On-board hydrogen generation for transport applications: the HotSpot™ methanol processor

Neil Edwards, Suzanne R. Ellis, Jonathan C. Frost, Stanislaw E. Golunski*, Arjan N.J. van Keulen, Nicklas G. Lindewald, Jessica G. Reinkingh

Johnson Matthey Technology Centre, Blount's Court, Sonning Common, Reading RG4 9NH, UK

Abstract

In the absence of a hydrogen infrastructure, development of effective on-board fuel processors is likely to be critical to the commercialisation of fuel-cell cars. The HotSpot™ reactor converts methanol, water and air in a single compact catalyst bed into a reformate containing mainly CO_2 and hydrogen (and unreacted nitrogen). The process occurs by a combination of exothermic partial oxidation and endothermic steam reforming of methanol, to produce 750 l of hydrogen per hour from a 245-cm^3 reactor. The relative contribution of each reaction can be tuned to match the system requirements at a given time. Scale-up is achieved by the parallel combination of the required number of individual HotSpot reactors, which are fed from a central manifold. Using this modular design, the start-up and transient characteristics of a large fuel-processor are identical to that of a single reactor. When vaporised liquid feed and air are introduced into cold reactors, 100% output is achieved in 50 s; subsequent changes in throughput result in instantaneous changes in output. Surplus energy within the fuel-cell powertrain can be directed to the manifold, where it can be used to vaporise the liquid feeds and so promote steam reforming, resulting in high system efficiency. The small amount of CO that is produced by the HotSpot reactions is attenuated to <10 ppm by a catalytic clean-up unit. The HotSpot concept and CO clean-up strategy are not limited to the processing of methanol, but are being applied to other organic fuels. © 1998 Elsevier Science S.A.

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1. Introduction

It now seems probable that internal-combustion powered vehicles will be superseded by electric vehicles, during the course of the first half of the next century. The incentives for this change come from stringent legislation for controlling local pollution, and from the global need for the responsible use of fuel. In the design of vehicles, the conflicting demands of high performance and environmental protection can be overcome by using a fuel cell to generate on-board electric power. The development of fuel-cell powered and hybrid vehicles is well advanced, but is not matched by progress in establishing an infrastructure for the distribution and supply of hydrogen. In the short to medium term, therefore, on-board generation of hydrogen from liquid or liquefied fuels can provide the answer.

Some of the earliest attempts at mobile hydrogen generation pre-date the current phase of development of electric vehicles. During the 1970s, the Jet Propulsion Laboratory proposed the concept of injecting hydrogen into an internal combustion engine [1], as a way of improving efficiency and lowering NO_x emissions. The work demonstrated the feasibility of generating a hydrogen-rich gas stream by on-board partial oxidation of gasoline [2]. In the following decade, Volkswagen tested a similar concept for methanol-combustion engines [3], again using some of the primary fuel to produce hydrogen in situ. In both cases, the reformate contained a high concentration of CO, which did not pose any problems in the particular application being targeted. However, the technology developed at that time cannot be directly used for the current target application of supplying hydrogen to solid polymer fuel cells, which will only tolerate very low CO concentrations (typically <40 ppm) [4].

The new fuel-processing technologies, which are being specifically tailored to fuel-cell applications, tend to be based on either partial oxidation or steam reforming. The Arthur D. Little multi-fuel processor comprises three con-

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* Corresponding author.

secutive stages (partial oxidation followed by a high- and low-temperature water-gas shift) [5]; Argonne National Laboratory describes its methanol processor as functioning by partial oxidation, but several other reactions (such as steam reforming, methanol decomposition, and water-gas shift) are also believed to be taking place [6]; both Toyota [7] and Daimler Benz [8] have successfully demonstrated on-board steam-reforming of methanol in prototype vehicles. Each approach has its advantages and its limitations.

- Partial oxidation offers compactness, fast start-up, and rapid responses.
- Steam reforming produces higher concentrations of hydrogen, and results in higher system efficiencies.

The ideal mobile fuel-processor should combine the advantages of both approaches.

