The temperature control unit design allowed the reactors to be operated in either heating or cooling modes, depending upon start-up, transient or steady state operation. Heating oil (''Fuchs Century 610T'') was used as the heat transfer medium. CO, CO$_2$ and O$_2$ analysis of the fuel stream, both pre- and post-reactor, was carried out during all experiments.

For reactor specification, see Fig. 2 and Table 2.

4. Experimental results

Operation of the dual stage reactor with fuel flow rates up to 20 kW$_e$ SPFC equivalents was performed. The steady state recorded CO exit concentrations from the reactor

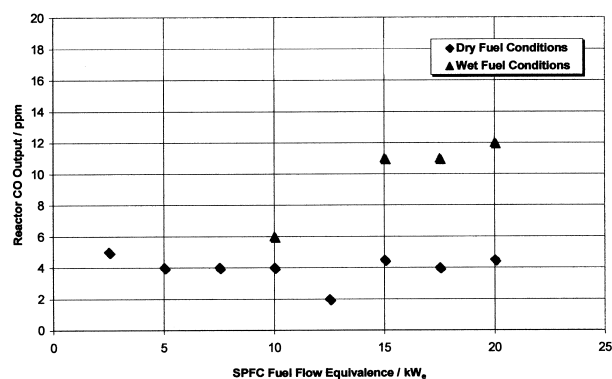Fig. 2. CO selective oxidation reactor (coated heat exchanger).

Fig. 3. CO output from the 4-litre dual stage reactor vs. fuel flow rate.
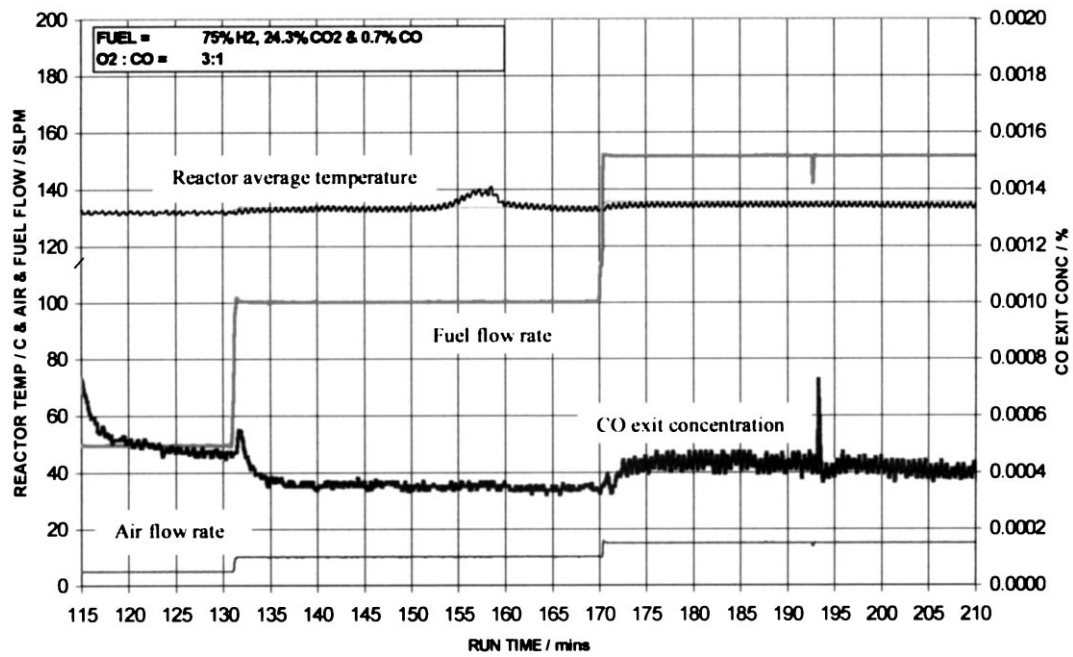
Fig. 4. CO oxidation performance of the 4-litre dual stage reactor with dry fuel.

w.r.t. fuel flow rate are shown in Fig. 3. Evaluation of the dual stage reactor with both dry (75% H_2, 24.7% CO_2 and 0.7% CO) and wet (69.4% H_2, 22.5% CO_2, 0.7% CO, 6.7% H_2O and 0.7% CH_3OH) reformed fuel compositions was carried out. A constant O_2:CO molar ratio of 3:1 was

utilised in all experiments, with a ratiometric air flow split of 2:1 between the first and second stage reactors, respectively.

