High yields of synthesis gas by millisecond partial oxidation of higher hydrocarbons [*]

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Cyclohexane, n-hexane, and isooctane were reacted with air in a Rh-monolith reactor and converted into synthesis gas ($H_2 + CO$) in yields exceeding 90%, with >95% conversion of fuels and 100% conversion of oxygen. The best catalyst was an 80 ppi washcoated alumina monolith containing 5 wt% Rh. There was a small effect of catalyst contact time on syngas selectivity and conversions for gas space velocities from 3×10^5 to 3×10^6 h^{-1}. Preheating the feed enhances syngas selectivities slightly, but no reactor preheat is necessary provided the fuel remains vaporized. Addition of 25 mol% toluene to isooctane also produces syngas, olefins, and methane with 90% yield, including ~70% yield to syngas. Partial oxidation of gasoline–air mixtures was attempted but the catalysts were poisoned after several hours, probably by sulfur and/or metals.

Keywords: syngas, millisecond partial oxidation, Rh-monolith reactor, hydrocarbon fuels, isooctane, gasoline

1. Introduction

There is large current interest in converting gasoline into synthesis gas or syngas ($H_2 + CO$) for several applications. The addition of small amounts of hydrogen to gasoline improves the overall performance of the automobile combustion engine [1–3] because H_2 provides combustible mixtures at ratios below the lean flammability limit of pure gasoline–air mixtures. Also, the lower temperatures that result from this hydrogen–gasoline–air mixture lead to less NO_x formation and lower heat transfer to the walls. Furthermore, the increased burning velocity associated with hydrogen–gasoline mixtures reduces flame-quenching distances and lowers hydrocarbon emissions [3]. Finally, mixture homogeneity and combustion efficiency are improved by the high molecular diffusivity of H_2 into air. Therefore, a combustion engine running with hydrogen enrichment can reduce fuel consumption and decrease emissions compared to standard combustion engines [4–6]. The CO in syngas, while not possessing as many desirable burning characteristics as H_2, still provides power for the engine in its exothermic combustion to CO_2.

The realization that hydrogen addition to a combustion engine has an overall positive impact on the combustion process has promoted research on both the generation of hydrogen and the delivery of hydrogen to the engine. Hydrogen should be generated on-board from gasoline for practical and safety reasons. Therefore, there have been studies [2–6] attempting to generate hydrogen from gasoline, including both steam reforming and partial-oxidation processes.

Another important automotive application of hydrogen and syngas is for on-board generation of electricity in fuel cells. Several companies are developing hybrid cars running on both conventional combustion power as well as electricity [7]. Hybrid technologies offer several advantages, including the ability to decide which source of power is appropriate for a given journey. Hybrid-engine cars reduce gasoline consumption and cut emissions and could therefore help reduce environmental pollution problems. Other technologies involving on-board fuel cells for auxiliary power have also been explored [8]. These systems take up extra power requirements in vehicles and can run even when the car's engine is turned off.

The successful production of syngas from the partial oxidation of methane [9–11,14,15], ethane [12], and n-butane [13] over Rh catalysts has been studied in detail. However, heavier fuels such as those contained in gasoline might not be expected to be partially oxidized selectively to CO and H_2 in millisecond catalytic reactors because higher hydrocarbons are more reactive than C_1–C_4 alkanes and may form olefins or react homogeneously to form CO_2 and soot. In this letter, we show that it is possible to convert higher hydrocarbons and air into very high yields of syngas in a Rh-coated ceramic-monolith reactor at millisecond contact times. The hydrocarbons studied include n-hexane, cyclohexane, toluene, isooctane, and gasoline.

The desired overall reaction of the general fuel C_xH_y and air is the formation of syngas

$$C_xH_y + \frac{x}{2}O_2 \rightarrow xCO + \frac{y}{2}H_2$$

which stoichiometrically is represented by C/O = 1. A competing reaction is the highly exothermic total oxi-

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dation of the fuel,

$$\mathrm{C}_x\mathrm{H}_y + \left(x + \frac{y}{4}\right)\mathrm{O}_2 \rightarrow x\mathrm{CO}_2 + \frac{y}{2}\mathrm{H}_2\mathrm{O}$$

Other possible reactions include olefin formation, steam reforming, and water–gas shift. We report both carbon-atom selectivities and hydrogen-atom selectivities calculated as the ratio of the moles of a specific product to the total moles of all products, with all species scaled by their number of C or H atoms. This definition accounts for the mole-number increase due to reaction and allows C-atom and H-atom selectivities to each sum to unity. Selectivities to CO and to H_2 are given by

$$S_{\mathrm{CO}} = \frac{\mathrm{CO}}{\sum_i m_i \mathrm{C}_{m_i}\mathrm{H}_{n_i}\mathrm{O}_{p_i}},$$

$$S_{\mathrm{H}_2} = \frac{2\mathrm{H}_2}{\sum_i n_i \mathrm{C}_{m_i}\mathrm{H}_{n_i}\mathrm{O}_{p_i}},$$

where m_i, n_i, and p_i are the number of carbon, hydrogen, and oxygen atoms, respectively, in each species and the summations are over all products $\mathrm{C}_{m_i}\mathrm{H}_{n_i}\mathrm{O}_{p_i}$. In the case that only the above two reactions occur, the selectivities are simply given by $S_{\mathrm{CO}} = \mathrm{CO}/(\mathrm{CO} + \mathrm{CO}_2)$ and $S_{\mathrm{H}_2} = \mathrm{H}_2/(\mathrm{H}_2 + \mathrm{H}_2\mathrm{O})$.

2. Experimental

The experimental apparatus and procedure were as described previously [9,16]. The reactor consisted of an 18 mm ID quartz tube containing an α-Al_2O_3 rhodium-coated monolith of 20, 45, or 80 pores per linear inch (ppi). The catalyst samples were prepared by soaking the monoliths in aqueous $Rh(NO_3)_3$ salt solutions, drying in air, and then calcining for ~6 h at 600 °C. In all experiments the monoliths were coated with 5–6 wt% Rh and in some experiments the monoliths were first washcoated with ~5 wt% γ-Al_2O_3. The washcoat, prepared from a γ-alumina slurry, consisted of a thin layer (25–50 μm) which roughens the catalyst surface and increases the surface area [13,17]. Two blank 45 ppi monoliths placed upstream and downstream of the active monolith served as axial heat shields. The three-monolith assembly was wrapped with thin Fiberfrax paper (alumina–silica fibers) to prevent bypassing of gases between the catalyst and the reactor wall. In the region of the catalyst, approximately one inch of high-temperature alumina–silica insulation was placed around the reactor tube to minimize radial heat losses.

