HotSpot™ Fuel Processor

ADVANCING THE CASE FOR FUEL CELL POWERED CARS

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The number of road vehicles in the world is set to double in the next twenty years. Such rapid growth threatens to destroy the clean air in regions where air pollution has not been a problem up to now, and to reverse the improvements in air quality that have resulted from the use of catalytic converters to clean-up exhaust emissions in traffic congested areas. Thus, there is a compelling need to develop high efficiency passenger cars, free of emissions. One very promising option is the use of the fuel cell, which generates energy efficiently by converting hydrogen to steam. However, there are major drawbacks to carrying and using hydrogen on vehicles, including the complexities of re-fuelling and the absence of a so-called hydrogen economy. Hydrogen fuelling of fuel-cell powered cars must be the ultimate goal and the most practical near-term solution is to use an on-board fuel processor to generate hydrogen from a liquid fuel while driving, and such a processor, the Hotspot™, is described here.

An on-board fuel processor must be fast-starting, compact, efficient, responsive and clean. Most fuel processors meet several of these requirements, but the HotSpot™ technology developed by Johnson Matthey can meet them all. It combines the speed and compactness of partial oxidation with the efficiency of steam reforming. The balance between these two processes can be adjusted to respond to the different demands on the vehicle during use. The technology is simple to scale-up, and the maximum required output is achieved by combining in parallel the appropriate number of basic reactor units, see Figure 1. Although HotSpot™ produces some carbon monoxide, this can effectively be eliminated by a clean-up reactor. So far, the technology is most advanced for methanol processing, but the HotSpot™ concept is also being applied to hydrocarbon fuels.

The Need for HotSpot™

While the human population has doubled since 1950, the number of cars in the world has increased 7-fold (1). In North America, Western Europe and Japan, the growth rate in car population is expected to stabilise soon at about one per cent per year, but the total road distance travelled in these regions is rising at a much faster rate (about four per cent per year in the U.S.A.). There is also an explosive rise in car traffic in some countries, for example, by the year 2010, the number of cars in China is predicted to grow 90-fold compared to the year 1990; while in India, the growth is expected to be 35-fold for the same period. Overall, the world car population could double from 400 million to 800 million in the next 20 years (1).

How can the detrimental effects to the atmosphere of such rapid growth in road traffic be minimised? The regulated emissions, produced by road vehicles, of carbon monoxide, hydrocarbons and nitrogen oxides, are responsible for localised pollution problems, such as poor air quality or photochemical smog. The major unregulated emission, carbon dioxide, contributes to the global greenhouse effect, which is implicated in climate change. In recent years, vehicle manufactures have fitted a catalytic converter into the car exhaust system to reduce localised pollution. Current noble metal containing catalytic converters are very effective at removing 90 to 95 per cent of the regulated
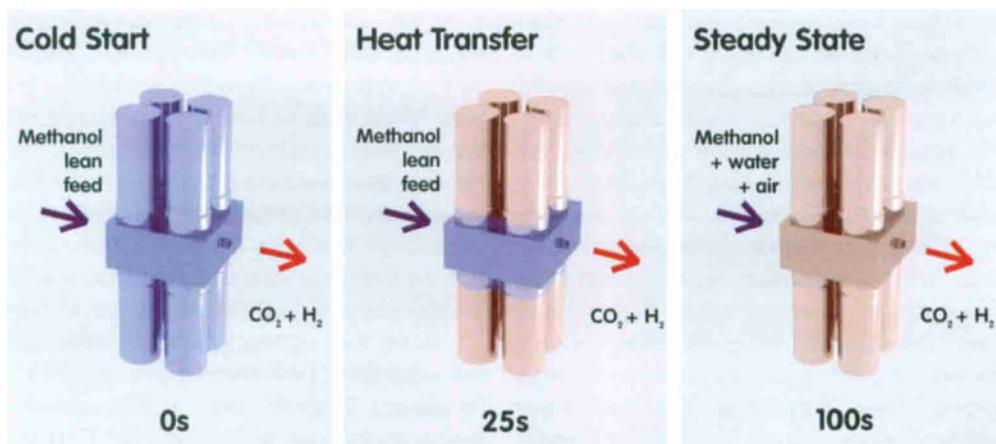
Fig. 1 An 8-unit HotSpot™ processor has a volume of 6 litres, weighs 8.8 kilograms and will produce 6000 litres per hour of hydrogen. Initially, the processor can be started by partial oxidation; after 25 seconds, heat is transferred from the reactors to the manifold; then after 100 seconds, the feed composition is changed to allow steam reforming as well as partial oxidation