The 4-litre dual stage reactor successfully demonstrated that the CO concentration present in typical methanol
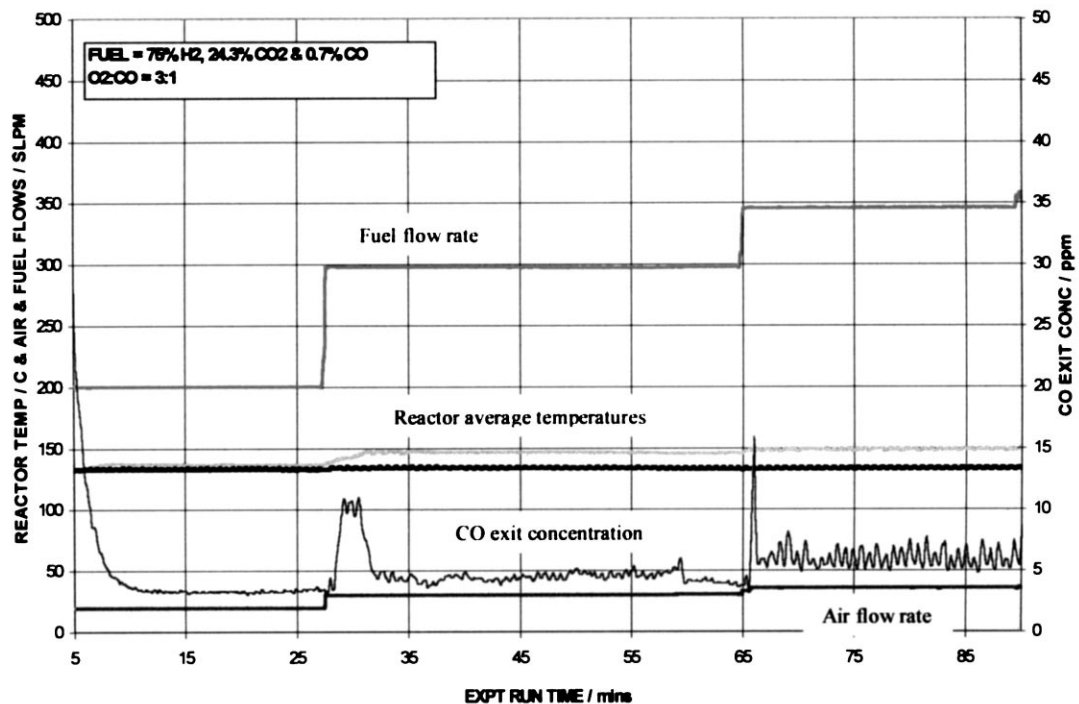

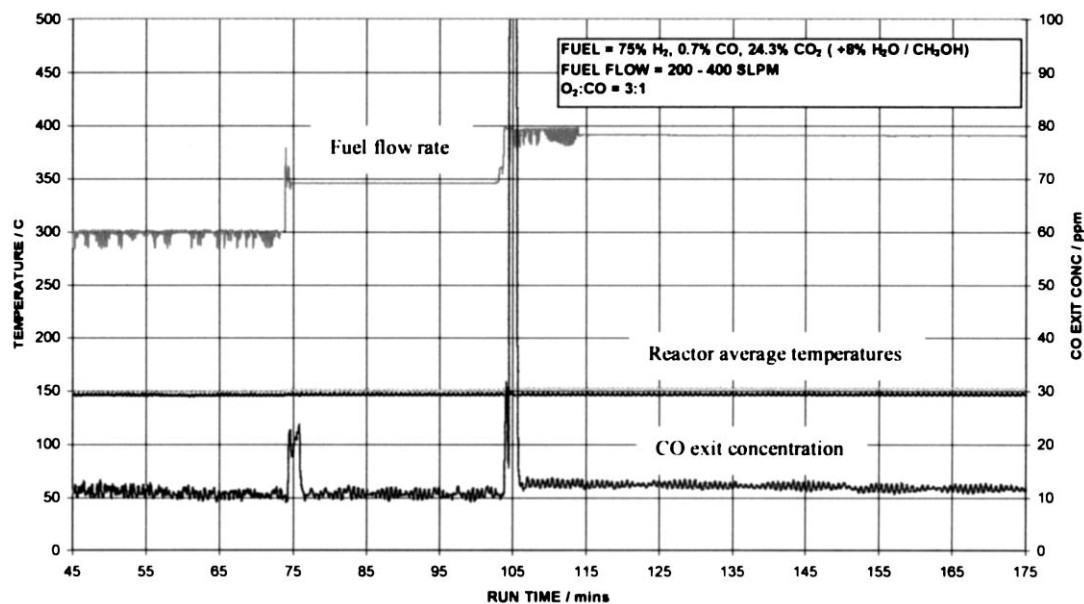Fig. 5. CO oxidation performance of the 4-litre dual stage reactor with dry fuel.

