The Hot Spot™ Reactor

HYDROGEN GENERATION USING A NOVEL CONCEPT

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Hot spots in chemical reactors are phenomena that the reactor designer would normally try to avoid. However, a reactor deliberately designed to incorporate a hot spot can possess attributes that make it very suitable for use in a self-contained hydrogen generator, small enough to be portable. We have successfully operated such devices under autothermal conditions, generating hydrogen gas from methanol (1), and methane and liquid hydrocarbons (2) at essentially complete single pass fuel conversion, and with excellent yields of hydrogen.

Much has been written in this Journal and elsewhere about a possible hydrogen based energy economy (3). Hydrogen gas, whether used directly as a fuel in internal combustion engines or indirectly to supply electricity using fuel cells, is inherently clean burning and yet highly reactive so that high thermal efficiencies can be obtained. When used in internal combustion engines the compression ratio can be increased markedly and yet because of its wide combustion limits hydrogen can be burnt in mixtures much leaner than is possible using conventional hydrocarbon/air mixtures. Thermal efficiencies of 35 to 40 per cent may thus be achieved, in comparison with the 25 to 30 per cent typical of a normal petrol fuelled engine (4).

Fuel cells are now an attractive reality in terms of potentially high energy conversion efficiencies, and for these hydrogen is orders of magnitude more reactive than any alternative fuel (5). The major impediments to the wider use of hydrogen as an energy source are the difficulties inherent in storage, distribution and transportation. In all of these areas liquid fuels have a clear advantage.

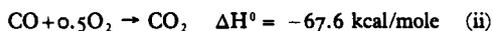Hydrogen is generally made by steam reforming fuels such as coal, methanol and particularly methane and higher hydrocarbons. The reactions are highly endothermic and require a large heat input. This in turn makes hydrogen generation both capital and energy intensive. The gas produced in this way is normally supplied as a high purity commodity, under high pressure in what are necessarily bulky and weighty gas cylinders. The complexities of this conventional means of hydrogen generation are such as to exclude this option as a portable energy source. However, it is pertinent to point out that the requirements of hydrogen which is to be used as a fuel, in the manner outlined above, are not the same as those normally supplied by high purity high pressure hydrogen. Specifically a gas at only slightly above atmospheric pressure is required, and this gas need not be pure hydrogen but could be merely hydrogen rich, say more than 20 per cent hydrogen. It should be noted that the theoretical debit for using 10 per cent rather than 100 per cent hydrogen in a fuel cell would be a loss of only 30 mV in open circuit cell potential, a trivial disadvantage.

The features that we consider to be essential for a portable or transportable hydrogen generator are shown in the Table. The use of a liquid fuel or methane has already been discussed. The need to eliminate as far as possible the requirements for external utility and power supplies coupled with the heat requirements of the conversion reaction, suggested that a partial oxidation process should be used. The "no water" requirement is based upon the need to minimise the overall weight and, of course, in a transportable system this includes fuel and all other consumables. A perceived need for rapid start-up again points towards an autothermal or partial oxidation process, rather than a conventional steam reforming route. However,

Perceived Requirements of a Portable Hydrogen Generator	
Fuel	Liquid: such as methanol, LPG or oil based
Operation	No utility requirements No power requirements No water requirements Rapid start-up
Equipment	Maximum hydrogen output : weight ratio Reliable Simple construction Inexpensive materials Compact
Product	Slight superatmospheric pressure More than 20 per cent hydrogen Complete fuel conversion per pass High hydrogen yield Low carbon monoxide yield

attempts at the homogeneous partial oxidation of methane, for example, usually lead to virtually complete oxidation of only part of the fuel. Thus the necessity of using a catalyst was indicated.

Dehydrogenation reactions are endothermic, and the provision of the necessary process heat can be made either by external means or, better, by the concurrent use of an exothermic reaction to drive the dehydrogenation. The oxidation of carbon monoxide, derived from the decomposition of the organic feedstock, appears to be a likely candidate. Thus the problem was to identify and use a catalyst which was capable of selectively oxidising carbon monoxide in the presence of hydrogen. Catalysts are known which are capable of oxidising carbon monoxide in the presence of hydrogen, so conceptually we began to think in terms of thermally decomposing methanol and producing the necessary heat by burning some of the carbon monoxide selectively using a suitable catalyst:

$$CH_3OH(l) \rightarrow CO + 2H_2 \quad \Delta H^0 = +30.6 \text{ kcal/mole} \quad (i)$$

$$CO + 0.5O_2 \rightarrow CO_2 \quad \Delta H^0 = -67.6 \text{ kcal/mole} \quad (ii)$$

Using air without water as reactant could result in a product gas with the composition hydrogen : carbon dioxide : nitrogen = 2:1:2 or 40 volume per cent hydrogen.