emissions, and are continuously being improved (2). The release of carbon dioxide is being tackled by edging-up vehicle efficiency from its present level of about 12 to 15 per cent, by improving the designs of the internal combustion engine and the vehicle structure. However, alternative technology, based on an electric motor powered by a fuel cell, is also being developed. The fuel cell offers the promise of vehicle efficiencies as high as 30 to 40 per cent, with no release of emissions other than pure steam.

The high intrinsic efficiency of a fuel cell arises from the fact that, as an electrochemical reactor, it produces mainly electrical energy while converting hydrogen and oxygen to steam (3). By contrast, an internal combustion engine generates mostly waste heat and only a small proportion of useful mechanical energy. Furthermore, internal combustion of gasoline or diesel fuel produces a complex mixture of products, including unreacted hydrocarbons, carbon monoxide (from the incomplete combustion of the fuel) and nitrogen oxides.

The major operational disadvantages of a fuel cell – its slow start-up and lack of response to short peak-loads – can be overcome by coupling it with a battery. Although the maximum efficiency is reduced to 25 to 35 per cent by this kind of hybridisation (1), it is still substantially higher than for a conventional internal combustion car.

In the past year both Toyota and Daimler Benz have exhibited experimental passenger cars, in which electrical power is generated by a solid polymer fuel cell (SPFC). The Daimler Benz (Mercedes A-class) car is powered entirely by the SPFC, while the Toyota (Rav 4) car uses a fuel cell/battery hybrid. Both cars carry methanol as fuel, which is catalytically processed on-board to produce a hydrogen-rich feed for the fuel cell.

On-Board Hydrogen Generation

The concept of generating hydrogen while driving is widely seen as the answer to the supply problem caused by the absence of a 'hydrogen economy'. However, the optimum choice of fuel and processor for this purpose is much more contentious. Daimler Benz and Toyota have demonstrated a commitment to using methanol and converting it to hydrogen by reaction with water (steam reforming). Other car companies would prefer to use existing motor fuels. With this aim, Arthur D. Little has recently demonstrated a compact fuel cell system, which produces hydrogen by reacting gasoline with a controlled amount of air (partial oxidation).

In fact, most of the fuel-processing technologies being looked at or developed for mobile use

are based either on partial oxidation or steam reforming. Partial oxidation is a fast process, resulting in small reactor size, fast start-up and rapid response to changes in load. Being exothermic, however, it can lead to low vehicle efficiency if the heat generated is wasted. By contrast, steam reforming is potentially more efficient, producing hydrogen from both the fuel and the water feed. Being endothermic, 'waste' energy from other parts of the system can be usefully recycled. Unfortunately, steam reforming is a slow process, requiring a large reactor and long response times. Thus, to achieve compactness and fast response requires compromise. Usually methanol conversion, and hence efficiency, is sacrificed in an on-board steam reformer.

The HotSpot™ reactor is a fitting alternative, as it combines the best features of both processing methods. It can be started up from cold by partial oxidation, so generating enough heat to drive the endothermic steam reforming process. Since both processes occur on the same HotSpot™ catalyst particles, heat transfer occurs over microscopic distances, so avoiding the need for complex heat-exchange engineering. When surplus energy becomes available from other parts of the system (for example hydrogen rejected by the fuel cell) it can be diverted to the HotSpot™ reactor(s) to increase the amount of steam reforming.

The reactors can be combined in parallel to produce a range of modular fuel processors with different maximum outputs, but identical response times. The relatively low concentration of carbon monoxide produced is removed catalytically by a small custom built reactor.

The History of HotSpot™

The original HotSpot™ reactor was invented in the mid 1980s (4). An oxygenate or a hydrocarbon was co-injected with air into a large bed of catalyst to produce a high yield of hydrogen (5). The name 'HotSpot™' refers to the small reaction sphere (~ 1 cm diameter) which formed around the point of injection, and in which most of the catalytic chemistry appeared to take place.

