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The conversion of gasoline to hydrogen for on-board vehicle applications

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Abstract

The autothermal reforming of model gasoline mixtures to produce hydrogen for fuel cell operations has been studied. Deactivation due to coking of a single Ni/Pt-based catalyst has been found to be significant, but operation using a platinum–ceria catalyst in line with a Ni-based steam-reforming catalyst allows acceptable efficiencies. Oxidation over the Pt/CeO_2 could be initiated at room temperature if the catalyst was pre-reduced. All oxygen was consumed and the bed temperature increased to about 580 °C. Subsequent steam reforming over a nickel-based catalyst gave ca. 70% conversion at a steam:carbon ratio between 2 and 3.4, with selectivity to hydrogen of between 65 and 70%. Application to fuel cell operations would require the selective removal of 1–2% carbon monoxide from the product gases.

Keywords: Gasoline; Hydrogen; On-board vehicle applications

1. Introduction

The control of vehicle exhaust emissions using catalytic converters has been highly successful [1]. However, increasingly stringent legislation demands emission control that is at or beyond the capability of conventional catalysts, and alternative means of reducing emissions are under consideration. Of these, fuel cell powered vehicles based on the polymer electrolyte membrane fuel cell (PEMFC) are favoured but these cells have the disadvantage of operating only on hydrogen as a fuel [2]. Since the distribution and on-board storage of hydrogen presents very real problems, attention has been focused on the conversion of more readily available fuels to hydrogen on-board the vehicle. The partial oxidation of hydrocarbons is one approach [3], namely

$$CH_4 + \tfrac{1}{2}O_2 \leftrightarrow CO + 2H_2, \quad \Delta H_{298} = -36\,\mathrm{kJ\,mol^{-1}} \quad (1)$$

Alternatively, conversion may be effected via steam or carbon dioxide reforming [3]:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2, \quad \Delta H_{298} = 206.2\,\mathrm{kJ\,mol^{-1}} \quad (2)$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2, \quad \Delta H_{298} = 247\,\mathrm{kJ\,mol^{-1}} \quad (3)$$

All reactions are favoured at high temperatures and require initiation, usually achieved by combusting part of the fuel [3]:

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O, \quad \Delta H_{298} = -802\,\mathrm{kJ\,mol^{-1}} \quad (4)$$

Exothermic partial oxidation is self-sustaining once initiated, while endothermic reforming reactions require continuing heat supplied by combustion (autothermal reforming [4]).

The production of hydrogen from methane [5], methanol [6] and light hydrocarbons [5] has been reported. The present studies are focused on the conversion of model hydrocarbons typical of gasoline, e.g.

$$C_8H_{18} + \tfrac{25}{2}O_2 \leftrightarrow 8CO_2 + 9H_2O, \quad \Delta H_{298} = -5100.6\,\mathrm{kJ\,mol^{-1}} \quad (5)$$

$$C_8H_{18} + 4O_2 \leftrightarrow 8CO + 9H_2, \quad \Delta H_{298} = -659.9\,\mathrm{kJ\,mol^{-1}} \quad (6)$$

$$C_8H_{18} + 8H_2O \leftrightarrow 8CO + 17H_2, \quad \Delta H_{298} = 1274.8\,\mathrm{kJ\,mol^{-1}} \quad (7)$$

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Table 1
Physical properties of the catalysts used

Properties	Pt/CeO$_2$	Ni-com	Pt/Ni-com
Metal content (wt.%)	2–3 as Pt	34 as NiO	2–3 as Pt/34 as NiO
BET surface area (m^2 g^{-1})	26.4 ± 0.3	11.0 ± 0.2	9.9 ± 0.8
Pore size diameter(BJH desorption) (nm)	7.6	21.2	17.5
Bulk density (g ml^{-1})	0.43	1.12	1.11

$$\mathrm{CO} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2}, \quad \Delta H_{298} = -41.2\,\mathrm{kJ\,mol^{-1}} \quad (8)$$

Studies of the partial oxidation of isooctane (reaction (6)) have been reported elsewhere [7] as have studies of the complete combustion of the fuel [8]. It was found that the optimal arrangement involved heat generation by total oxidation on a supported Pt-based catalyst, followed by steam reforming over a Ni-based catalyst. A similar arrangement was found to be optimal in the present system.