In the original version of the Johnson Matthey HotSpot reactor, an oxygenate [9] or hydrocarbon [10] fuel was co-injected with air into a large catalyst bed, where hydrogen was formed by partial oxidation within a highly localised reaction zone (the hot spot). When the feed was methanol/air (mol ratio = 1:2.5), a self-starting and self-sustaining reaction began to take place immediately. From cold start-up, the reaction took 25–30 min to reach a steady state, at which the temperature within the hot spot was constant at ca. 600°C, and the hydrogen concentration in the reformate stabilised at 41%. The reaction was most closely represented by the following overall stoichiometry [11]:

$$CH_3OH + 0.5\,(O_2 + 3.76N_2) \rightarrow CO_2 + 2H_2 + 1.88N_2 \qquad (1)$$
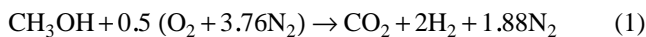
In this steady state, a maximum specific hydrogen-output of 12 l/h per litre of catalyst was produced.

We have since concentrated on improving the performance of the HotSpot reactor for processing methanol. Our decision to focus on methanol was based on several factors:

- it contains a high H/C ratio, which means it has a lower propensity for soot formation than hydrocarbons;
- it is a relatively clean fuel, in terms of its production and its composition;
- it can be made from renewable sources;
- a great deal of expertise in its use as a fuel already resides within the car companies and vehicle subsystem manufacturers.

Through an iterative process of reactor engineering and catalyst design, we have intensified the output of our methanol HotSpot reactor and reduced its start-up time, while maintaining 99–100% conversion and low CO. Using a modular approach to scale-up, these qualities are not compromised by the construction of high power fuel-processors. We have also designed and developed the complementary technologies (for cleaning the reformate, and using the hydrogen rejected by the fuel cell) that allow HotSpot to be integrated into a vehicle drivetrain.

2. Individual hotspot reactor performance

The current methanol HotSpot reactor is a small cylinder (volume = 245 cm^3), with inlet and outlet connections in the base. The reactor will start to function if methanol is supplied in the form of liquid or spray. However, for the high throughputs required for mobile applications, the liquid feeds (methanol and water) are best pre-vaporised and mixed with air, before being supplied to the reactor. The vaporisation and mixing are carried out in a heated chamber, which is maintained at a temperature of 130–150°C (see Section 3).

When the feed contains only methanol and air (mol ratio = 1:2.5), the reactor functions purely by partial oxidation to produce a reformate containing 41% hydrogen when dried. As shown in Eq. (1), partial oxidation produces 2 mol H$_2$/mol methanol consumed. By including water in the feed, and reducing the amount of air, the hydrogen concentration in the reformate can be increased to 58% (dry gas analysis), corresponding to 2.42 mol H$_2$/mol methanol consumed. Under these conditions, the reactor is functioning by a combination of partial oxidation and steam reforming. The endothermic contribution of the methanol + water reaction lowers the catalyst bed temperature (to 400°C maximum), resulting in excellent durability. As both the exothermic and endothermic reactions occur on the same catalyst particles, heat transfer occurs over very short (microscopic) distances. This is in contrast to conventional designs for autothermal processors, in which heat is exchanged between two separate reactor stages, each containing a different catalyst that needs to operate at its own optimum temperature and space velocity.

Using a feed (vaporised methanol/water + air) intended to achieve near autothermal operation, a cold reactor will start to produce hydrogen immediately, and will reach its steady-state output in 2–5 min (depending on the exact reactant stoichiometry). However, the start-up time can be accelerated simply by using a leaner reactant feed until the maximum temperature in the catalyst bed reaches 400°C, before switching to the standard feed. As shown in Fig. 1, when starting-up with a reactant feed required to produce 625 l/h of hydrogen, the reactor takes 70 s to reach 75% of the steady-state output and 170 s to reach 100%. Increasing the air feed rate by 20% during start-up (before switching to the standard feed when the bed temperature approaches 400°C) results in the reactor reaching 75% output in only 20 s, and 100% in 50 s.