When methanol was the processed fuel, the catalyst bed was prepared in two layers: the first

was a base metal partial oxidation catalyst; the second a noble metal total oxidation catalyst. The injection point was at the centre of the first layer. When methanol and air were injected into the cold reactor, total oxidation (to carbon dioxide and steam) began spontaneously as the reactants reached the lower layer. Transfer of heat back to the first layer initiated partial oxidation (to carbon dioxide and hydrogen) around the injection point and a hot spot began to form.

A steady state (characterised by stable product composition) was reached after about 25 to 30 minutes. Thereafter, the temperature within the hot spot was stable at around 600°C. In this steady state there was complete conversion of methanol by partial oxidation, to produce 2 molecules of H_2 for each molecule of CH_3OH consumed (6). The process was entirely self-sustaining. The reactor produced up to 12 times its own volume of hydrogen per hour.

Although work has been done with hydrocarbon fuels, priority is presently being given to developing HotSpot™ for on-board methanol processing, as we subscribe to the view, held in particular by the major German car manufacturers, that methanol merits careful consideration as a fuel for SPFC powered vehicles. This view comes from the facts that methanol:
- contains a high H/C ratio
- is a relatively clean fuel, both in terms of its production and composition, and
- can be made from renewable sources, and so need not add to the net carbon dioxide in the atmosphere.

Through an iterative process of reactor engineering, catalyst design and performance mapping, the performance of the HotSpot™ reactor has been dramatically improved for methanol processing. The reactor now contains a single-bed of multicomponent noble metal/base metal catalyst. It produces hydrogen as soon as a feed of methanol/air or methanol/water/air enters, and it can reach steady state within a minute. The output has been improved by over two orders of magnitude, so that the current reactor produces 50 times its own volume of hydrogen per minute. Over the past 18 months, the design and construction of large HotSpot™

methanol processors for integration into SPFC systems has been undertaken, with the development of other key components, such as a clean-up unit (to remove carbon monoxide) and a catalytic afterburner (to use the hydrogen rejected by the fuel cell) being part of the work.
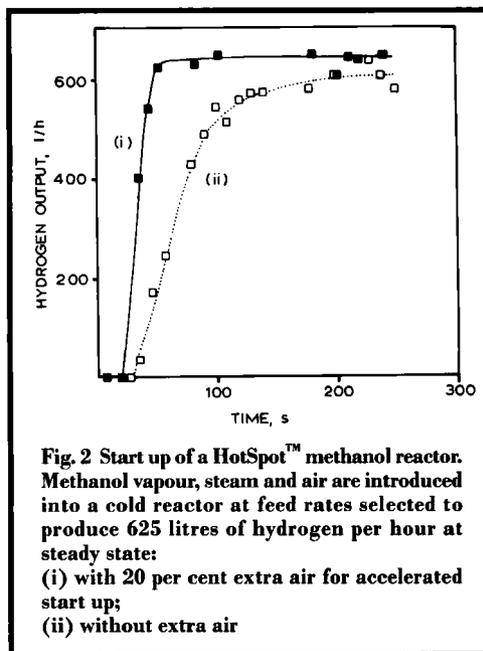
The HotSpot™ Methanol Processor

The current HotSpot™ reactor operates most efficiently when it converts methanol by a combination of (exothermic) partial oxidation and (endothermic) steam reforming. By supplying a feed of methanol/water/air, the two processes can be made to sustain each other. Under these autothermal conditions, as much as 2.4 moles H_2 are produced for each mole of CH_3OH consumed. Also, the maximum temperature inside the reactor is only 400°C, giving excellent catalyst durability. If very low rates of hydrogen production are required, the methanol and water can be supplied as droplets or spray, while, for the high rates needed for vehicle applications, the liquid feeds should be vaporised.

When a feed of steam, vaporised methanol and air (in the proportions needed for autothermal operation) is supplied to a cold reactor, hydrogen starts to form immediately and stabilises after several minutes. As shown in Figure 2, start-up can be accelerated by adding more air to the feed at first to promote partial oxidation. When the catalyst bed temperature approaches its optimum (after 40 seconds, see Figure 2(i)), the amount of air can be cutback, and the reactor rapidly reaches a steady state. Once there, any change in feed rate produces an instant change in hydrogen output. With the present design of processor, the maximum hydrogen output is 750 litres per hour, from a 245 cm³ reactor. This is equivalent to a power density of 3 kW per litre for each reactor, assuming that 1000 litres of hydrogen per hour will produce 1 kW of SPFC power.