Furthermore, the requirement for rapid start up from ambient may be satisfied by the addition of a small quantity of platinum group metal catalyst to the base metal dehydrogenation catalyst. Near complete oxidation of methanol can occur over such catalysts from ambient conditions. Once sufficient heat has been generated to sustain the endothermic dehydrogenation only the Equations (i) and (ii) are significant.

Reactor Design

Initially we were interested in relatively small rates of hydrogen production, which entailed using a small reactor, and therefore we knew that heat losses would be a problem. In an effort to overcome this we placed some reduced copper on silica catalyst inside a domestic vacuum flask and passed the methanol/air vapours in through a dip tube. The presence of a small quantity of platinum or palladium catalyst enabled the reaction to light off at room temperature, and tests showed that high conversion of methanol and an excellent yield of

hydrogen were possible. However when we carried out the experiment using the same catalyst mixture in a conventional through flow reactor much poorer yields were obtained and these were not improved even with external heating of the tube. Using a through flow reactor in which the reactants were injected directly into the middle of the catalyst bed again gave selective results. Clearly point injection had a major beneficial effect and it is interesting to consider possible reasons for this.

Upon ignition of a highly exothermic reaction such as this the reaction increases in intensity and the reaction zone moves upstream towards the incoming reactants. With a conventional fixed bed reactor the reaction front stabilises at the leading edge of the catalyst bed. With point injection, however, the reaction front again moves towards the incoming reactant flow but as it approaches the inlet the reactant velocity increases to such an extent that the front remains within the catalyst bed where selective oxidation can be maintained. This very high gas velocity also means that it is much more difficult for the desired hydrogen product to back-diffuse and be consumed in the inlet region where oxygen partial pressure is higher.

In the case of point injection, heat utilisation is also improved as heat transferred either by convection or radiation from the combustion zone is absorbed by the catalyst, and is then available to promote subsequent endothermic reactions. With a planar reaction front, heat is lost much more readily to the reactor walls and this loss must be made up by the consumption of desired hydrogen, thus reducing the overall hydrogen yield.

A further interesting question that arises is whether steam reforming might give higher yields of hydrogen than partial oxidation. Certainly this is true in conventional plants in which external heat is supplied. However, the addition of water to the feed not only adds to the weight penalty but also increases the amount of heat required to vaporise the feed and bring the vapour to the reaction temperature. For an autothermal process this heat must arise from the combustion of part of the fuel or indirectly perhaps from burning some of the desired hydrogen end product. Thus in such a situation, some product would be consumed in order to make more product. Clearly the net effect will depend upon the precise details of the reactor design and the amount of water required. Conventional methane/steam reformers customarily use a large excess of steam, 5 to 7 mole ratio, which assists the heat flux and helps to maintain catalyst activity by limiting carbon formation. We have evaluated this new type of reactor both with and without water and have shown that at a 1:1 mole ratio with methanol there is little net benefit to be gained in hydrogen yield, although the carbon monoxide yield was significantly reduced by the addition of water.

Results of Small Reactor Studies

Three series of experiments were carried out, all with methanol charged at 10g/h and using a 3 weight per cent copper/silica catalyst in an upstream zone and a physical mixture of this catalyst and a 5 weight per cent palladium/silica catalyst, in the ratio of 9:1, in a downstream zone which comprised 20 per cent of the total catalyst bed volume. For one series of experiments water was injected along with the methanol at a rate of 6g/h. The reactor consisted of 50g of catalyst held in a tube of 4cm internal diameter, and into which the methanol/air/water feed was injected 4cm below the catalyst bed surface through a 6mm tube. For comparison purposes a conventional tubular reactor was used, made from 1cm internal diameter tubing. The temperature was that measured by a thermocouple 1cm downstream from the reactant inlet.

