

Catalytic partial oxidation of higher hydrocarbons at millisecond contact times: decane, hexadecane, and diesel fuel

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Abstract

The catalytic partial oxidation of *n*-decane and *n*-hexadecane with air over a Rh-coated monolith produces synthesis gas (H_2 and CO) in selectivities exceeding 80%, with > 99% conversion of fuels and 100% conversion of oxygen at catalyst contact times from 5 to 25 ms. The high boiling hydrocarbons were delivered as liquids using an automotive fuel injector into a heated chamber where they vaporized in the presence of air. This system creates temperature and concentration gradients that allow safe mixing of fuel with air at temperatures above the autoignition of the fuel. Fuel-rich feeds beyond the syngas ratio produced olefins with selectivities as high as 80% in the case of *n*-hexadecane. The distribution of these olefins goes from primarily ethylene to large α -olefins as oxygen feed is decreased. Partial oxidation of low sulfur diesel fuel was also carried out successfully, producing synthesis gas at > 98% fuel conversion with several hours of stable operation.

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Keywords: Syngas; Olefins; Partial oxidation; Rh-monolith reactor; Hydrocarbons; Hexadecane; Diesel fuel

1. Introduction

Reforming hydrocarbons is important in many applications to produce fuels, such as H_2 , and chemical intermediates, such as synthesis gas, and olefins [1–6]. It is accomplished either by steam reforming or steam cracking which involve reaction with H_2O in endothermic processes or by partial oxidation which involves reaction with O_2 in exothermic processes. Conversion of methane to syngas [1–3] and ethane to olefins [4,5] by both processes is well established, and reactions of alkanes up to isooctane have been demonstrated [6,7].

While steam reforming and steam cracking of higher alkanes, such as diesel fuel, can be accomplished under suitable conditions, the partial oxidation of higher alkanes presents several problems, such as flames during vaporization and mixing, soot formation associated with combustion of fuel-rich gases, and coke formation on reactor walls and on catalysts.

Currently there is considerable interest in reforming logistic fuels such as diesel and JP-8 (similar to kerosene

and used as a military fuel) into light alkanes and especially H_2 for devices such as fuel cells, which function either exclusively on H_2 (the proton-exchange membrane fuel cell) or which function best with H_2 in the fuel (the solid oxide fuel cell). Since a major interest is in fuel cells for transportation vehicles, gasoline and diesel are essential fuels in the next generation of fuel cell vehicles.

There is also considerable interest in fuel reforming for pollution abatement in automotive applications with internal combustion engines. Reforming of gasoline or diesel into H_2 and other small molecules creates a fuel that burns very efficiently, thus reducing or eliminating exhaust emissions of hydrocarbons, CO, and particulate matter [8–10]. The abatement of NO_x in diesel engines is especially difficult because, unlike a spark ignited engine, in a lean burn environment there is insufficient H_2 , CO, and small hydrocarbons to react with NO_x in the catalytic converter. Therefore, reforming part of the fuel and using it to react with NO_x could be important in diesel emissions control.

We describe here the reforming by partial oxidation of two of the major components of diesel fuel: *n*-decane and *n*-hexadecane. These fuels can be quantified by detailed mass balances to determine conversions and selectivities to various products. We also demonstrate the partial oxidation

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of a low sulfur grade of diesel fuel. Since this is a mixture, quantitative analysis of reactants and products is more complicated, as is specification of the C/O ratio.

Our primary objective in this paper is to demonstrate the feasibility of this reaction in short contact time reactors using a fuel injector for fuel vaporization and mixing with air. We offer qualitative arguments regarding the mechanisms that lead to successful operation, but further experiments and modeling will be required to characterize these partial oxidation processes quantitatively, especially with diesel fuel mixtures.