The flow rates of the high-purity (99.9+%) gases (oxygen and nitrogen) entering the system from high-pressure cylinders were adjusted using mass-flow controllers that are accurate to ±0.1 SLPM (standard liters per minute). The liquid hydrocarbons were high-purity HPLC grade, except for gasoline, which was a regular 87-octane automotive fuel. Liquid fuels were metered with an ISCO syringe pump and vaporized by a fluidized-bed heater. Catalyst light-off was achieved by temporarily preheating to the ignition temperature, which was approximately 250 °C for almost all experiments. Autothermal temperatures at the front and back faces of the catalytic monolith were measured to within ±10 °C with chromel–alumel thermocouples. The reactor pressure was maintained at 1.2 atm with a downstream valve. The product gas composition was monitored by a gas chromatograph (HP 6890 GC), and by using inert N_2 as the calibration standard, carbon and hydrogen balances typically closed within ±5%. All product gases were incinerated in a fume hood and vented.

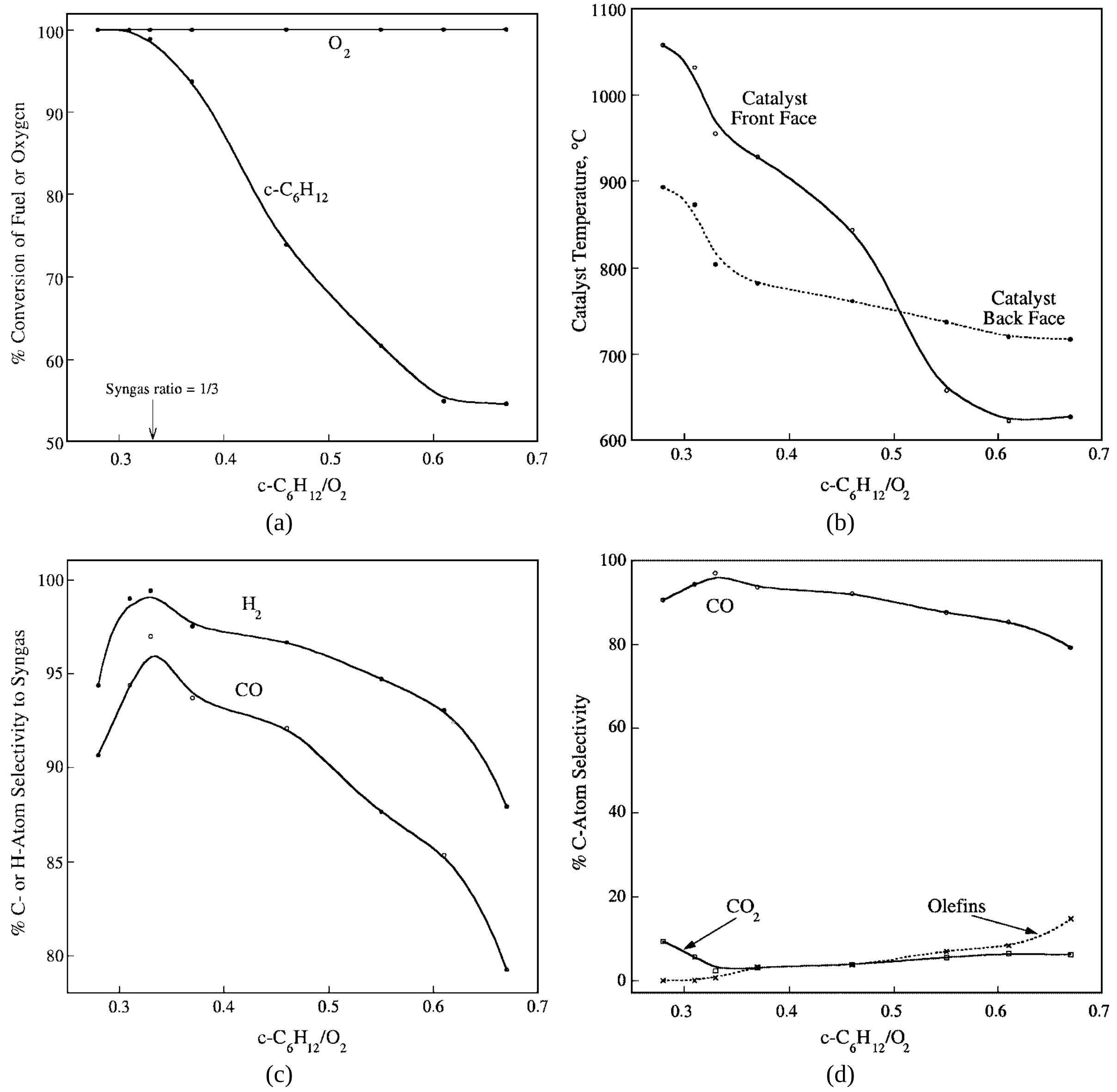
3. Results

3.1. Cyclohexane

Cyclohexane (research octane number, RON = 83) and air were fed to the Rh-monolith reactor at varying fuel/oxygen ratios. A Rh-coated 80 ppi monolith with a washcoat was chosen because this catalyst is optimal for syngas production from methane [13]. The cyclohexane/oxygen molar feed ratio was varied from 0.28 to 0.67 with the total flow rate of cyclohexane and air fixed at 2.5 SLPM (gas space velocity of 7.3×10^5 h^{-1}), the reactor pressure $P = 1.2$ atm, and the feed temperature $T_0 = 250$ °C. The stoichiometric ratio for the production of syngas from cyclohexane is c-$C_6H_{12}/O_2 = 1/3$, while the combustion ratio is 1/9.