The manner in which the reaction temperature varied as the air rate was increased, is shown in Figure 1, for the three sets of experiments. Temperatures were somewhat lowered when water was added, reflecting the additional heat requirement, but were substantially lower in the case of the tubular reactor where the heat losses became so much greater. Figure 2 shows how the methanol conversion paralleled the changes in reaction temperature. The
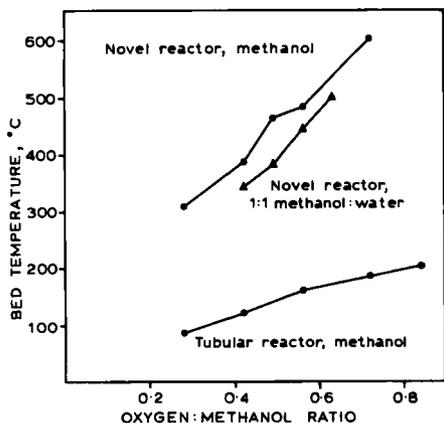
Fig. 1 The catalyst bed temperature is shown to be dependent on the type of reactor, as well as on the oxygen : methanol ratio; when water is added the temperature of the bed is lowered somewhat
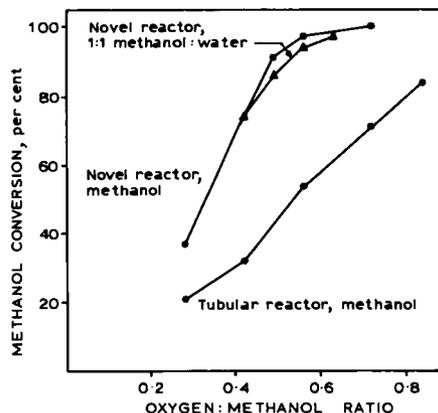
Fig. 2 The conversion of methanol to hydrogen depends on the oxygen : methanol ratio but also on the type of reactor used, and parallels the changes in the reaction temperature. At an oxygen : methanol ratio of 0.5 the conversion in the novel reactor reached 90 per cent
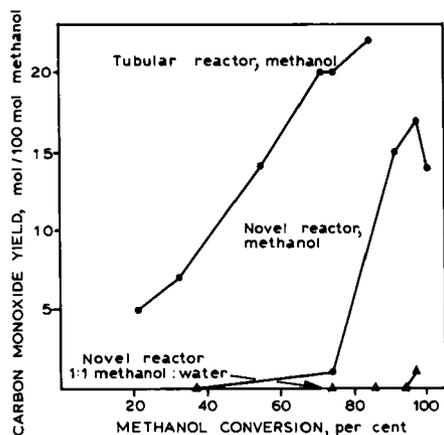
Fig. 3 The carbon monoxide yield depends on the methanol conversion; the yield being lowest in the novel reactor when water is added to the methanol
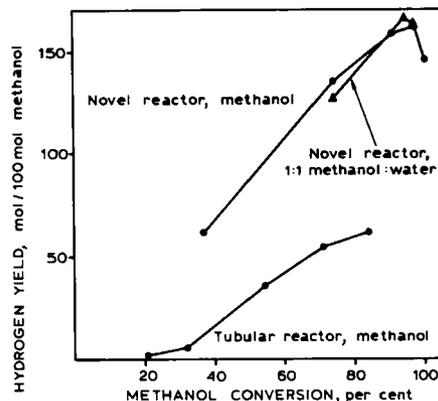
Fig. 4 The yields of hydrogen using the novel reactor are roughly the same with and without added water, and are much superior to the yield from the tubular reactor

methanol conversion reached 90 per cent when the oxygen:methanol ratio was 0.5, in line with the stoichiometry given in Equation (i).

The carbon monoxide and hydrogen yields as the methanol conversion increased are shown in Figures 3 and 4, respectively. The carbon monoxide yields were significantly lower from the novel reactor, especially when water was added. This reflects the influence of the carbon monoxide shift reaction in the cooler parts of the reactor. The hydrogen yields were similar with and without added water, but again much superior for this reactor compared to the tubular reactor. This reflects the greater heat losses from the tubular reactor and the need to compensate by burning some extra feed or
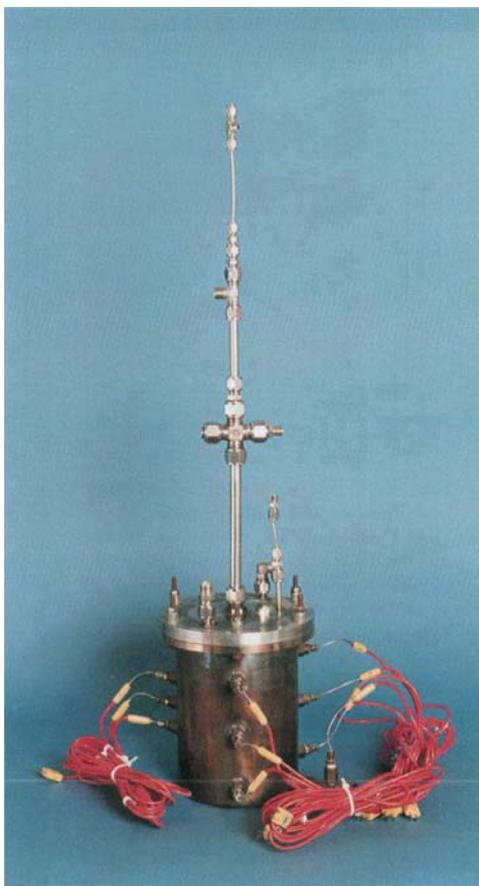
Fig. 5 A scaled up reactor of 2 litres capacity successfully demonstrated the commercial possibilities of this means of generating hydrogen gas. The vertical injector pipe penetrated midway into the catalyst bed. The temperature was measured by thermocouples at nine positions