2. Experimental

The conversion of artificial gasoline to hydrogen was studied over three catalysts. Initial experiments were completed over a commercial steam-reforming catalyst doped with platinum. The catalyst was found to coke easily, and further experiments were carried out in a two-bed system consisting of platinum on ceria followed by a commercial steam-reforming catalyst.

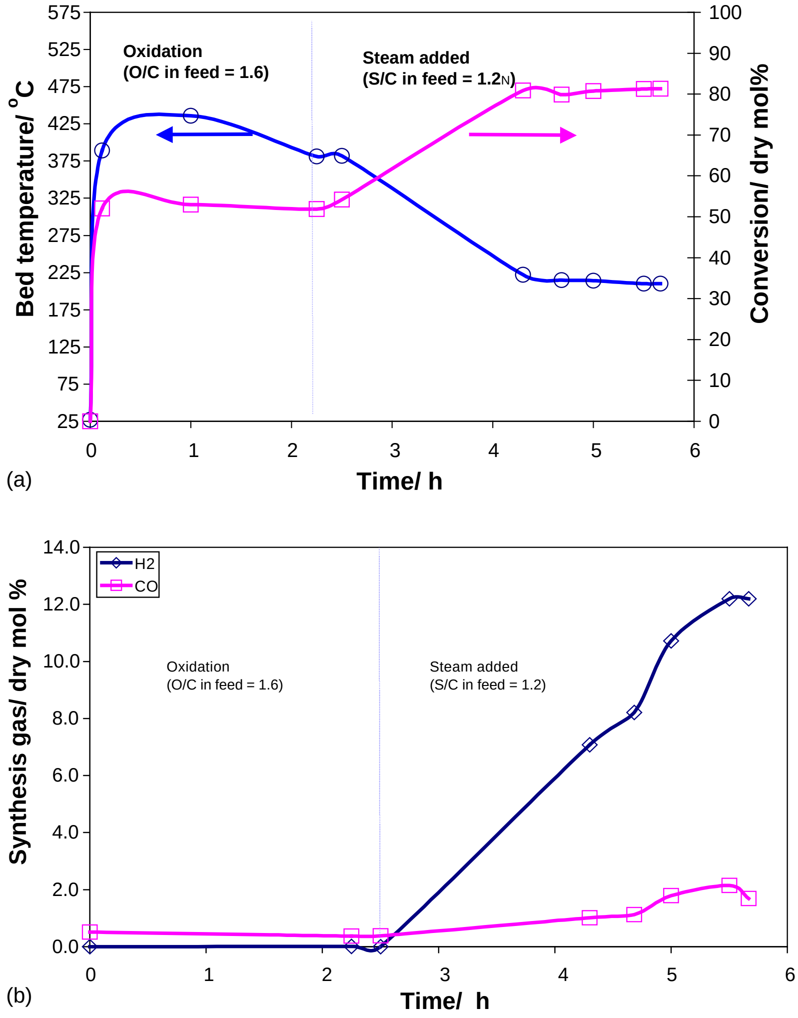

Fig. 1. (a) Catalyst bed temperature and isooctane conversion (total dry gas 141 ml min^{-1}; water 3 ml h^{-1}; Pt/Ni-com catalyst loaded 0.1 g). (b) Synthesis gas product distribution (total dry gas 141 ml min^{-1}; water 3 ml h^{-1}; Pt/Ni-com catalyst loaded 0.1 g; O:C = 1.6:1).