Figure 1(a) shows the conversion of fuel (cyclohexane) and oxygen for these experiments. Oxygen was completely converted for all ratios. The cyclohexane conversion was 100% for c-$C_6H_{12}/O_2 < 1/3$ and ~99% at the syngas ratio. For richer feeds, fuel conversion fell, dropping to 55% for c-$C_6H_{12}/O_2 = 2/3$. Figure 1(b) shows both the front-face and back-face catalyst temperatures. At the syngas ratio, the front face was ~950 °C while the back face was ~800 °C. The difference of 150 °C between front and back faces suggests that the chemistry was shifted towards the entrance of the catalytic monolith. The abrupt increase of temperatures below the syngas ratio can be attributed to the total oxidation of some of the fuel, as indicated by the production of CO_2 (figure 1(d)), a highly exothermic reaction. For richer (c-$C_6H_{12}/O_2 > 1/2$) conditions, the back face was hotter, while for a fuel/oxygen ratio of approximately 1/2, the entrance and exit of the catalyst were both at ~750 °C.

Figure 1(c) shows the selectivities to synthesis gas for these experiments. Hydrogen-atom selectivities to H_2 and carbon-atom selectivities to CO are reported. There was a clear optimum at the syngas ratio in both H_2 (99% selectivity) and CO (97% selectivity). Even at c-$C_6H_{12}/O_2 = 2/3$, twice as fuel-rich as the syngas ratio, selectivities of 88% to H_2 and 79% to CO were attained. Figure 1(d) (carbon products) shows that mixtures leaner than the syngas ratio tended to form combustion products, while richer mixtures favored the formation of olefins at the expense of CO. The



(a) (b)

(c) (d)

Figure 1. Partial oxidation of cyclohexane with air over an 80 ppi Rh monolith (with washcoat). The space velocity was 7.3×10^5 h^{-1}, the feed temperature 250 °C, and the reactor pressure 1.2 atm.

olefins produced were primarily ethylene, propylene, cyclohexene and benzene, and soot production was apparently minimal.

3.2. *n*-hexane

The difference between linear and cyclic fuels was explored by feeding *n*-hexane (RON = 25) and air over the same catalyst and at the same reactor conditions. The fuel/oxygen feed ratio (n-C_6H_{14}/O_2) was varied again from 0.28 to 0.67. The stoichiometric ratio for the production of syngas from *n*-hexane is n-$C_6H_{14}/O_2 = 1/3$, while the combustion ratio is 0.105. Figure 2 shows that *n*-hexane partial oxidation was similar to that of cyclohexane. At the syngas ratio, nearly 100% conversion of fuel was achieved, with 99 and 96% selectivities to H_2 and CO, respectively. There was no oxygen breakthrough for any value of n-C_6H_{14}/O_2. Trends in selectivities to CO_2 and cracked olefins (not shown) were also similar to those for cyclohexane. The loss in syngas selectivity was due to CO_2 and H_2O formation for n-$C_6H_{14}/O_2 < 1/3$ and due to olefin production for n-$C_6H_{14}/O_2 > 1/3$.

3.3. Isooctane

The effect of branching in the fuel was investigated by feeding isooctane (2,2,4-trimethylpentane, RON = 100), a standard reference fuel for gasoline. The isooctane/oxygen ratio (i-C_8H_{18}/O_2) was varied from 0.225 to 0.50, which is roughly the same range of carbon/oxygen atom ratios (C/O) as for the previous experiments. Again, a Rh-coated 80 ppi washcoated monolith was used, and reactor conditions were set at 7.3×10^5 h^{-1} space velocity (isooctane + air), $P =$