desired hydrogen product. At essentially complete methanol conversion the gas composition was 35 volume per cent hydrogen, 20 volume per cent (carbon monoxide + carbon dioxide) and 45 volume per cent nitrogen, with a net hydrogen flow of 12 l/h, quite sufficient for the applications which we have discussed.

Reactor Scale-Up

After the successful demonstration of the novel properties of the concept on a bench scale reactor it was necessary to scale up the operations in order to:

[a] Demonstrate that the advantageous features of the concept were applicable on a commercial sized device

[b] Demonstrate that hydrogen gas could be generated continuously on demand on a scale of commercial interest

[c] Further elucidate the catalytic chemistry involved.

To this end a stainless steel reactor with a capacity of two litres was constructed, as shown in Figure 5. The reactor shell was blanked off at the base and a one inch diameter pipe in the bottom wall acted as a take off pipe for the make gas. The top of the reactor was flanged with a centrally mounted injector pipe which penetrated midway into the catalyst bed. The catalyst was mounted on a gauze base positioned to give clearance above the gas take off pipe. Temperatures in the catalyst bed were measured at nine points by thermocouples mounted in drillings through the reactor shell. By this means both axial and radial temperature distributions were monitored.

The reactor was supplied with feedstock air and purge nitrogen which were metered by mass flow controllers supplying up to 500 Normal litres/minute (N l/min) each. Methanol was delivered by a calibrated diaphragm pump at rates up to 100 ml/min. The methanol and air reactants were only brought together in the injector inside the reactor. After reaction over the catalyst the product gases were cooled in an efficient condenser and the condensate collected. The dry product gas was then analysed by gas chromatography and the flowrate measured by mass flowmeter before venting.

Scale-Up Data

The temperatures in the catalyst bed are shown as a function of time, that is from the start of air injection, in Figure 6. The reaction was initiated from ambient conditions and commenced within a few minutes; steady state temperatures were achieved within 0.75h. Analysis showed that hydrogen gas was generated within 30 minutes of start. A noticeable feature of Figure 6 is the eventual formation of a hot spot in the region adjacent to the injector. A temperature of about 450°C was

Fig. 6 The temperature distributions across the 2 litre catalyst bed are shown after start-up. The hot spot which developed near the injector can be seen.
Thermocouple 3 was located at the top wall
Thermocouple 5 was located at the bottom wall
Thermocouple 6 was located near the injector exit
Thermocouple 8 was located at the bottom centre
Thermocouple 11 was located below the hot zone
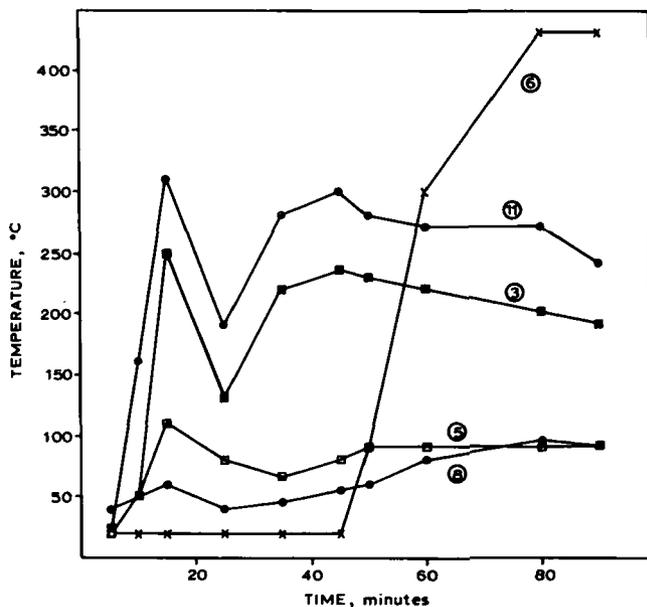
observed in this region, while temperatures in the remainder of the reactor were much cooler, generally in the range 200 to 300°C.

The thermal conditions in the bed, and hence temperature distributions, are the result of numerous factors including feedrate, extent and selectivity of the reaction, thermal capacity of the bed and reactor design. Consequently neither temperature nor pressure (close to ambient in all cases) can be considered as process variables useful for reactor evaluation in this strongly adiabatic, thermally heterogeneous environment. It is useful to assess reactor performance in terms of the effect of the oxygen:methanol molar ratio on the reaction parameters, since this ratio will have the greatest bearing on the extent of the reaction (conversion) and the reaction selectivity.