The CO concentration in the HotSpot reformate is highly dependent on the catalyst bed temperature. This means that in the first few seconds after cold start-up, the CO concentration is negligible, before rising to a maximum of 2–3% (of dry reformate) as the reactor reaches its near autothermal steady state. During changes in throughput, the CO concentration does not change, providing the reactant stoichiometry is not altered. Similarly, the concentrations of the other components of the reformate remain unchanged, even
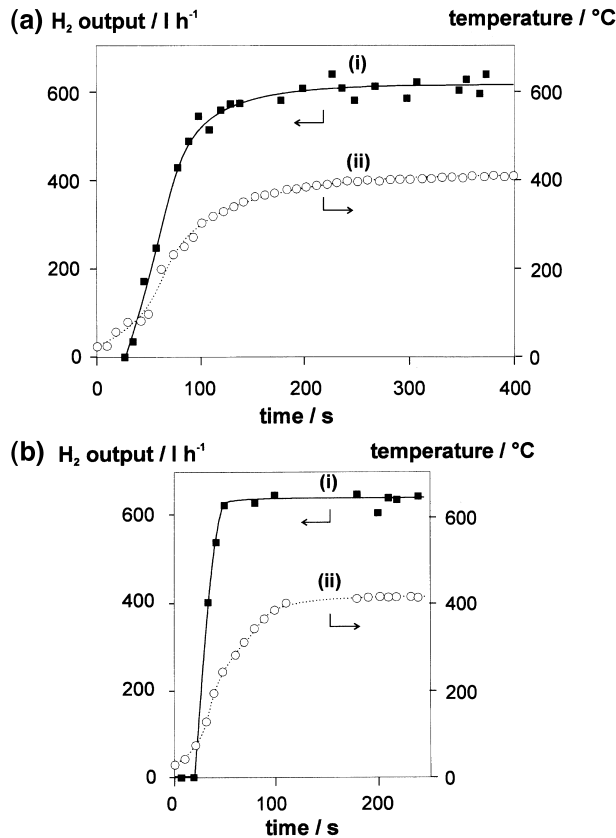
(a) H₂ output / l h⁻¹   temperature / °C

(b) H₂ output / l h⁻¹   temperature / °C

Fig. 1. Start-up of HotSpot reactor: (a) using steady-state conditions (methanol/O_2 = 4.4); (b) using extra air (methanol/O_2 = 3.7 when bed temperature < 400°C; methanol/O_2 = 4.4 when bed temperature reaches 400°C).

though the flow-rate responds immediately to changes in throughput.

Based on the assumption that 1000 l of H_2/h is equivalent to 1 kW$_e$, each HotSpot reactor is currently rated at 750 W of fuel cell power. Although the maximum output can be increased (Fig. 2), it is at the cost (i) of methanol conversion (which drops below 99% at ca. 850 l/h of H_2) and then (ii) of low CO (which approaches 4% at 1000 l/h of H_2).

3. Modular processor design

A key feature of HotSpot is its modular design. Hydrogen output is scaled-up by combining the appropriate number of individual reactors, which are fed in parallel from a central manifold. Fig. 3 shows a 6-kW processor, comprising a quartet of reactors on each side of a flat manifold, but other arrangements and shapes are possible. The liquid feeds are vaporised and mixed with air in a chamber inside the manifold. An identical pathlength to each reactor ensures equal distribution of reactants, so that the start-up time and transient response of a large processor are the same as for a single reactor.

The manifold has the additional function of heat exchange, allowing surplus energy to be used to vaporise

the liquid feed, so ensuring high efficiency of the overall system. During fast start-up under partial oxidation conditions, the exothermic heat of reaction produced by the Hot-Spot reactors is conducted through the manifold to heat the incoming feed. When the temperature inside the vaporisation chamber reaches its optimum for steady-state operation (130–150°C), the feed can be changed to a mixture of methanol, water and air. Under conditions, where the Hot-Spot reactors are running endothermically, the heat input can be provided by the hydrogen rejected by the fuel cell. In our present design, this is achieved by combusting the anode-reject gas in a separate catalytic afterburner, and circulating the hot exhaust-gas within the manifold.

As the afterburner will combust methanol at ambient temperature, it can also be used to provide rapid heat during start up.

Another advantage of the modular design is that it provides an extra control option. Instead of changing the hydrogen output by turning-up or turning-down the feed rates, the output can be stepped up or down simply by changing the number of active reactors (or banks of reactors). This option is particularly useful at very low output (<10% of the maximum), where using a low feed rate to each reactor can result in methanol slip and above average CO concentrations.

4. CO clean-up

There are several well tried methods for removing CO from a mixed gas stream. These include (i) methanation, (ii) preferential oxidation and (iii) the use of hydrogen permeable membranes. In the context of a fuel-cell system, each has its limitations.