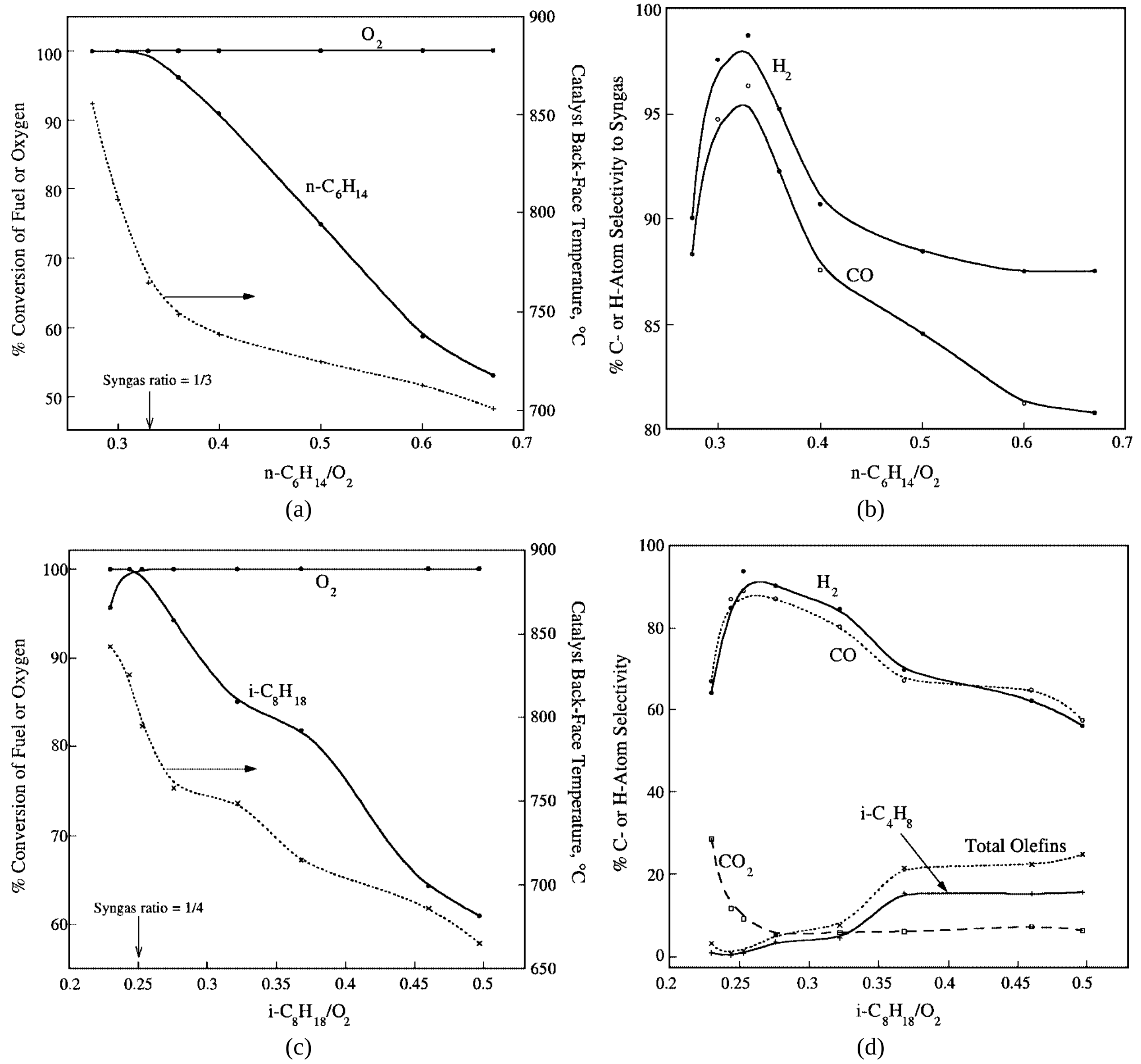


Figure 2. Partial oxidation of n-hexane (a, b) and isooctane (c, d) with air over an 80 ppi Rh monolith (with washcoat). The space velocity was $7.3 \times 10^5\ h^{-1}$, the feed temperature 250 °C, and the reactor pressure 1.2 atm.

1.2 atm, and $T_0 = 250$ °C. The syngas ratio for isooctane is i-$C_8H_{18}/O_2 = 1/4$ and the combustion ratio is 0.08.

Figure 2(c) shows that fuel conversion was 100% for i-$C_8H_{18}/O_2 \leqslant 1/4$ and dropped to ~60% at i-$C_8H_{18}/O_2 = 1/2$. Catalyst back-face temperatures show the same qualitative trend as seen for the C_6 alkanes, and the temperature at the syngas ratio (795 °C) was comparable. Oxygen conversion was complete at the syngas ratio but dipped to 96% for $C_8H_{18}/O_2 = 0.225$. Selectivities of 94% to H_2 and 89% to CO (figure 2(d)) were observed at i-$C_8H_{18}/O_2 = 1/4$. At i-$C_8H_{18}/O_2 = 0.225$, CO_2 selectivity jumped to 28% as syngas formation decreased. Olefin production was very important for i-$C_8H_{18}/O_2 > 0.3$. The dominant olefin produced was isobutylene, which was 15% selective for fuel/oxygen ratios exceeding 0.35. Other products included propylene and methane, which were 8 and 10% selective, respectively, at i-$C_8H_{18}/O_2 = 1/2$.

3.4. Catalyst pore size and washcoat

The density of the catalytic pores or channels contained in the α-Al_2O_3 monolith was varied from 20 to 80 pores per linear inch (ppi). The average pore diameter of a blank monolith is the porosity (~80%) divided by the number of pores per inch, and the actual pore diameter (table 1) is lower by twice the thickness of the catalyst film (and washcoat if present). Experiments were performed with an isooctane–air feed at the syngas ratio (i-$C_8H_{18}/O_2 = 1/4$) with a space velocity of $7.3 \times 10^5\ h^{-1}$, feed temperature of 250 °C, and reactor pressure of 1.2 atm. Results are compared in table 1 for catalyst geometries of 20, 45, and 80 ppi. An 80 ppi catalyst with a washcoat (~5 wt% γ-Al_2O_3 and 25–50 μm film thickness) was also tested. All catalysts had Rh loadings of 5–6 wt%.

Table 1
Effect of catalyst support.[a]

Rh catalyst pore density	Pore diameter (μm)	Surface area (m^2)	Back-face T (°C)	Selectivity (%) CO	CO_2	H_2
20 ppi	∼800	0.2–0.4	930	75	11	70
45 ppi	∼350	0.2–0.4	910	78	10	74
80 ppi	∼200	0.2–0.4	843	83	9	84
80 ppi with washcoat	100–150	2–5	795	90	9	93

[a] Isooctane–air feed at the syngas ratio and conditions as stated in text. Conversions of both fuel and oxygen were nearly 100% for all catalysts.

Conversions of both fuel and oxygen were nearly 100% for all four catalysts at these conditions. Selectivities to syngas improved as the pore diameter was reduced from 800 μm (20 ppi) to 200 μm (80 ppi). Without a washcoat, the 80 ppi monolith was 8% more selective to carbon monoxide and 14% more selective to hydrogen than the 20 ppi monolith. The washcoat significantly improved the production of syngas, raising the H_2 and CO selectivities by 9 and 7%, respectively, over the non-washcoated 80 ppi catalyst support. Catalyst exit temperatures increased as the pore density decreased from 80 to 20 ppi. The larger pores in the 20 ppi monolith cannot catalytically consume O_2 as quickly, driving up the measured back-face temperature.

3.5. Contact time

The effect of varying the total gas space velocity (or catalyst contact time) over a factor of ten was explored by feeding isooctane and air at flow rates from 1 to 10 SLPM at the syngas ratio of $i\text{-}C_8H_{18}/O_2 = 1/4$ ($T_0 = 250\,°C$). These flow rates translate into gas space velocities from 3×10^5 to 3×10^6 h^{-1} (calculated at reactor inlet conditions). The catalyst contact time τ, which depends on reaction conditions, ranged from 20 to 2 ms over these space velocities. A Rh-coated 80 ppi washcoated monolith, optimal for syngas production as shown above, was used.

The conversions of both isooctane and oxygen were essentially complete for all flow rates (figure 3(a)). The catalyst exit temperature varied widely, from 630 °C at 3×10^5 h^{-1} to 920 °C at 3×10^6 h^{-1}. Selectivities to synthesis gas, approximately 85–90% for all flow rates studied, were relatively insensitive to contact time (figure 3(b)). The significant changes in back-face temperature could not have been due to changes in the chemistry. At 3×10^5 h^{-1}, the selectivity to CO_2 was 13%, meaning more total oxidation was occurring which should increase temperatures; yet the lowest back-face temperature was observed at 3×10^5 h^{-1}. The temperature behavior was instead a result of the differing heat transfer through the monolith. As the flow rate increased, the reaction heat was more effectively carried to the catalyst back face, and the reactor operated closer to adiabatic. Operation at even higher flow rate should be possible with little loss in performance.