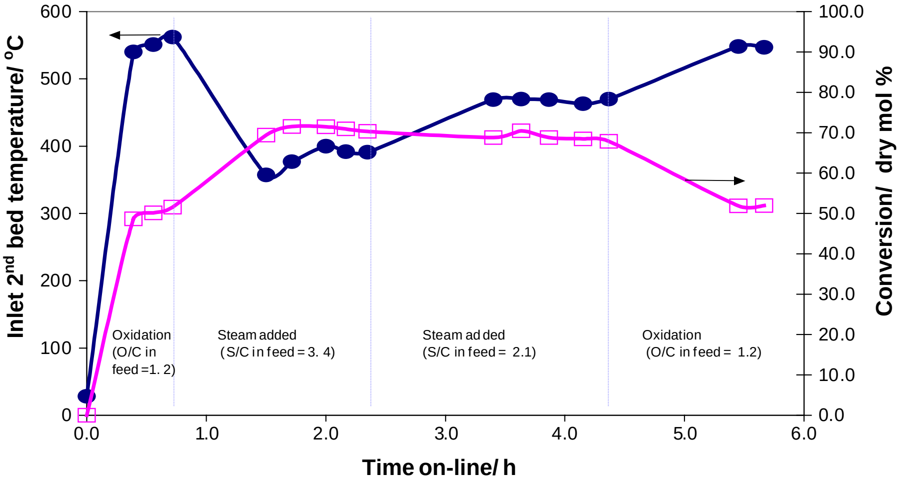

Fig. 2. Combined catalyst bed temperature and artificial gasoline conversion from all runs (total dry gas flow 377 ml min^{-1}; two bed system with total catalyst loaded = 0.5 g).

The initial catalyst was prepared by impregnation of a Ni/MgO/Al_2O_3 catalyst with a solution of tetraamine platinum chloride. The catalyst was dried (120 °C: 12 h) and calcined (500 °C: 4 h) before use. Catalyst characteristics are summarised in Table 1. 0.1 g of catalyst (300–425 µm) was diluted with x-alumina particles of the same size in the ratio 1:9 before loading the reactor.

The preparation of the Pt/ceria catalyst has been previously described [8]. 0.2 g catalyst was mounted upstream of 0.3 g Ni/MgO/Al_2O_3 (both 300–425 µm) in the reactor. Characteristics of all catalysts are summarised in Table 1.

Catalyst testing was carried out using a flow system. Hydrocarbons were vaporised from two saturators maintained at 20 °C using nitrogen as a carrier gas. Water was supplied using an ISCO 260D syringe pump. All gases were metered using Brooks 5850 mass flow controllers and heated to 200 °C before entering the reactor.

The stainless steel reactor (10 mm i.d.) was loaded and placed in the constant temperature zone of an electrically heated furnace. The reactor was fitted with thermocouple well, allowing the measurement of the axial temperature distribution along the bed.

Product analysis was carried out using three gas chromatographs. Permanent gases were separated on a 1.8 m CTR-1 column (40 °C) and analysed using a TCD. Hydrocarbons were separated using a 3 m WH/OV-101-chromosorb column (temperature programmed from 40 to 120 °C) and analysed using an FID detector. Hydrogen was separated using