1. Methanation requires three molecules of hydrogen for each molecule of CO. This means that the hydrogen loss is equivalent to at least 3 times the concentration of CO removed. Furthermore, selective methanation of CO is
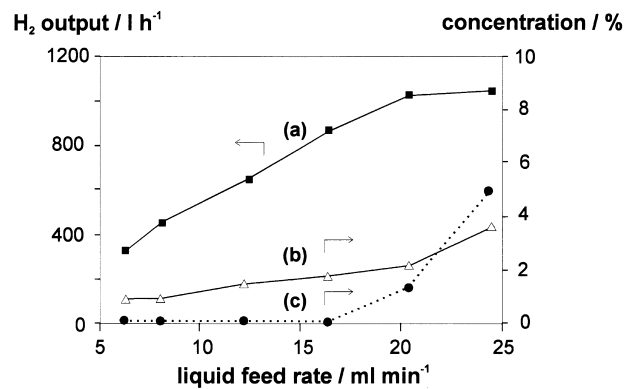
H₂ output / l h⁻¹   concentration / %

Fig. 2. Effect of throughput on steady-state performance of HotSpot reactor (liquid feed = 55% methanol/45% water, by mass; methanol/O_2 = 5.0; manifold temperature = 150°C). (a) Rate of hydrogen output, (b) CO concentration of reformate, (c) methanol concentration of reformate.

very difficult to achieve and control in the presence of a large excess of CO_2 [12]. When pure hydrogen is required in the chemical process industry, any CO_2 is first removed (using an alkaline absorber) before the CO is methanated [13], but this is not practical on board a vehicle.

2. Several catalysts are known for the selective oxidation of CO in the presence of hydrogen, but some require such low temperatures [14] or such a narrow temperature window [15] that the clean-up reactor would require very careful cooling and temperature control. In general, catalysts for preferential CO oxidation owe their selectivity to the fact that H_2 oxidation is blocked by CO adsorption [16]. However, H_2 oxidation will begin to predominate at low partial pressures of CO, when relatively few catalytically-active sites are blocked. In practice, this means that the preferential oxidation of CO can become increasingly difficult as the CO concentration declines.

3. Palladium (and Pd-alloy) diffusers are highly effective at excluding all other gases apart from hydrogen, but require a high pressure differential (10–20 bar) and a relatively high temperature (300–400°C) to allow hydrogen to permeate at a sufficiently high rate [17]. The performance of the HotSpot reactor is largely insensitive to pressure changes, but its operation at high pressure would require a multi-stage compressor, which would have an adverse impact on system efficiency. Another penalty in efficiency would arise from the need to heat either the HotSpot reformate, which emerges from the manifold at 180°C, or the membrane.

Having carefully assessed these methods, the strategy we have developed is based on the concept that CO can be removed more effectively in several small and highly selective catalytic stages, than in one large catalyst bed. Initially, we demonstrated this on a microreactor scale, using a synthetic reformate, containing 5% CO, 15% CO_2, 40% H_2 and 40% N_2. The reformate was passed through a water saturator (at room temperature) before being fed to an isothermal multi-stage reactor with air injection. As shown in Table 1, the reactor could be tuned to achieve extremely low CO concentrations at the expense of very little hydrogen,
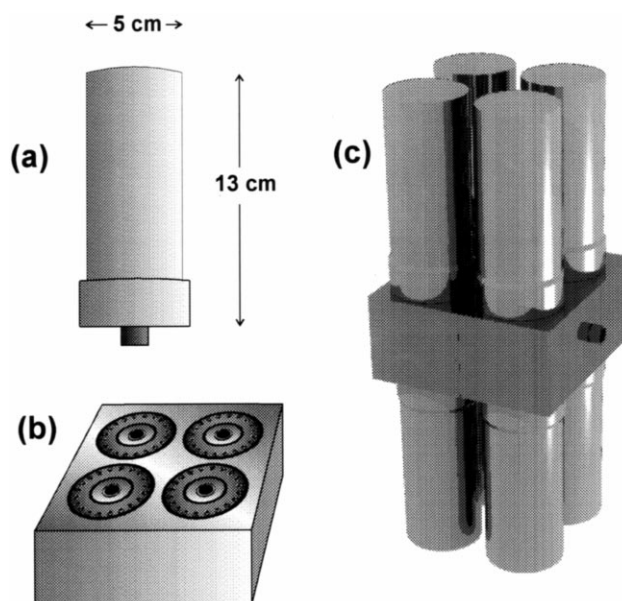

Fig. 3. Modular HotSpot assembly: (a) individual reactor, (b) manifold, (c) 6-kW methanol-processor.

with no sign of de-activation. Based on this performance, we predicted that if linear scale-up proved possible, a clean-up unit would be about 20% of the volume of a HotSpot methanol processor, and that 95% of the hydrogen would emerge from the unit.