3.6. Preheat

The effect of varying the reactor feed temperature from 110 to 300 °C was explored by feeding 2.5 SLPM of isooctane and air (7.3×10^5 h^{-1} or $\tau = 8$ ms) at the syngas ratio, again over a Rh-coated 80 ppi washcoated monolith. The preheat temperature was adjusted with heating tape wrapped around the reactor tube upstream of the catalyst. At a reactor pressure of 1.2 atm, 110 °C is just above the boiling point of isooctane.

The conversions of both isooctane and oxygen were complete for all feed temperatures. The catalyst front face varied from 950 °C at $T_0 = 110\,°C$ (no preheat) to 1085 °C at $T_0 = 300\,°C$, while the back face increased only ∼15 °C (figure 3(c)). This result suggests that at these conditions the reaction zone was located near the front of the catalyst. Syngas production was favored by preheating the reactants (figure 3(d)). No preheat gave 85% H-atom selectivity to H_2 and 83% C-atom selectivity to CO. These numbers increased and began to level off at $T_0 = 250\,°C$, reaching 93 and 90% selectivities to H_2 and CO, respectively.

3.7. Aromatics

Gasoline usually contains aromatics for octane enhancement, and toluene (RON = 120) is typically the largest aromatic component of gasoline. California Phase II fuel contains 25% aromatics [19]. To examine the influence of aromatic fuels in the partial oxidation to synthesis gas, we added 25 mol% (18 liquid vol%) toluene to isooctane and fed the mixture with air over a washcoated 80 ppi Rh catalyst. The space velocity, feed temperature, and reactor pressure were set to 7.3×10^5 h^{-1}, 250 °C, and 1.2 atm. The isooctane/oxygen molar ratio was first fixed at 1/4 with the toluene added, producing a mixture slightly richer (C/O $\approx$ 1.2) than the syngas composition. In a separate experiment, the stoichiometric amount of air was calculated for each hydrocarbon and summed so that the carbon/oxygen atom ratio C/O was unity for the overall fuel.

Table 2 summarizes the results of toluene addition to isooctane. The conversions of isooctane and oxygen were both nearly complete in these experiments. For C/O = 1.2, the conversion of toluene was 82%, while the selectivity to H_2 was 62% and to CO was 69%. At the syngas ratio (C/O = 1), the conversion of toluene increased to 88%, and the selectivity to syngas increased to 65% for H_2 and 71% for CO. The catalyst back-face temperature also increased slightly to 826 °C. When shutting down the reactor, solid carbon accumulated at the exit of the downstream blank monolith, but at steady state there was no apparent accumulation of coke. Small amounts of carbon buildup were observed on the thermocouple wires downstream of the catalyst.

3.8. Commercial gasoline

In these experiments the millisecond reactor has been proven to be able to partially oxidize a wide variety of