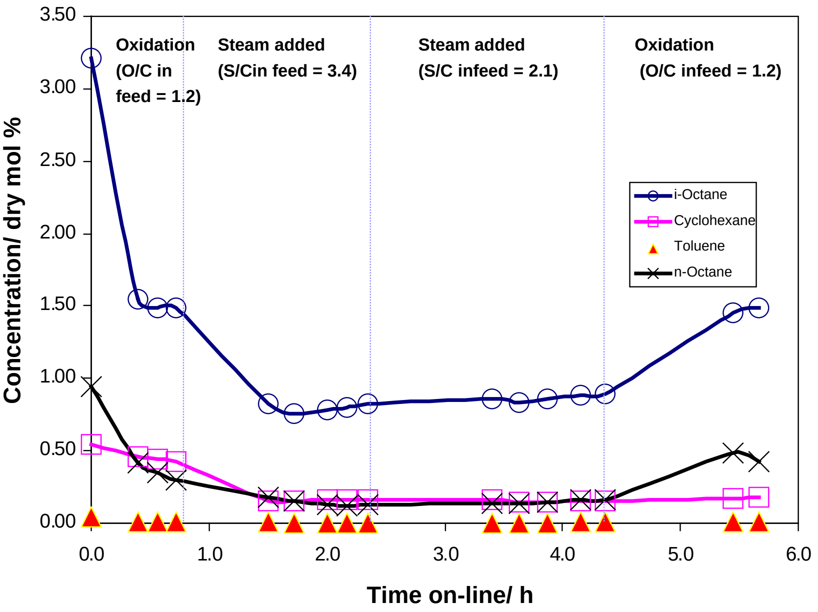

Fig. 3. Combined feed concentration profile for the autothermal reforming of artificial gasoline (total dry gas flow 377 ml min^{-1}; two-bed system with total catalyst loaded = 0.5 g).

a 13X column (40 °C) and analysed using a TCD. Carbon balances were accurate to within ±15%.

The catalysts were either pretreated in oxygen–nitrogen at ambient before use, or reduced in 20% hydrogen/nitrogen (600 °C: 4 h).

Initial experiments were completed using gasoline, but heavy coking was observed. As a result, a hydrocarbon mixture based on analyses of Australian gasoline by Duffy and Nelson [10] was used as a model for gasoline. It contained cyclohexane (5%), isooctane (35%), *n*-octane (20%), toluene (35%) and hexene (5%).

3. Results and discussions

First experiments were carried out with isooctane, in order to establish reaction conditions. Previous studies [7,9] had indicated approximate operating conditions.

The Pt/Ni catalyst was loaded into the reactor and reduced. 1% isooctane in nitrogen was then passed over the catalyst for 2 min and oxygen was admitted to give an O:C ratio of 1.6 in a total flow of 140 ml min^{-1}. As shown in Fig. 1a, the bed temperature rose rapidly to ca. 430 °C and attained a steady-state value of 380 °C. Although there was a possibility that hydrogen could be produced by partial oxidation (reaction (6)), the absence of this product showed that the reaction was unimportant in this case.

3 ml h^{-1} of water was then pumped into the evaporator, to give a steam:carbon ratio of 1.2 in the reactor. As expected, endothermic steam reforming (reaction (3)) was favoured and, as a result, the temperature of the bed dropped (Fig. 1b). Isooctane conversion increased to ca. 80% and both hydrogen and carbon monoxide were observed (H_2:CO = 6:1). The increased ratio above the value expected from reaction (7) was probably due to coke formation.

Post-run analysis of the catalyst showed that significant amounts of coke had been formed, and this could not be avoided without working at high steam:carbon ratios. This infers the necessity to carry a larger amount of water on a vehicle, at a cost to fuel efficiency. As a result, attention was focused on the two-bed ($\mathrm{Pt.CeO_2 + Ni/MgO{-}AlO_3}$) system, which proved more resistant to coke formation.

The initial experiments with gasoline used the same approach as with isooctane, first oxidising and then steam reforming the fuel (Fig. 2). Since a vehicle-mounted catalyst would have to survive many stop–start operations, several cycles of experiments were carried out. These can be conveniently summarised using the same graphs (Figs. 2–4).

A mixture of gasoline, oxygen and nitrogen was first admitted to the reduced catalysts. The bed temperature rapidly increased and about 50% of the inlet hydrocarbons was combusted (Fig. 2). Although water was formed by oxidation, the amount produced was insufficient significantly to affect the subsequent steam:carbon ratio. In contrast to isooctane, some hydrogen was produced even in this oxidation stage (Fig. 4).

Product analysis clearly showed that all oxygen was consumed (Fig. 4) and that various components of the gasoline oxidised to a greater or lesser extent (Fig. 3). Octanes and toluene were extensively oxidised, but cyclohexane was more inert.