Fig. 6. CO oxidation performance of the 4-litre dual stage reactor with wet fuel.

steam reformate could be reduced from at least 7000 ppm to ≤ 12 ppm for fuel flows up to 400 SLPM (20 kW$_e$ SPFC power equivalent). The optimum average reactor temperature for such levels of CO removal was 150–160°C.

The reactor response in terms of thermal excursions and CO exit concentrations, related to fuel flow changes was recorded. Results for dry fuel flow in the range 50 to 350 SLPM are presented in Figs. 4 and 5, and results for wet conditions up to 400 SLPM are shown in Fig. 6. For dry fuel flow rate changes of 50 → 100 → 150 and 200 → 300

→ 350 SLPM, no excursions in the reactor temperatures occurred. While some momentary increase in the CO output concentration was recorded, CO levels were still maintained below 20 ppm. The high heat transfer efficiency of the reactor design was peculiarly effective in keeping the reactor at its optimum temperature during the flow changes.

For moist fuel changes of 300 → 350 → 400 SLPM, no excursions in reactor temperature were recorded, more noticeable increases in the CO output did occur compared

Table 3
Four litre dual stage reactor — CO input and O$_2$:CO molar ratio characteristics

CO inlet inlet/%	Od2:CO molar molar ratio	2/1 Air HEX split	2/1 Air HEX split	2/1 Air HEX split	1/1 Air HEX split	1/1 Air HEX split	1/1 Air HEX split
		HEX 1 average temperature/°C	HEX 2 average temperature/°C	CO exit/ppm	HEX 1 average temperature/°C	HEX 2 average temperature/°C	CO exit/ppm
0.2	1	138	138	1175	140	140	1240
0.2	2	140	140	550	142	142	700
0.2	3	140	142	50	142	142	240
0.2	4	141	141	8	144	144	17
0.5	1	142	140	3520	142	142	3620
0.5	2	140	140	2650	142	142	2850
0.5	3	154	154	300	154	154	500
0.5	4	152	154	8	160	160	23
0.7	1	153	153	4650	153	153	5000
0.7	2	153	152	2800	153	153	3350
0.7	3	167	165	75	153	154	400
0.7	4	166	166	6	155	155	28
1.0	1	160	153	6000	153	153	6700
1.0	2	158	153	3500	153	153	4100
1.0	3	166	166	50	153	153	350
1.0	3.5	168	172	6	149	162	37

(1) Fuel flow rate: 300 SLPM (15–20 kW$_e$ SPFC equivalent), (2) fuel composition: 69.4% H$_2$, 0.2–1.0% CO, 0.7% CH$_3$OH, 6.7%% H$_2$O and balance CO$_2$, (3) HEX: heat exchanger.
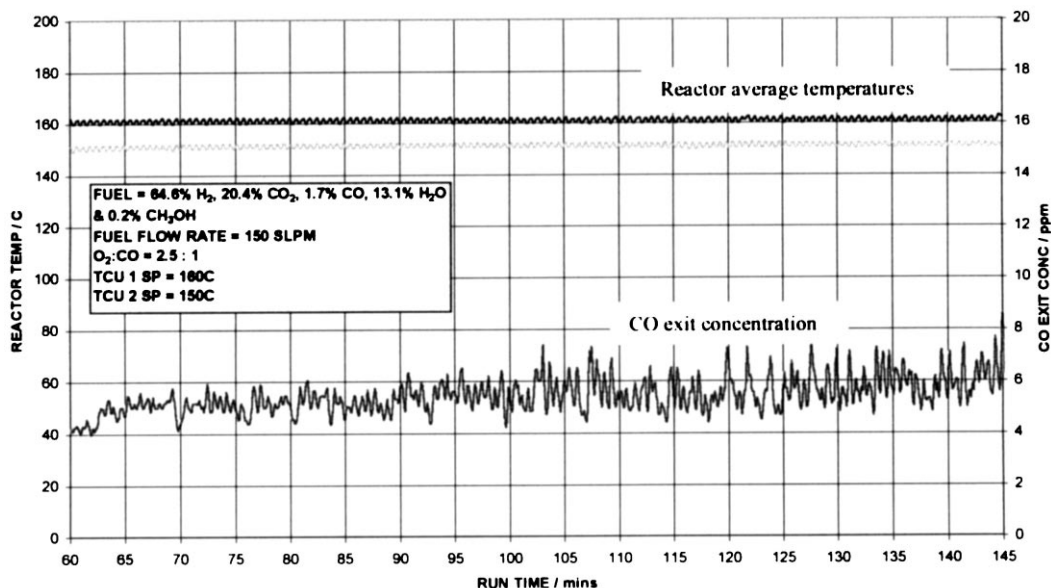
Fig. 7. CO oxidation performance with revised reformat at 150 SLPM flow rate.