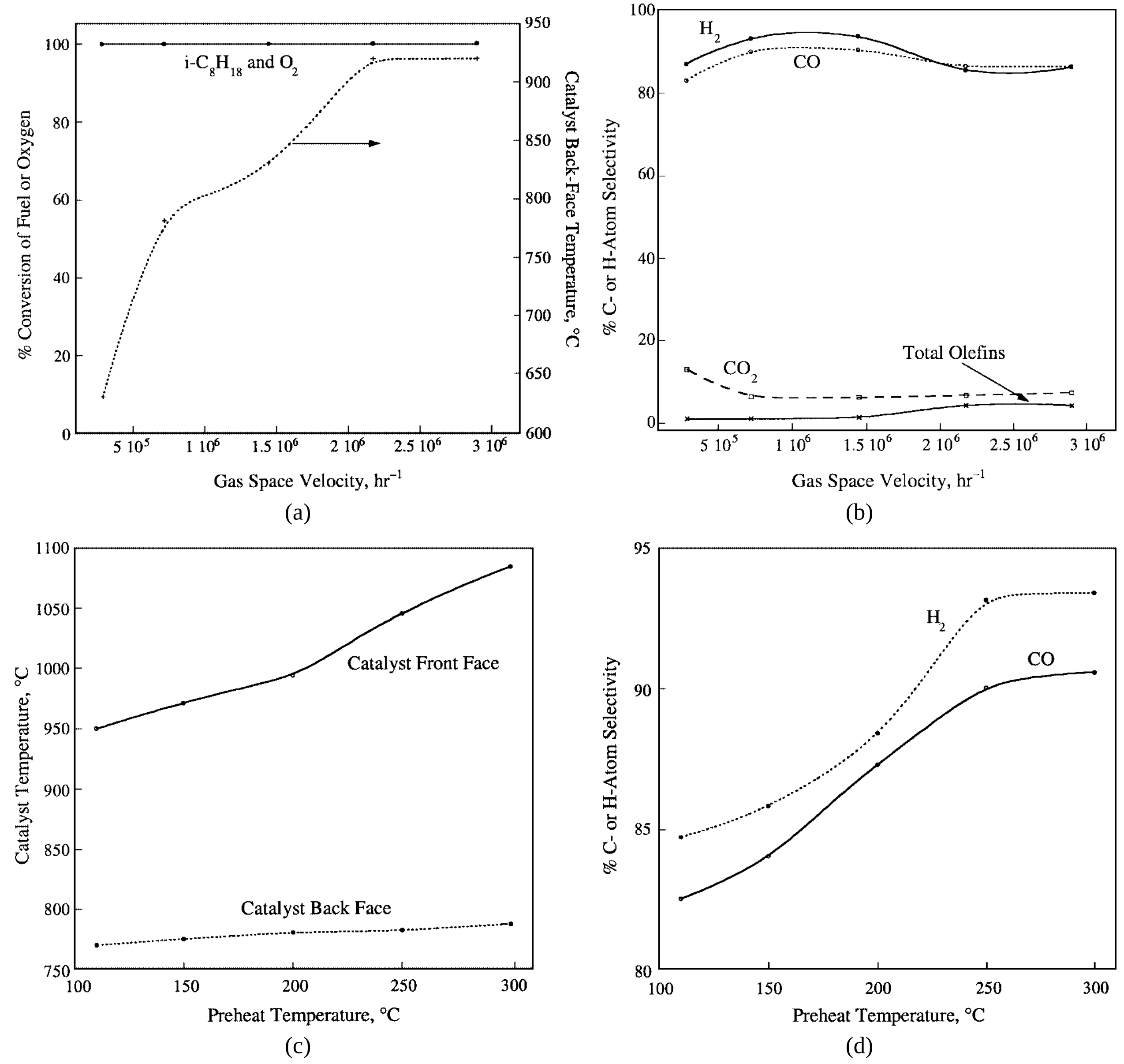


Figure 3. Effects of varying the gas space velocity (a, b) at $T_0 = 250\,^{\circ}\mathrm{C}$ and the preheat temperature (c, d) at a space velocity of 7.3×10^5 h^{-1}. The isooctane and air were fed at the syngas ratio ($i\text{-}C_8H_{18}/O_2 = 1/4$) over a washcoated 80 ppi Rh monolith with a reactor pressure of 1.2 atm. For the preheat experiments, conversions of both fuel and oxygen were nearly complete.

Table 2
75% isooctane–25% toluene partial oxidation.[a]

C/O	Conversion			Back-face	Selectivity (%)	
	Oxygen	Isooctane	Toluene	temperature (°C)	CO	H_2
1.2	100	100	82	812	69	62
1.0	100	100	88	826	71	65

[a] Catalyst was a washcoated 80 ppi Rh monolith with reactor conditions as stated in text.

feed streams to synthesis gas. It would of course be economically attractive if existing gasolines could be directly converted to syngas in this process. To examine the explicit performance of commercial automotive fuels, we fed regular 87-octane gasoline (BP Amoco) and air over an 80 ppi Rh washcoated monolith at varying air concentrations. It is difficult to calculate fuel conversions due to the large number of hydrocarbons, many of which are unknown. Because the water peak was unreliable in the GC analysis, H_2 selectivities could not be estimated without knowing fuel conversion. We report here the $CO/(CO + CO_2)$ ratio, which has ranged from 0.85 to 0.95 in the experiments described so far.

There is no obvious syngas ratio for gasoline as for individual fuels. We attempted to experimentally locate the optimum fuel/air ratio for syngas production by varying the air flow rate from 1 to 4 SLPM while keeping the fuel delivery rate constant at 100 ml h^{-1}. The optimum air flow rate was 1.8 SLPM, which gave $CO/(CO + CO_2) = 0.77$ for an 80 ppi washcoated Rh monolith (table 3). The value of $CO/(CO + CO_2)$ varied from 0.44 for 1 SLPM air to

Table 3
Gasoline partial oxidation.[a]

Rh catalyst pore density	% oxygen conversion	Back-face temperature (°C)	$CO/(CO + CO_2)$
20 ppi	99.8	795	0.74
80 ppi with washcoat	99.5	744	0.77

[a] The liquid flow rate of gasoline was 100 $ml\,h^{-1}$ and the air flow rate was 1.8 SLPM. Reactor conditions were as stated in text.

0.19 for 4 SLPM. A 20 ppi monolith at the same flow rate and inlet concentrations produced $CO/(CO + CO_2) = 0.74$. Possible reasons why gasoline did not perform as well as isooctane are discussed below.

4. Discussion

We find that higher alkanes give higher selectivities to syngas and higher hydrocarbon conversions than does methane. This result is surprising because the higher alkanes should have more tendency to undergo homogeneous reactions that should readily form coke and soot, which are never observed, even at high fuel/O_2 ratios. Homogeneous combustion of higher alkanes is much faster because the weaker C–H bonds give faster flame induction times and higher flame velocities. The flame induction time for methane is $\sim$10 ms, while for higher alkanes it is $\sim$1 ms.

The higher alkanes also give temperatures up to 200 °C cooler than for methane, which might be expected to lower conversions and syngas selectivities while stopping the reaction without breaking all C–C bonds. Higher alkanes are capable of easily forming olefins while CH_4 is not. Scission of C–C bonds forms an olefin and a smaller alkane, and noble-metal catalysts (particularly Pt) are capable of oxidative dehydrogenation of C_2H_6 and higher alkanes with >60% carbon atom selectivity. While we observe as high as 10–20% olefins at high fuel/O_2 ratios, at the syngas ratio olefin production is much less than 1%.

4.1. Comparison of alkanes

At the syngas ratio ($C_6/O_2 = 1/3$), both cyclohexane and n-hexane were reacted with air over Rh to produce synthesis gas at >95% selectivities to both H_2 and CO. Trends for both C_6 alkanes were similar. Compositions leaner than the syngas ratio produced CO_2 and H_2O, while feeds richer than $C_6/O_2 = 1/3$ tended to form parent and cracked olefins. The production of high-octane olefins is probably more beneficial than the formation of complete-combustion products for this technology. Isooctane (2,2,4-trimethylpentane), a model gasoline component defined with an octane number of 100, could also be successfully converted to syngas (94% selectivity to H_2 and 90% to CO) in our process. Isooctane exhibited a narrower optimum in syngas selectivity with respect to fuel/oxygen ratio, compared to cyclohexane or n-hexane. For $C/O = 2$, the C_6 alkanes still produced >80% selectivities to H_2 and CO while isooctane oxidation became $\sim$60% selective for syngas. The dominant olefin produced from isooctane was isobutylene, which also has a high octane rating.