Steady state was reached after ca. 45 min, when 24 mL min^{-1} of water (steam:carbon = 3.4:1) was added. As expected, the temperature of the bed dropped and the amount of gasoline consumed increased (Fig. 2). Significantly more

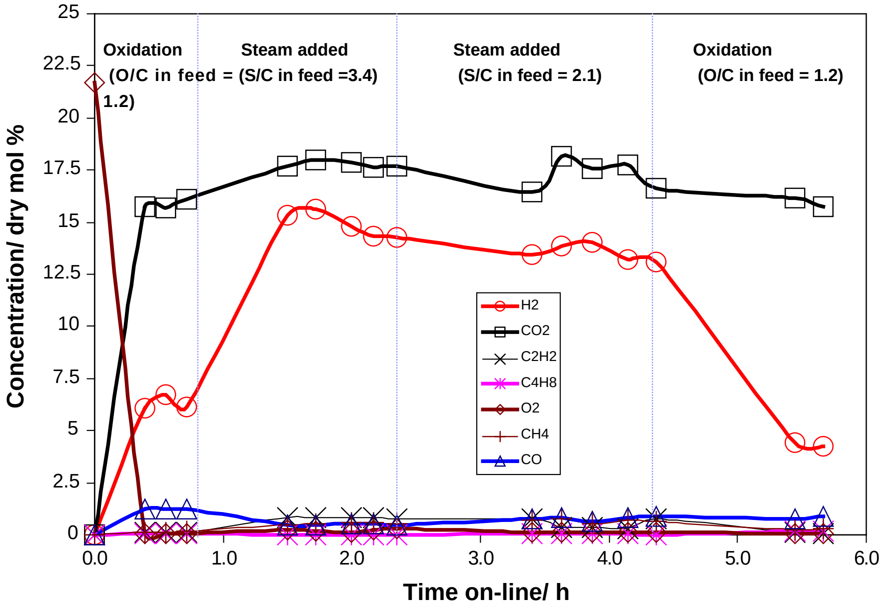

Fig. 4. Combined product distribution for the autothermal reforming of artificial gasoline (total dry gas flow 377 ml min^{-1}; two-bed system with total catalyst loaded = 0.5 g).

Table 2
Results observed and simulated from the autothermal reforming of artificial gasoline

	Run		
	1	2	3
Feedstock			
O:C	1.2	1.2	1.2
H_2O:C	0	3.4	2.1
GHSV[a] (h^{-1})	27000	60800	47700
T_1[b] (°C)	562	391	470
T_2[c] (°C)	584	n/a	566
Conversion (mol%)	51.6	70.3	67.9
RHPE[d] (%)	n/a	26.9	33.1
Product yield, (mol/atom carbon fed) × 100%			
H_2	16.6	44.0	39.1
CO_2	43.5	54.5	49.8
CO	3.4	1.5	2.6
CH_4	0.5	1.6	2.0
C_2H_2	0.3	2.4	2.2
C_4H_8	0.2	0.1	0.1
H_2, mol% in dry gas	6.1	14.3	13.1
H_2 selectivity (mol H_2/atom carbon consumed) ×100%	34.2	70.1	66.3

n/a: not available.
[a] Based on total catalyst volume.
[b] Inlet second bed.
[c] Outlet second bed.
[d] RHPE: (observed value of hydrogen produced) × 100% (calculated hydrogen based on thermodynamics).

isooctane was consumed, but all other components of the gasoline also reacted (Fig. 3). The amount of hydrogen produced increased by about 2.5 times (Fig. 4).

Previous studies have used the relative hydrogen process efficiency (RHPE: the ratio between the amount of hydrogen produced and the calculated maximum hydrogen production based on thermodynamics) to assess the process efficiency [1,2]. Results reported in Table 2 show a value of 27% for this period.