Our scale-up prediction has so far been tested on the 6 kW scale, where we have constructed a clean-up unit for the eight-unit processor shown in Fig. 3. The unit, which is 40% of the size of the processor, is larger than predicted. However, the additional volume is largely accounted for by the engineering, and not by an increase in the number of catalytic stages or in their relative size. The unit will attenuate CO to below 10 ppm with high selectivity, even when the inlet CO concentration is comparatively high (see Table 2).

5. Efficiency of the integrated system

The efficiency of a fuel-cell drivetrain will depend both on the performance of the individual components and on the way in which they interact within the integrated system. One of the key factors is the nature of the hydrogen supply. The decision to produce reformate in situ, instead of using pure hydrogen, has implications at several points throughout the system. Losses in efficiency can take place:

1. inside the fuel processor (by incomplete conversion, or waste of fuel by combustion instead of the desired partial oxidation, steam-reforming and water-gas shift reactions);
2. during CO-removal (by associated loss of hydrogen);

Table 1

CO clean-up performance of the multistage microreactor. Inlet composition of synthetic reformate with added air: 33.7% H_2, 2.7% O_2, 4.2% CO, 12.7% CO_2, 43.7% N_2, 3% H_2O; feed rate: 46 cm^3/min; total mass of catalyst: 200 mg; space velocity: 14 000 cm^3/g_{cat} per h

Elapsed time (h)	Outlet CO concentration (dry) (ppm)	Outlet H_2 concentration (dry) (%)
43	3	32.3
72	2	32.6
96	2	32.5
120	3	32.5

Table 2

CO clean-up performance of a 6-kW unit. Composition of reformate produced by a 6-kW processor operating at 80% throughput: 45.6% H_2, 2.6% CO, 16.6% CO_2, 18.2% N_2, 17% H_2O; flow-rate: 11 400 l/h; rate of air addition: 35 l/min

Outlet CO concentration (dry)	8 ± 5 ppm
Outlet H_2 concentration (dry)	43%
Rate of H_2 output	4900 l/h
H_2 converted	5.77%

3. in the fuel cell (by incomplete utilisation of the hydrogen in the reformate);
4. by the parasitic power requirements of ancillary components (such as pumps, valves and compressors).

In our system design (Fig. 4), hydrogen rejected by the fuel-cell anode is combusted in a catalytic afterburner, which provides energy to pre-heat the HotSpot feeds, and so promotes the endothermic steam-reforming reaction. Operated in this way, the steady-state efficiency of the HotSpot reactors is 95.4%, while that of the CO clean-up unit is 93.5%, resulting in a value of 89% for the conversion of fuel to usable reformate (higher heating value of H_2 supplied to the fuel cell × 100%/higher heating value of methanol consumed). Our simulations indicate that the overall fuel-cell efficiency for our system (net kW_e/higher heating value of methanol consumed) could be as high as 40%. This is comparable with the figure that we predict for a fuel cell supplied by a methanol steam-reformer, which in turn is 1.25 times as efficient as a fuel cell supplied by pure partial oxidation.

6. Conclusions

The HotSpot methanol processor has many of the qualities required of a mobile hydrogen source for electric cars. It is compact, fast starting, efficient and responsive. It needs, however, to be coupled with a clean-up strategy to achieve the low CO-concentrations tolerated by solid polymer fuel cells. Although the size and selectivity of our catalytic CO clean-up unit have yet to be optimised, the unit already allows HotSpot to meet the fuel-processing targets for CO-concentration (<10 ppm steady state; <100 ppm transient) and specific output (0.75 kW_e/l of fuel-processing system), set by the US Partnership for a New Generation of Vehicles [18].