to reactor operation with dry fuel. CO output concentrations were re-established within 1 to 2 min of the imposed fuel flow rate change.

The performance of the 4-litre dual stage reactor was evaluated in terms of the expected CO concentrations produced from the reformer, under typical operating conditions. The air input required to the dual stage reactor (and flow split ratios) was also investigated, in order to achieve acceptable CO concentrations. The results obtained, under steady state conditions, are summarised in Table 3.

It was found that by using a total air flow rate equivalent to an $O_2:CO$ molar ratio of $\geq 3.5:1$, CO exit concentrations of < 10 ppm were achievable for reformate CO concentrations ranging from 2000 to 10,000 ppm (1%). Once again, a ratiometric air split of 2:1 between the first and second stage reactors produced increased levels of CO oxidation, compared to an equal air split between the two reactors.

Reactor set-point temperatures of 160°C and 150°C were employed for the first and second stages, respec-
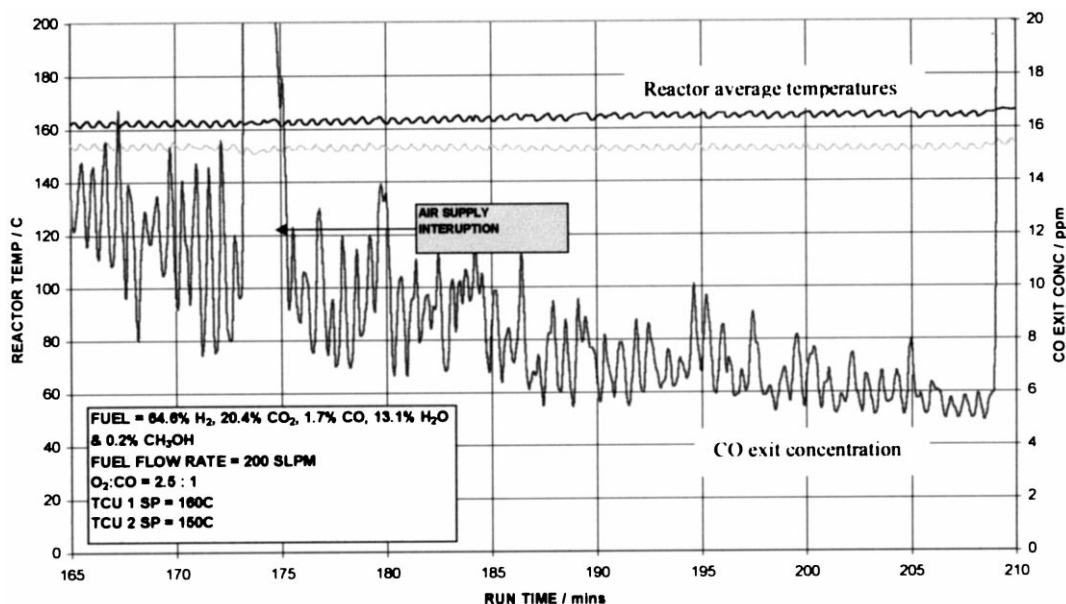