The exit gas composition is shown as a function of the oxygen : methanol ratio in Figure 7. It can be seen that the gas composition was largely independent of this ratio, the average gas composition over the range depicted being: hydrogen 42, nitrogen 37 and (carbon monoxide+carbon dioxide) 21 volume per cent. Since the extent of methanol conversion was strongly dependent on the oxy-

gen : methanol ratio, as expected, the reaction selectivity was largely independent of methanol conversion.

Under these conditions selectivity to hydrogen, defined as the fraction of hydrogen bound up in converted methanol which appears
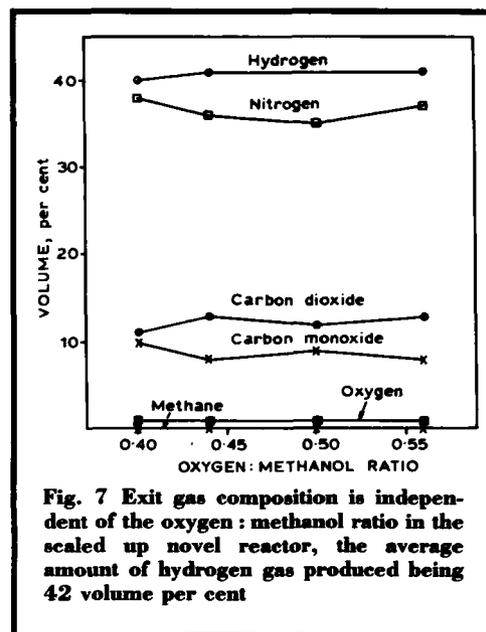
Fig. 7 Exit gas composition is independent of the oxygen : methanol ratio in the scaled up novel reactor, the average amount of hydrogen gas produced being 42 volume per cent

as molecular hydrogen in the product, was in excess of 85 per cent. Alternatively expressed, the molar ratio hydrogen:methanol converted reached 1.71. A limiting value of 2.0 was anticipated based on the reaction stoichiometries from Reactions (i) and (ii). A maximum hydrogen output of 3.28 N m^3/h was achieved at an oxygen : methanol ratio of 0.56. The hydrogen yield reached 1.20 N m^3 hydrogen per kilogram methanol fed to the reactor. A limiting value of 1.40 was anticipated, based on the expected reaction stoichiometry. Methanol conversion was strongly dependent on the oxygen : methanol ratio and under the conditions of maximum hydrogen output a methanol conversion of 94 per cent was observed.

Very low oxygen concentrations in the exit gas are also indicated in Figure 7. In fact the analytical method did not distinguish between oxygen and argon present in the atmosphere. However, by making a comparison between the ratio (oxygen + argon) : nitrogen provided by experimental data and the ratio of argon : nitrogen present in the atmosphere, it was estimated that the residual oxygen concentrations in the exit gas were usually in the range 1000 to 2000 ppm. The data given in Figure 7 suggest that carbon monoxide concentrations in the exit gas are less than 10 volume per cent. The observed concentration range was 4 to 10 volume per cent depending on the conditions. Such levels may be diminished even further by the incorporation of water into the feed. The catalyst was extremely efficient for the water gas shift reaction under these temperature conditions. In fact concentrations of carbon monoxide in the exit gas as low as 2 volume per cent have been recorded under such conditions.

Conclusions from Scale-Up Data

The data presented above show that the attractive features of this novel reactor, first demonstrated on a bench scale reactor, have been proven on a scale of commercial interest. These are:

[1] High methanol conversion at high selectivity to hydrogen

[2] Negligible oxygen breakthrough

[3] Potentially low carbon monoxide make

[4] Auto-ignition from ambient.

The observed exit gas compositions are very close to those expected from an overall reaction stoichiometry:

$$CH_3OH + 0.5O_2 \rightarrow CO_2 + 2H_2$$
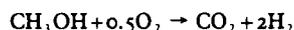
The fact that gas compositions were largely independent of the oxygen:methanol ratio suggests that oxygen had little part to play in the primary reforming step, and that the reaction sequence was:

$$CH_3OH \rightarrow CO + 2H_2$$

$$CO + 0.5O_2 \rightarrow CO_2$$
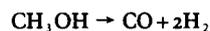
Thus the high selectivity to hydrogen observed using this process was due to the successful competition for oxygen displayed by carbon monoxide, in preference to hydrogen, over this catalyst under these conditions:
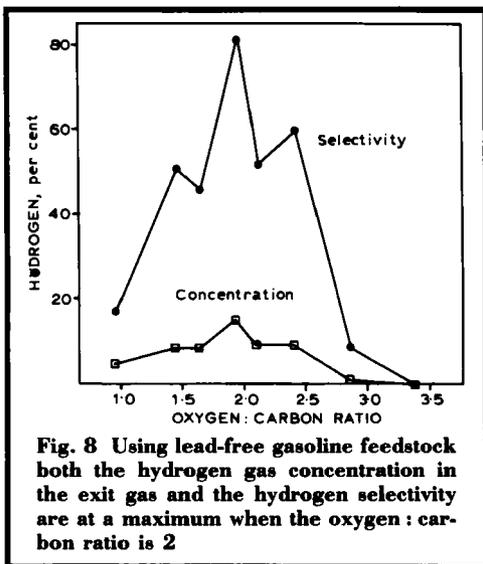
$$H_2O \xleftarrow{H_2} 0.5O_2 \xrightarrow{CO} CO_2$$
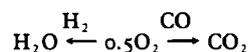
The Use of Hydrocarbons as Fuels

With the ready availability of hydrocarbon fuels, their use as feedstocks in this novel reactor concept would be an attractive option. Methane (natural gas), propane (LPG), n-hexane, 60–80 petroleum ether, lead-free gasoline and commercial diesel have all been evaluated as feedstocks using the bench scale reactor described previously. The catalyst used in all these cases was a more active 1 per cent platinum-3 per cent chromium/silica formulation. All of these fuels have been successfully reformed although here discussion will be restricted to the liquid hydrocarbons.

None of the hydrocarbons was capable of auto-ignition with the catalyst employed. However, the reactions could be initiated readily from ambient in the usual way using either methanol or product hydrogen, and then be sustained by introducing the hydrocarbon and switching off the initiator.

With the use of liquid hydrocarbon fuels such as gasoline and diesel, where a great multiplicity of compounds are present, the use of molar oxygen:hydrocarbon ratios for reactor

Fig. 8 Using lead-free gasoline feedstock both the hydrogen gas concentration in the exit gas and the hydrogen selectivity are at a maximum when the oxygen : carbon ratio is 2

of the oxygen:carbon ratio using lead-free gasoline as feedstock are shown in Figure 8. The latter was a premium test gasoline containing a maximum 45 per cent aromatics, a maximum 20 per cent olefins with the balance saturates. A difference in performance between this and the analogous data obtained using methanol is immediately apparent. With the latter the gas composition was largely independent of the oxygen : carbon ratio, but with the gasoline feed the gas composition—as reflected by the hydrogen gas concentration—was ratio dependent. The selectivity to hydrogen reached a maximum of about 80 per cent at an oxygen : carbon ratio in the region of 2.0.

This situation is the same when using any of the other hydrocarbon fuels tested. Figure 9 gives a comparison of the four liquid hydrocarbon fuels and shows that hydrogen was abstracted from all the fuels except diesel with similar efficiency, reaching similarly high hydrogen selectivities at an oxygen:carbon ratio close to 2.0. The inference is that hydrocarbon species whether aliphatic, aromatic, naphthenic, saturated or unsaturated were all reformed with equal facility. Quite clearly, a
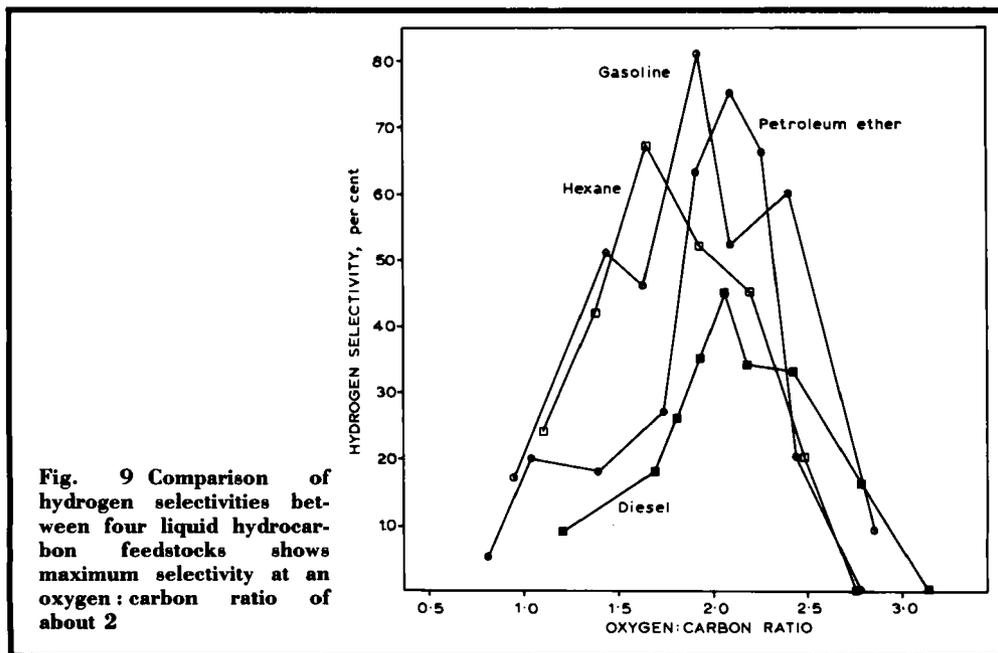
assessment was not possible. However, with a knowledge of the carbon analysis for the fuel the oxygen:carbon atomic ratio could be calculated and used for reactor/catalyst evaluation.