2. Experimental

2.1. Fuel injector for fuel vaporization and mixing

For methane and other light alkanes the fuel is a gas at room temperature or it can be vaporized before mixing by heating to $< 100\text{ }^{\circ}\text{C}$ [1,11]. However, the autoignition temperature of normal alkanes decreases as the chain length increases and is as low as $\sim 200\text{ }^{\circ}\text{C}$ for alkanes above *n*-decane. Since the boiling point increases with the hydrocarbon chain length, the boiling point exceeds the autoignition temperature for alkanes higher than *n*-decane. During vaporization and mixing of fuel with oxygen, the interface between the vaporized fuel and oxygen necessarily produces mixtures varying from pure fuel to pure oxygen. Since the temperature of vaporization is above the autoignition temperature, the mixture could spontaneously ignite, producing flames and explosions. Diesel fuel contains mostly linear alkanes ranging from C_8 to C_{20} , most of which have higher

boiling point than autoignition temperatures. In these experiments we therefore found it essential to use an automotive fuel injector to facilitate vaporization and mixing of reactants before the catalyst.

2.2. Reactor

The reactor consists of a quartz tube with 19-mm inner diameter and 55-cm length as shown in Fig. 1a. The fuel is delivered at the top of the reactor using an automotive fuel injector. Air is also admitted at the top of the reactor. The conical dispersion of the 100- μm fuel droplets creates a thin film of liquid fuel on the heated inner walls of the reactor, which were heated to between 250 and $400\text{ }^{\circ}\text{C}$, depending on the fuel boiling temperature. This film absorbs heat and vaporizes near the wall where there is little oxygen because of the fuel vapor boundary layer. Since vaporization and mixing of the fuel with air occurs simultaneously, this avoids or reduces regions containing a combustible mixture at a temperature above the autoignition temperature.

Pressurized fuel at 5 psig feeds the injector, which is computer-operated at frequencies between 3 and 10 Hz and at duty cycles from 0.5 to 10% (the percentage of the time that the injector remains open). Thus, the liquid flow rate delivered by the injector is controlled accurately by the pressure in the fuel supply tank and by the duty cycle. The fuel delivery rate was calibrated at different pressures, frequencies, and duty cycles and is accurate to within $\pm 2\%$.

Two blank 80 ppi monoliths placed immediately upstream and downstream from the catalyst acted as axial heat shields and promote additional radial mixing as shown in Fig. 1a. The monoliths were wrapped with Fiberfrax alumina-silica paper to avoid bypassing of gasses between

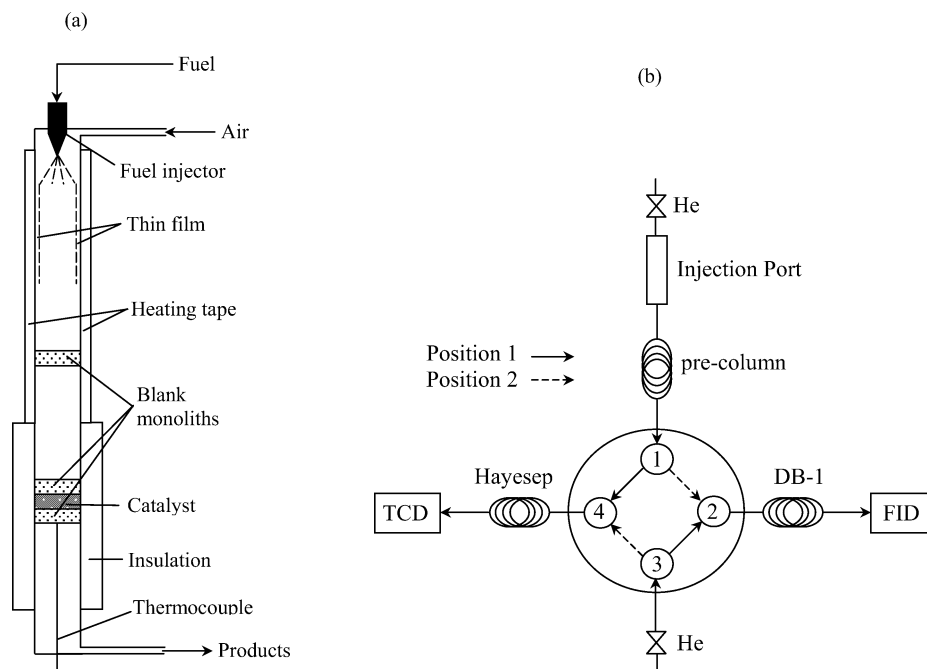


Fig. 1. Schematic of the reactor (a) and gas chromatograph (b).

the monoliths and the reactor wall. A chromel–alumel k-type thermocouple was placed between the backside blank monolith and the catalyst to measure the back-face temperature. Alumina–silica insulation was placed around the reactor to reduce radial heat losses. The flow rates of the high purity N_2 and O_2 entering the reactor from high-pressure cylinders were adjusted using mass flow controllers accurate to ± 0.05 SLPM (standard liters per minute).