4.2. Toluene + isooctane

Toluene, added to isooctane to simulate the aromatics contained in fuels, was converted to syngas moderately well and did not induce coking in the reactor or visible soot formation. For a 75 mol% isooctane + 25 mol% toluene blend at $C/O = 1$, the toluene conversion was 88%, isooctane was completely converted, and selectivities of 65% to H_2 and 71% to CO were attained. The lower conversion of toluene compared to isooctane is probably due to the absence of secondary or tertiary C–H bonds that facilitate adsorption and reaction. The carbon–hydrogen bonds on the aromatic ring are over 20 kcal/mol stronger than the primary C–H bonds on the methyl group, so initial H atom abstraction from toluene should occur at the methyl group. Hydrogen abstraction rates generally increase in the order phenyl < primary < secondary < tertiary. Isooctane has a weak tertiary C–H bond which should be attacked quickly so that, overall, isooctane is more reactive than toluene.

It is perhaps surprising that hydrogen-deficient toluene does not form soot or coke. Apparently the toluene that does undergo initial abstraction loses its aromatic stabilization quickly so that carbon-containing species can desorb from the surface. Although the production of syngas decreased with toluene addition, olefins (such as propylene) and methane, rather than CO_2, were produced. The selectivities to total-oxidation products were comparable to those with pure-isooctane feeds ($CO/CO_x \approx 0.9$ with and without 25 mol% toluene).

4.3. Gasoline

Partial oxidation of gasoline poses several challenges. First, there is not a unique "syngas ratio" as for distinct hydrocarbon molecules. The stoichiometric carbon/oxygen atomic ratio for converting oxygen-containing hydrocarbons to syngas is greater than unity, meaning that the proper C/O ratio for gasoline with oxygenated components is greater than one. In any case, gasoline is composed of many different hydrocarbons, and it can be difficult to calculate an average stoichiometric formula for computing the proper flow rates. Second, sulfur-containing compounds can poison noble-metal catalysts such as rhodium. Typical gasolines contain anywhere from 50 to 500 ppm sulfur [17]. Third, metal contaminants in gasoline can also poison catalysts. Finally, compounds such as detergents and anti-oxidants are usually added by refiners to gasoline.

Experimentally, gasoline oxidation over Rh could not be made to be as selective to syngas. One possible reason is that, while any of the individual fuels in gasoline would work well at their respective syngas ratios, there is no way to operate with an appropriate amount of air to partially oxidize (selectively to syngas) every fuel present. The 87-octane gasoline we tested contained C_4–C_9 alkanes, olefins, aromatics, and 10 vol% ethanol (winter fuel in Minnesota). Since the syngas ratio for ethanol is relatively rich ($C/O = 2$ feed ratio of ethanol/air), ethanol oxidation could account for some of the CO_2. Indeed, ethanol, and oxygenates in general, are often added to gasoline as "clean-burning" fuels because they readily form CO_2 due to internal oxygen. While we cannot expect to achieve complete conversion of gasoline with high syngas selectivities, it should be possible to operate fuel-rich so that CO_2 formation is minimized. By varying the overall fuel/air concentrations over a fourfold range in gasoline/O_2, it was found that CO_2 formation was always significant and that $CO/(CO + CO_2) = 0.77$ was the best selectivity observed. Compared to isooctane, which at its syngas ratio produced $CO/CO_x = 0.94$ and 0.87 for 80 and 20 ppi, respectively, gasoline oxidation did not perform as well in selectively producing syngas. Gasoline (table 3) did show the same trend with respect to pore size as isooctane (table 1).

All individual fuels, when operated richer than the syngas ratio, produced small amounts of CO_2 (figures 1 and 3). Yet no matter how rich we fed gasoline–air, carbon dioxide and water were always produced in relatively large amounts, indicating that gas-phase reactions (unselective to syngas) were probably important. The incomplete oxygen conversion for gasoline oxidation implies that something was preventing all the O_2 from adsorbing onto the rhodium surface. If oxygen consumption is not rapid, oxidation channels to CO_2 and H_2O become favored. Catalyst ignition temperatures for gasoline in air gradually increased over time to $>300\,°C$, as opposed to $\sim 250\,°C$ for all individual hydrocarbons studied, indicating less catalytic activity. Moreover, syngas selectivities at constant gasoline/O_2 and reactor conditions steadily declined a period of several (~ 10) hours. All of these factors suggest some type of catalyst deactivation as the underlying problem. Although aromatics tend to form soot at high temperatures, the gasoline tested contained ~ 10 mol% aromatics, much less than in the isooctane–25 mol% toluene mixture which did not lead to visible coke formation on the catalyst.

The likely deactivation mechanism was poisoning by sulfur-containing compounds, because the gasoline used contained ~ 0.5 wt% sulfur [18], mostly as thiophenic derivatives. Rh catalysts are known to be sensitive to small (~ 100 ppm) levels of sulfur contaminants, and energy dispersive X-ray spectroscopy of the used catalyst surface showed strong evidence of poisoning by S as well as other metals such as Fe, V, Mg, and Ti that probably originated from the crude oil (which can contain up to 1 wt% metals [18]) or additives. As environmental regulations become stricter and gasolines become cleaner, sulfur and metal poisoning should be reduced.

4.4. Catalyst and reactor conditions

The size of the Rh-coated catalyst channels had a significant effect on syngas selectivities for isooctane–air oxidation at the syngas ratio (i-$C_8H_{18}/O_2 = 1/4$). As the pore size was decreased (pore density increased) from 20 to 80 ppi, the H-atom selectivity to H_2 improved by 14% and the C-atom selectivity to CO increased by 8%. Total oxidation is much more exothermic than partial oxidation, so higher catalyst temperatures were observed for larger pores. Rh promotes $CO + H_2$ (at short contact times) while gas-phase reactions lead to $CO_2 + H_2O$. Therefore, smaller pores, by consuming oxygen more rapidly than larger pores, favored the syngas route.

Addition of a γ-Al_2O_3 washcoat to an 80 ppi α-Al_2O_3 monolith further enhanced the selectivity to syngas by 9% for H_2 and 7% for CO. This improvement can be explained by the increased mixing in the boundary layer due to the surface roughening by the washcoat, improving mass transfer of the limiting reactant (oxygen) to the catalytic surface. These results are very similar to trends observed with methane and n-butane partial oxidation [13].