The hydrogen gas concentration in the exit gas, and the hydrogen selectivity as a function

Fig. 9 Comparison of hydrogen selectivities between four liquid hydrocarbon feedstocks shows maximum selectivity at an oxygen : carbon ratio of about 2
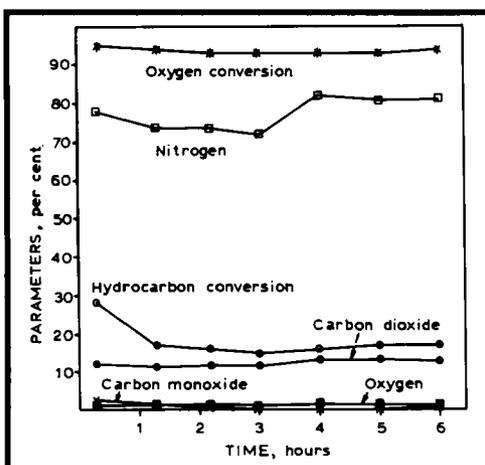
Fig. 10 The catalyst durability over the course of a day using a lead-free gasoline feedstock at an oxygen : carbon ratio of 0.27 is shown by the constancy in the six measured parameters

Figure 10 shows the constancy of the six measured parameters over the course of an operation lasting for a day. On discharge parts of the reactor and the thermocouple showed signs of coking; the catalyst was free of carbon.

commercial device using a hydrocarbon fuel would be required to operate at an oxygen:carbon ratio of 2.0.

Hydrocarbon conversions were uniformly high in the range 80 to 90 per cent, and were less dependent on the oxygen : carbon ratio than those using methanol feed. Hydrogen yields obtained from the liquid hydrocarbon fuels were:

n-hexane: 1.09 N m³ hydrogen/kg (limiting value 1.82 N m³/kg)

petroleum ether: 0.83 N m³ hydrogen/kg (limiting value 1.21 N m³/kg)

gasoline: 1.28 N m³ hydrogen/kg (limiting value 1.31 N m³/kg).

Commercial diesel fuel was also reformed but the results were erratic and further development work is required.

Because hydrogen is abstracted from these fuels with similar efficiency the maximum hydrogen yield observed is largely a reflection of the degree of unsaturation of the fuel at constant hydrocarbon conversion.

There was a perceived threat of coking from these highly unsaturated fuels, especially when the reactor was operated under rich conditions, that is at oxygen : carbon ratios less than 2. This could occur for example on start up, shut down or on changing conditions. Consequently a durability run was carried out using lead-free gasoline as feed at an oxygen : carbon ratio of 0.27, an extremely oxygen deficient condition.

Conclusions from the Hydrocarbon Data

In principle the use of natural gas, LPG, naphtha, and lead-free gasoline provide options for feedstocks in the present technique although they have not been demonstrated on a commercial scale reactor. These feedstocks show little tendency to cause coking even under ultra rich conditions. The use of diesel fuel must await further development.

Auto-ignition is not achieved using hydrocarbons alone, but is readily effected using either methanol or hydrogen gas.

Gas compositions and especially hydrogen selectivity are more sensitive to the oxygen : carbon ratio than is methanol reforming. Hydrogen selectivity greater than 80 per cent, at a hydrocarbon conversion greater than 90 per cent, was achieved at the stoichiometric oxygen : carbon ratio of 2 using gasoline feedstock.