Eliminating Carbon Monoxide

In common with other fuel processors, the HotSpot™ methanol reactor produces some carbon monoxide (CO). But, unlike some other technologies, it does not produce large spikes

Fig. 2 Start up of a HotSpot™ methanol reactor. Methanol vapour, steam and air are introduced into a cold reactor at feed rates selected to produce 625 litres of hydrogen per hour at steady state:
(i) with 20 per cent extra air for accelerated start up;
(ii) without extra air

of CO at any stage during normal operation. In fact, the rate of CO production by HotSpot™ is highly dependent on the catalyst bed temperature. In practice, this means that the product gas contains negligible CO during the first few seconds of start-up from cold. As the reactor approaches steady state, the CO concentration rises and stabilises at about 2 per cent.

Carbon monoxide is a poison for SPFC at concentrations above about 40 ppm, therefore, it is necessary to remove most of the CO from the processed gas stream. On assessing the usual removal methods, each was found lacking:
• catalytic methanation (reaction with hydrogen to form methane) – at best it consumes 3 molecules of useful hydrogen for each molecule of CO it removes, and at worst it can waste all the hydrogen if it converts the carbon dioxide in the processed gas as well;
• catalytic preferential oxidation – like methanation it is difficult to ensure that very little hydrogen is wasted;
• palladium (or palladium alloy) diffusers – they require a high pressure differential and high temperature, both of which can impact badly on the overall efficiency of the system.

In view of these limitations, we have developed an advanced clean-up reactor, comprising several catalytic stages. Initially, we demonstrated, on a microreactor scale, that CO can be more effectively removed by a succession of small but highly selective stages, rather than by one large bed containing either a methanation or a preferential oxidation catalyst. The clean-up reactor has now been scaled-up to cope with the output from our largest current HotSpot™ processor (18 kW). The scaled-up reactor, which is less than half the size of the processor, reduces the CO concentration from > 2 per cent to < 10 ppm at the expense of 6 per cent of the hydrogen output. Based on kinetic studies of the underlying reaction rates, and on reactor simulations, it is thought possible to ultimately construct a clean-up reactor 20 per cent of the processor size which will allow 99 per cent of the hydrogen to pass through unreacted.

System Integration

Apart from its intrinsic design, HotSpot™ is also distinguished by its modularity. Output is scaled-up by feeding the required number of individual reactors from a common manifold. For example, in Figure 1, a 6 kW methanol processor has 8 HotSpot™ reactors fed in parallel from a central manifold block. The reactors are connected to the block by inlet and outlet connections in the base of each reactor. Liquid methanol and water are sprayed at the required feed rates, using liquid-fuel injectors, into a central chamber inside the manifold, where they mix with a regulated flow of air. The manifold is maintained at 150°C, ensuring the complete vaporisation of the liquid feeds. From the central chamber, the reactant mixture of methanol vapour, steam and air divides and travels an identical distance to each of the reactors. As a result, all the reactors and the complete processor have identical response to changes in input. The processed gas streams emerging from each reactor enter a common channel, which leads to a single exit port from the manifold.

In the first few methanol processors that were constructed, the temperature of the manifolds could be raised to 150°C, by electrical cartridge heaters, before the reactant feeds were introduced. The use of electrical heating during start-up remains an option, as some battery power will be available on all SPFC vehicles. However, as electrical power will be required by several components (such as pumps, compressors, electronic controls, lights) when the vehicle is started from cold, other options for heating the manifold would lessen the load. One strategy is to generate heat internally, by first carrying out mainly partial oxidation in the HotSpot™ reactors. As the hot processed gas emerges from the reactors it transfers heat to the manifold. Once the manifold has reached 150°C, the water feed can be switched on, the methanol:air ratio can be altered to induce steam reforming as well as partial oxidation, and the feed rates can be increased. Another start-up approach is to combust methanol in a separated catalytic afterburner, with the resulting heat being transferred to the manifold. In one processing system currently being tested, hot exhaust gas from the afterburner is circulated within the manifold through a long internal loop.