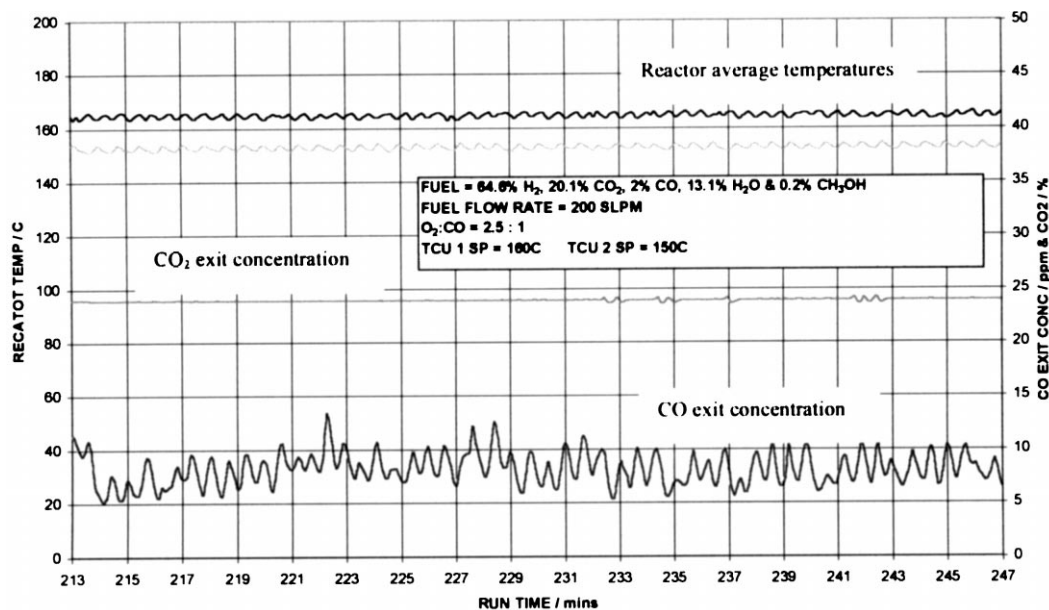Fig. 8. CO oxidation performance with revised reformat at 200 SLPM flow rate.

Fig. 9. CO oxidation performance with revised reformat at 200 SLPM flow rate.

tively. An air split ratio of 2:1 was used between the first and second stages, with a total air flow supplied to both the reactors equivalent to an O_2:CO molar ratio of 2.5:1.

Steady state data, showing the reactor performance with a revised fuel composition and with fuel flow rates of 150 and 200 SLPM, is presented in Figs. 7 and 8. Evaluation of the reactors performance with fuel flow rates > 200 SLPM (10 kW_e SPFC equivalent) was not possible, due to the upper limit of the CO mass flow controller being exceeded.

In addition, the reactor performance was also evaluated using a CO input concentration of 2% at a fuel flow rate of 200 SLPM (10 kW_e SPFC equivalent) which is composed of 64.6% of H_2, 2.0% of CO, 20.1% of CO_2, 13.1% of H_2O and 0.2% of CH_3OH. Reactor set-point temperatures of 160°C and 150°C and an air split ratio of 2:1 (O_2:CO = 2.5:1) were again employed. Results showing the reactor steady state performance are given in Fig. 9. The 4-litre dual stage reactor has, therefore, been demonstrated as having the capacity to reduce CO concentrations in a methanol reformate fuel stream from up to 2% to levels < 10 ppm.

5. Conclusions

A compact and lightweight gas clean-up system (GCU) for the selective oxidation of carbon monoxide present in reformed methanol has been developed. The prototype unit scaled for a 20 kW_e fuel cell was 3.7 l in volume and weighed 4.9 kg. To date approximately 100 h of operation at 20 kW_e equivalent flow rates have been achieved using synthetic reformate with CO output levels below 15 ppm.

The design and construction of the GCU has involved the critical assessment of a number of candidate catalyst formulations for selective CO oxidation and heat transfer technologies suitable for catalyst washcoating and ultimately GCU automotive applications.

Catalyst screening has been performed at the micro and bench scale reactor level. The most promising catalyst formulations have subsequently been applied to heat transfer substrates for further evaluation. A formulation based upon platinum and ruthenium was selected for use in the final GCU reactor design.

The compact CO selective oxidation unit was based on a dual stage reactor design. Each reactor was of 2 l (2.5 kg) in volume and the process stream chamber was washcoated with a platinum–ruthenium catalyst formulation. Each reactor was supplied with its own regulated air supply for CO oxidation. Each reactor had approximately 1 l available for reaction of the fuel stream with oxygen and 1 l for cooling via the re-circulation of heat transfer fluid.

Preliminary GCU response trials, relating to fuel flow rate changes, have shown that due to the high thermal transfer efficiency of the reactors, no transients in the reactor temperature appear to occur. Small excursions in CO level (up to 16 ppm) were observed using dry reformate, larger excursions (up to about 160 ppm lasting for up to 2 min) were observed using moist reformate.

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