The suggestion of a stoichiometric oxygen : carbon ratio suggests the participation of oxygen in the primary reforming reaction, which is not the case with methanol. The observations argue for an overall stoichiometry for all hydrocarbon fuels:
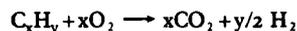
$$C_x H_y + x O_2 \longrightarrow x CO_2 + y/2\ H_2$$

Acknowledgement

References

1 J. W. Jenkins, *U.S. Patent* 4,789,540; 1988, *European Appl.* 217,532; 1987
2 J. W. Jenkins, *European Appl.* 262,947; 1988, *U.S. Patent* to be published
3 J. O' M. Bockris, *Environment*, 1971, **13**, 51
4 "The Boston Reformed Fuel Car", M. S. Newkirk and J. L. Abel, SAE Paper 740600, 1974; "Combustion Characteristics of Hydrogen Fuelled Spark Ignition Engine", S. Furuhama et al., JSAE Paper No. 6, 1973. "On-Board Hydrogen Generation for Automobiles", J. Houseman and D. J. Cerini, 11th IECEC, SAE Paper 769001,

1976; "On-Board Steam-Reforming of Methanol to Fuel the Automotive Hydrogen Engine", F. L. Kester, A. J. Konopka and E. H. Camara, IECEC 759175, 1975; B. Lindner and K. Sjöström, *Fuel*, 1984, **63**, 1485; Li Jing-Ding, Lu Ying-Qing and Du Tian-Shen, *Int. J. Hydrogen Energy*, 1986, **11**, (10), 661; "Lean Mixture Operation of Hydrogen-Fuelled Spark Ignition Engines", J. S. Wallace, L. Segal and J. F. Keffer, SAE Paper 852119, 1985

5 S. Srinivasan, *J. Electrochem. Soc.*, 1989, **136**, (2), 41C–48C

Platinum-Modified Coatings on Gas Turbine Blades

PROMISING TRIALS ON LONG-RANGE MARITIME PATROL AIRCRAFT

First-stage high pressure blades on advanced gas turbine engines must operate at elevated temperatures under highly stressed conditions in extremely oxidising environments which, in many cases, contain fuel contaminants such as sulphur and vanadium, and also ingested salts. Under such conditions the blades may be degraded by the phenomenon known as hot corrosion. One way of maintaining the properties of such blades is to coat the base metal superalloy with a protective outer layer, and aluminide coatings are widely used for this purpose. Platinum aluminides offer improved corrosion resistance, however (1).

Having experienced an unacceptable rejection rate of high pressure turbine blades, the Australian Department of Defence initiated a programme to find a protective layer which was more durable than the conventional aluminide coating applied to first-stage blades by engine manufacturers, and the results of a metallographic examination of platinum-modified aluminide coatings after 750 hours of engine operation have been reported (2). The same researchers have now presented a comparative study of the behaviour of various coating systems on the first-stage high pressure blades in the engines of two long-range maritime patrol aircraft (3).

In their experience, approximately 60 per cent of the first-stage turbine blades coated with conventional nickel aluminide were rejected after 2000 hours due to failure of the coating, and almost all of the remainder were discarded after a further 2000 hours. With the aim of finding a coating that would serve for 4000 engine operating hours they have assessed: nickel aluminides supplied by two different vendors, platinum-modified aluminide, platinum-plus-rhodium-modified aluminide,

silicon-modified aluminide, and manganese-plus-chromium-modified aluminide layers. After 1000 hour trials certain behavioural trends were evident, and the condition of the blades coated with the noble metal-modified aluminides was generally better than that of the others. Only minor degradation was apparent on the blades coated with the two noble metal-modified aluminides, and it was concluded that they may be able to achieve the required lifetime of 4000 hours.

References
1 R. G. Wing and I. R. McGill, *Platinum Metals Rev.*, 1981, **25**, (3), 94
2 J. L. Cocking, G. R. Johnston and P. G. Richards, *Platinum Metals Rev.*, 1985, **29**, (1), 17
3 J. L. Cocking, P. G. Richards and G. R. Johnston, *Surf. Coat. Technol.*, 1988, **36**, (1–2), 37

New Sensor for Carbon Dioxide

None of the traditional methods of determining carbon dioxide in atmospheres is particularly applicable to development in cheap, portable sensors. However, a recent paper describes an amperometric sensor which offers these desirable features. Based upon a porous electrode in a three-electrode cell, the electrolyte consists of a copper diamine complex in aqueous potassium chloride (J. Evans, D. Pletcher, P. R. G. Warburton and T. K. Gibbs, *Anal. Chem.*, 1989, **61**, (6), 577).

The working and counter electrodes consist of porous polytetrafluoroethene disks spray coated with a platinum layer. The cathode is held at a constant potential; when the solution is contacted by a carbon dioxide-containing atmosphere its pH decreases, this results in the formation of Cu^{2+}, and a current which is strongly dependent on carbon dioxide concentration is observed from the sensor.