The addition of water requires extra weight for a vehicle, but a steam:carbon ratio of ca. 2 is required to avoid coking [4]. As a result, steam intake was reduced to 0.81 mol h^{-1} (steam:carbon = 2.1). Surprisingly, this reduced conversion only by about 2% (Fig. 2) and had no major effect on product distribution (Figs. 3 and 4). Small traces of acetylene, butene and methane were observed, probable due to small amounts of hydrocarbon cracking and of nickel-catalysed methanation. Carbon monoxide production increased from

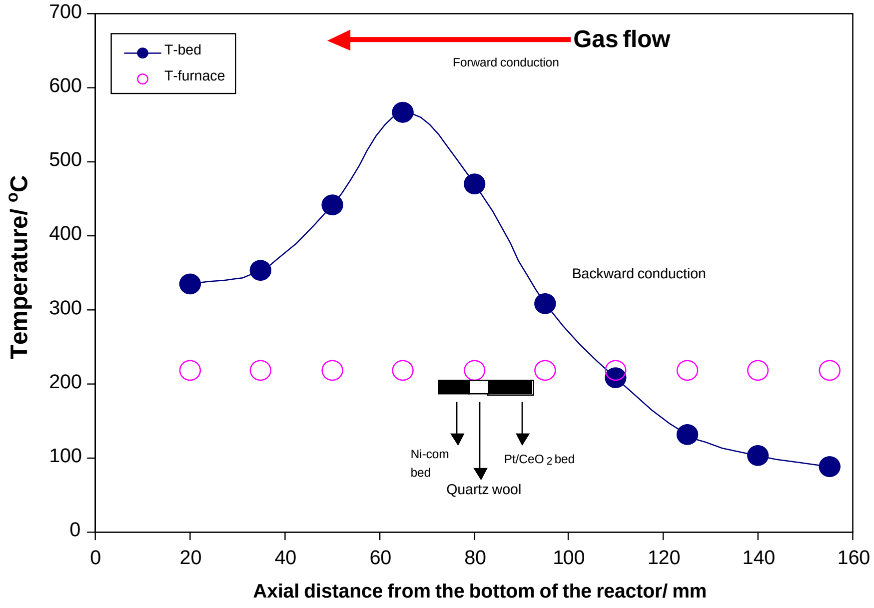

Fig. 5. Temperature profile of the catalyst bed.

0.5% (steam:C = 3.4) to 0.8% (steam:carbon = 2.1), reflecting the decreased importance of the water-gas shift reaction at lower steam concentrations.

The axial temperature distribution along the reactor during operation with a steam:C ratio of 2.1 in shown in Fig. 5. Thermal conduction along the walls of the reactor and the thermowell are seen to distribute the heat provided by the initial oxidation along the length of the reactor, providing sufficient heat to drive the endothermal reforming reactions.

The final cycle involved returning the system to the operating conditions of the first hour (Figs. 2–4). It is seen that the overall conversion returned to the original value, although some 30% less hydrogen was produced (Fig. 4). This was suggested to be due to coke formation, and a second set of experiments was carried out without the final oxidation. Three percent of oxygen in nitrogen was then passed over the catalysts maintained at 500 °C. Calculated 3% carbon dioxide was generated over about 3 h decoking, confirming partial deactivation by coke.

The system was taken through the same cycles several times, with no major changes in results. Figs. 2–4 present results that are typical of all start ups and cycles.

In further experiments, the catalyst bed was cooled to ca. 100 °C and reactants admitted without pre-reduction. No sign of oxidation was observed, until the catalysts were heated to ca. 175 °C, when the exothermic oxidation raised the bed temperature to ca. 580 °C. Previous studies with isooctane have shown that an oxidised catalyst would not light off to ca. 200 °C [7] and these results confirmed the observation for the gasoline mixture.

Although hydrogen yields and selectivities were higher with higher steam:C ratios (Table 2), the extra weight to be carried by the vehicle would reduce fuel consumption. However, lower steam:C ratios do produce sufficient hydrogen for fuel cell operation (Table 2). The production of carbon monoxide is too high for fuel cells, and selective removal of the potential poison [2] will be required.

4. Conclusions

The study shows that the autothermal reforming of a model hydrocarbon gasoline mix to produce hydrogen is feasible using a two-bed system with Pt/CeO_2 catalyst as an initiator. The catalysts must be reduced (probably using hydrogen stored from a previous run) or heated to ca. 200 °C before use.

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