The predicted efficiency of an electric drivetrain, comprising a HotSpot methanol processor (+CO clean-up), fuel cell and electric motor, overlaps with the top end of the range projected for advanced internal-combustion engines. Critically, though, HotSpot does not produce the particulate and NO_x emissions, which the designers of the most efficient diesel engines are struggling to control at realistic cost. Other emissions (CO, CO_2, organics, SO_x) are also substantially lower than for the best internal-combustion engines, irrespective of whether the analysis starts at the fuel tank or at the oil well [19].

One of the most topical issues is whether the fuel for on-board processors should be methanol or petroleum-derived. The strongest argument in favour of gasoline-type fuels is the existence of a global infrastructure for their distribution and supply. By contrast, the infrastructure for methanol is limited and localised. However, the development of com-
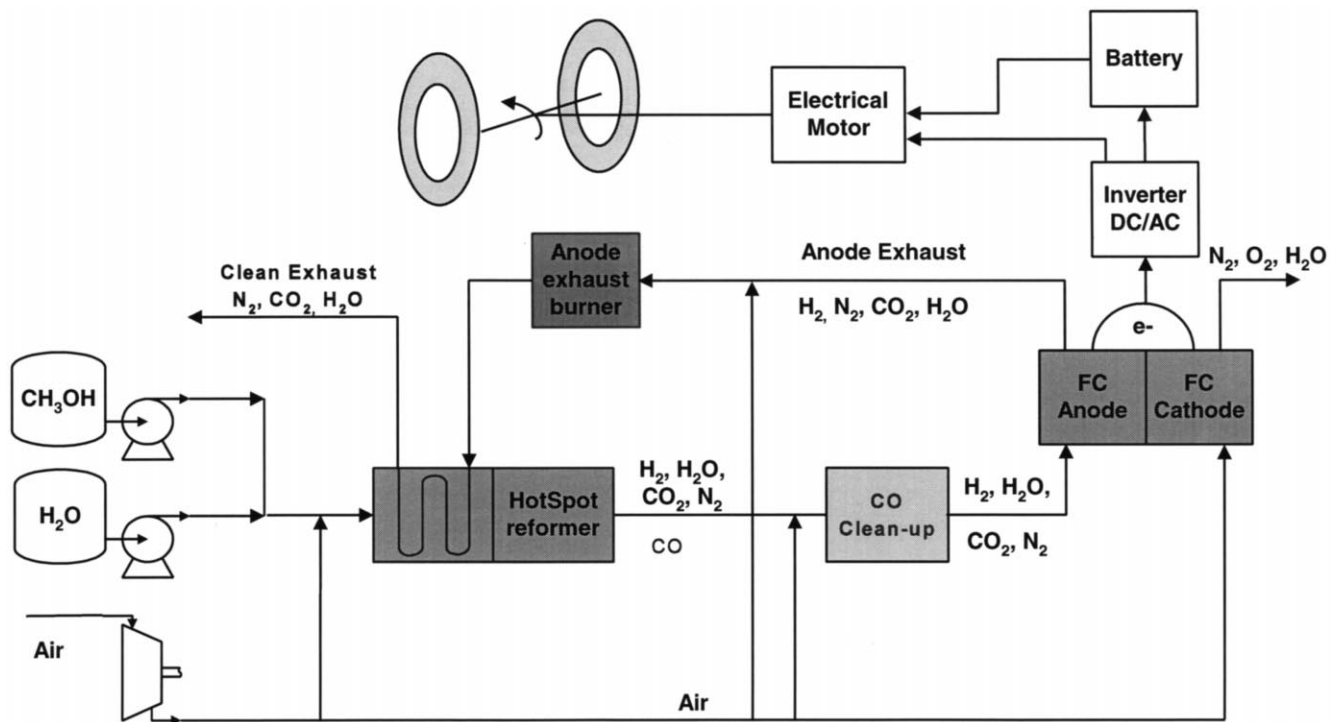

Fig. 4. Design for electric drivetrain incorporating HotSpot methanol-processing technology.

plete vehicle drivetrains based on methanol processing is further advanced, with demonstration vehicles already being exhibited by Toyota and Daimler Benz. Although the work at Johnson Matthey has so far focused on methanol processing, we believe that HotSpot technology (including CO clean-up) can be adapted to other fuels. Apart from striving to optimise our methanol processor, we have begun to design the catalysts and reactors that should allow us to develop HotSpot processors for alternative fuels.

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