Using the optimal washcoated 80 ppi Rh catalyst, the gas space velocity of isooctane and air (at i-$C_8H_{18}/O_2 = 1/4$) was varied from 3×10^5 h^{-1} ($\tau = 20$ ms) to 3×10^6 h^{-1} ($\tau = 2$ ms) at $T_0 = 250\,°C$. Additionally, the feed temperature was varied from no preheat ($T_0 \approx 110\,°C$) to $T_0 = 300\,°C$ at 7.3×10^5 h^{-1}. The catalyst did not extinguish at 3×10^6 h^{-1}, the highest space velocity studied in our experimental system. Low flow rates promote formation of carbon dioxide and water due to the long catalyst contact times (>10 ms). At higher space velocities, syngas selectivities decreased by $\sim 5\%$, but the decrease was due to olefin formation rather than CO_2 production. Preheating the feed gases by nearly 200 °C increased syngas selectivities by 5–10%, probably due to enhanced reaction and mass-transfer rates. Inlet temperatures higher than approximately 250 °C did not significantly affect syngas selectivity.

4.5. Mechanism

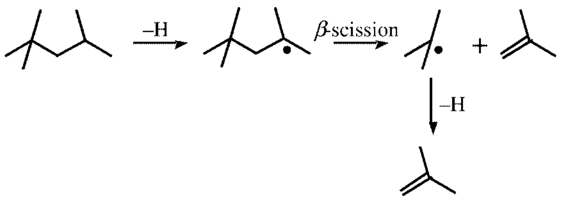
The Rh-surface chemistry of the general fuel molecule C_xH_y and oxygen should be qualitatively similar to methane partial oxidation [9–11,14,15]:

$$\begin{gathered} C_xH_{y,s} \rightarrow C_xH_{y',s} + (y - y')H_s \\ O_{2,g} \rightarrow 2O_s \\ 2H_s \rightarrow H_{2,g} \\ C_s + O_s \rightarrow CO_s \rightarrow CO_g \end{gathered}$$

The fuel necessarily undergoes multiple dehydrogenation and C–C cleavage reactions. The hydrogen on the surface desorbs to form gas-phase molecular H_2. Adsorbed oxygen reacts with carbon to form CO which desorbs or possibly reacts further. Direct reactions of fuel fragments or CO with adsorbed oxygen can lead to CO_2 and H_2O. However, some total oxidation may be necessary to generate heat and keep the catalyst ignited.

Alkanes and probably olefins should follow this general scheme. With hydrogen-deficient aromatic hydrocarbons, H-atom abstractions quickly lead to carbon-rich material that will coke the catalyst surface if the aromatics are not oxidized with oxygen. Although there is less hydrogen in aromatic compounds, the selectivity to H_2 will not necessarily be affected because $OH^{\cdot}$ formation ($C_xH_{y,s}+O_s \rightarrow C_xH_{y-1,s}+OH_s$ or $H_s+O_s \rightarrow OH_s$) should be reduced, thus leading to less water ($OH_s+H_s \rightarrow H_2O_g$). Aromatics should only lower syngas selectivities if they deactivate the surface through coking and allow oxygen breakthrough and subsequent gas-phase total-oxidation reactions. Oxygenates, as discussed above, could cause increased CO_2 formation on the surface because abstractions may lead to surface CO rather than C, thus favoring the $CO_s + O_s \rightarrow CO_{2,g}$ reaction.

A significant difference between methane and larger fuels is that all C–H bonds are not equivalent in most fuels as in methane. The large selectivity to isobutylene (~15%) from isooctane partial oxidation emphasizes this fact. Isooctane contains five primary carbon sites and one secondary, one tertiary, and one quaternary site. H-atom abstraction rates are highest for tertiary C–H bonds [20]. Isobutylene results from abstraction of the tertiary hydrogen followed by β-scission of the parent molecule into isobutylene and an isobutyl radical i-$C_4H_9^{\cdot}$,



The isobutyl radical has nine equivalent primary H atoms, and the abstraction of one of them leads to another isobutylene molecule. At fuel-rich conditions, isobutylene is not further broken down and is a significant product from isooctane.

5. Summary

A wide variety of fuels were fed with air to a Rh-coated monolith reactor at millisecond contact times, and we find that they can produce synthesis gas (CO and H_2) in very high yields. Cyclohexane,n-hexane, isooctane, and toluene, representing model cyclic, linear, branched, and aromatic hydrocarbon fuels, respectively, could all be partially oxidized to syngas. Optima with respect to fuel/oxygen ratios occurred at the stoichiometric ratio for syngas ($C/O = 1$) for each fuel. Yields of syngas from cyclohexane and n-hexane exceeded 95%, while those from isooctane surpassed 90%. Addition of 25 mol% toluene to isooctane lowered syngas yields to <70%, but most of the non-syngas products were high-octane olefins. Partial oxidation of commercial 87-octane gasoline resulted in ~80% CO_x selectivity to CO, but sulfur-containing contaminants and/or metals in the gasoline poisoned the Rh surface. Because environmental regulations continue to limit the acceptable amounts of sulfur and metals in gasoline, there is promise of utilizing commercially available fuels for generating syngas on-board automobiles.

The catalyst pore size had a considerable effect on syngas selectivities, with the highest production of syngas observed for 80 ppi Rh-coated ceramic monoliths containing a washcoat. The reactor performance was not significantly altered by an order-of-magnitude change in space velocities from 3×10^5 h^{-1} ($\tau \approx 20$ ms) to at least 3×10^6 h^{-1} ($\tau \approx 2$ ms), indicating that catalyst geometry rather than surface area was responsible for the effect of pore size. Preheating the feed enhanced syngas selectivity by several percent, but no reactor preheat was necessary other than that required to ignite the catalyst and vaporize the fuel.

Liquid throughputs in these experiments were about one-tenth those of gasoline consumption rates in a typical automobile journey (60 mi h^{-1} and 30 mi gal^{-1}), which corresponds to approximately 2 kW of syngas. Although space velocities higher than 3×10^6 h^{-1} should be possible, higher fuel flow rates can be handled simply by scaling up to a larger catalyst at the same contact time; an order-of-magnitude increase in throughput capacity requires increasing the monolith diameter to ~5 cm. Waste heat, readily available in an engine, should easily provide the heat requirements for fuel vaporization and preheat and probably allow for H_2O injection to increase H_2 production.

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