One drawback of using processed gas, instead of neat hydrogen, to feed a fuel cell is that some of the hydrogen will emerge unreacted. Typically, a fuel cell rejects 20 to 30 per cent of the hydrogen in a processed gas stream. This need not have a substantial impact on efficiency, if the energy contained within the rejected hydrogen can be usefully recycled. HotSpot™ provides a very effective sink for this energy. By combusting the hydrogen, the heat produced can be transferred to the manifold and hence to the reactants, so encouraging more steam reforming. In effect, this allows more water to be converted to hydrogen.

To simplify the system design, a noble metal catalyst which allows the same afterburner to be used for combusting both hydrogen and methanol has been developed, see Figure 3. The catalyst is so active that light-off begins as soon as cold methanol is sprayed into an air stream entering the afterburner. When rejected hydrogen becomes available, it can be fed to the afterburner in place of the methanol. This afterburner, therefore, not only enables fast start-up,
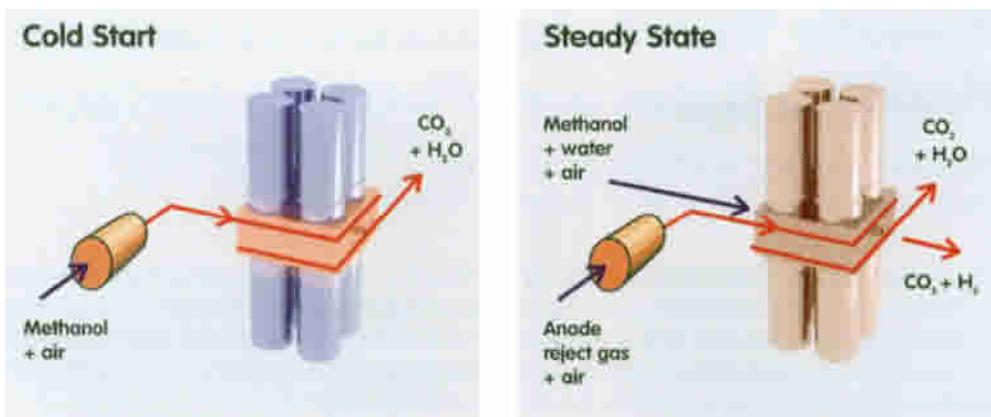
Fig. 3 Here, the manifold is heated by energy generated externally, either by heat supplied by the combustion of methanol in the afterburner during a cold start, or by heat supplied by the combustion of surplus hydrogen in the afterburner during steady state operation

but also increases the steady-state operating efficiency, and ensures that only carbon dioxide and water are released into the atmosphere.

Future Prospects

The hydrogen output from a single HotSpot™ methanol reactor results in a very high power density (3 kW per litre). This drops to just over 1 kW per litre for a modular processor, because of the spacing between reactors and the extra volume required by the manifold. As the processor must be coupled with a clean-up reactor to eliminate carbon monoxide, the power density is reduced further to 0.75 kW per litre. This value already meets the target for fuel processors that has been adopted by U.S. car manufacturers (7); and yet, HotSpot™ is far from optimised. In the immediate future, the design and performance of the HotSpot™ processor will be improved by:

- increased output from individual reactors
- reduced manifold size
- reduced size of the clean-up reactor
- increased selectivity in the clean-up reactor

- improved integration of the components.

The question of whether methanol is the correct fuel for SPFC vehicles does not have a simple answer. Methanol is highly suited for onboard processing, but hydrocarbons have the advantage, being the established vehicle fuels with a global infrastructure for their supply and distribution. We are sure, though, that HotSpot™ is the right processing technology. From our work on methanol, we know that HotSpot™ can match the efficiency of steam reforming and can substantially exceed that of partial oxidation. In its speed of start-up and rate of response to changes in load, HotSpot™ matches partial oxidation and outperforms steam reforming.

The fuel debate is unlikely to be resolved soon; so we are preparing for the possibility that SPFC-vehicle manufacturers will offer more than one choice of fuel, probably between methanol and a more conventional vehicle fuel. In the meantime, research and development of HotSpot™ technology will continue, aimed at achieving an ideal methanol processing system and a novel hydrocarbon processor.

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