The liquid hydrocarbons were high-purity HPLC grade (99+%), except for diesel fuel, which was a California phase 2 low sulfur diesel. An analysis of this diesel showed that it consists of 90.2% alkanes, 2.1% alkenes, and 7.9% aromatics, with less than 10 ppm sulfur and average molecular formula of $C_{14.5}H_{31}$. The reactor was operated at atmospheric pressure.

2.3. Catalyst

The catalysts consist of 18-mm diameter and 10-mm length α - Al_2O_3 ceramic foams with 80 pores per linear inch. The monoliths were wash-coated with ~ 5 wt% γ - Al_2O_3 to roughen the catalyst surface and increase its surface area [12]. The wash-coated monoliths were coated with 4 to 5 wt% Rh by soaking them in an aqueous $Rh(NO_3)_3$ solution and calcining for ~ 6 h at 600 °C. In these experiments a total of 150 runs were performed using eight catalysts. Each catalyst operated for ~ 10 h, and no catalyst deactivation was observed if exit temperatures were maintained at < 1000 °C.

2.4. Product analysis

The product stream consists of a mixture of permanent gases, liquids (after cooling), and unreacted fuel. Analyzing this mixture using a gas chromatograph or mass spectrometer is challenging because columns that separate permanent gases retain larger molecules for long periods of time and columns that can separate liquids cannot separate permanent gases. Therefore a dual-column system was designed and installed in a 5890 series II Hewlett-Packard GC as shown in Fig. 1b. The sample is injected into a DB-1 capillary precolumn (15-m length, 0.32-mm id, 0.25 μ m film) at the injection port. The permanent gases travel faster through the precolumn than the hydrocarbons. The four-way switching valve is initially at position 1, where the permanent gases are sent to a Heyesep D-packed column (9-m length, 2.2-mm id). This column separates the permanent gases at room temperature. After the permanent gases have left the precolumn, the valve is switched to position 2 sending the hydrocarbons to a DB-1 capillary column (60-m length, 0.32-mm id, 0.25 μ m film). The permanent gases are analyzed using a TCD (thermal conductivity detector) and the hydrocarbons using an FID (flame ionization detector). Nitrogen was used as the calibration standard, carbon and hydrogen balances typically closed within $\pm 8\%$ error. All products were incinerated in a fume hood and vented.

This GC system was insufficient to analyze the larger hydrocarbon products ($> C_{10}$) that resulted from the partial oxidation of *n*-hexadecane because the large number of GC peaks made the analysis intractable. Therefore, a GC mass spectrometer was used to analyze heavier products in a separate analysis. The hydrocarbon products were condensed in acetone and analyzed. In all cases the results showed that most of the hydrocarbon products were α -olefins. The GC-MS also quantified alkanes and olefin fractions.

2.5. Startup and shutdown

Oxygen and nitrogen at the air ratio were admitted to first heat the catalyst and walls of the reactor. Fuel was then admitted using the injector. The catalyst typically ignited within ~ 15 s, and a sample was collected once the back-face temperature stabilized, usually ~ 30 min later. The reaction was shut down by stopping oxygen flow first, then the fuel. The oxygen flow was occasionally turned back on soon after to burn off coke that might have formed on the catalyst surface.

3. Results

3.1. *n*-Decane

n-Decane and air were fed to the Rh-monolith reactor at several flow rates. The carbon/oxygen feed ratio was varied from 0.7 to 2.5 at total flow rates of 2, 4, 6, and 8 SLPM. These flow rates correspond to catalyst contact times of 24, 12, 8, and 6 ms, respectively, estimated at an average catalyst temperature of 800 °C. The reactor pressure was kept at 1 atm and the feed temperature was 250 °C which is above the boiling point of *n*-decane, 174 °C. The combustion ratio for *n*-decane is $C/O = 0.323$ and the syngas ratio is $C/O = 1$.

Fig. 2 shows the conversion of *n*-decane and oxygen and the catalyst back-face temperature at the total vapor flow rates studied. The oxygen conversion was $> 90\%$ for all ratios and flow rates. The *n*-decane conversion was $> 99\%$ for $C/O < 1.2$ at high flow rates and it decreased slightly as the feed became more fuel rich for all flow rates. The catalyst back-face temperature increased with increasing flow rate because at higher flow rates the rate of heat generation increases causing the reactor to operate closer to adiabatic. As predicted, the catalyst back-face temperature decreased as the fuel conversion decreased.

Fig. 3 shows the selectivities to synthesis gas (CO and H_2), combustion products (CO_2 and H_2O), and olefins for these experiments. The optimum yield in both H_2 and CO for all flow rates occurred at $C/O = 0.8$, a ratio slightly lower than syngas stoichiometry. The shift in the C/O ratio at which the optimum syngas yield occurs could be attributed to the presence of homogeneous chemistry, which

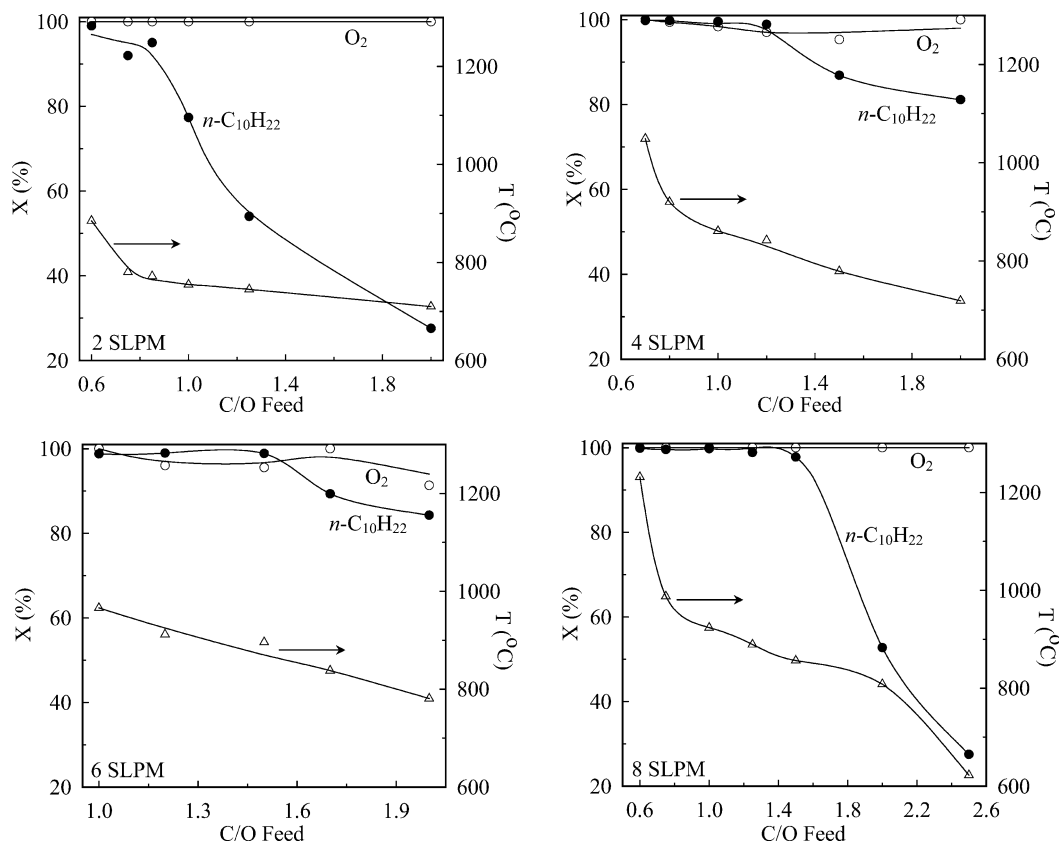


Fig. 2. Effect of n -decane/oxygen feed ratio on the fuel and oxygen conversions and the catalyst back-face temperature at 2, 4, 6, and 8 SLPM.

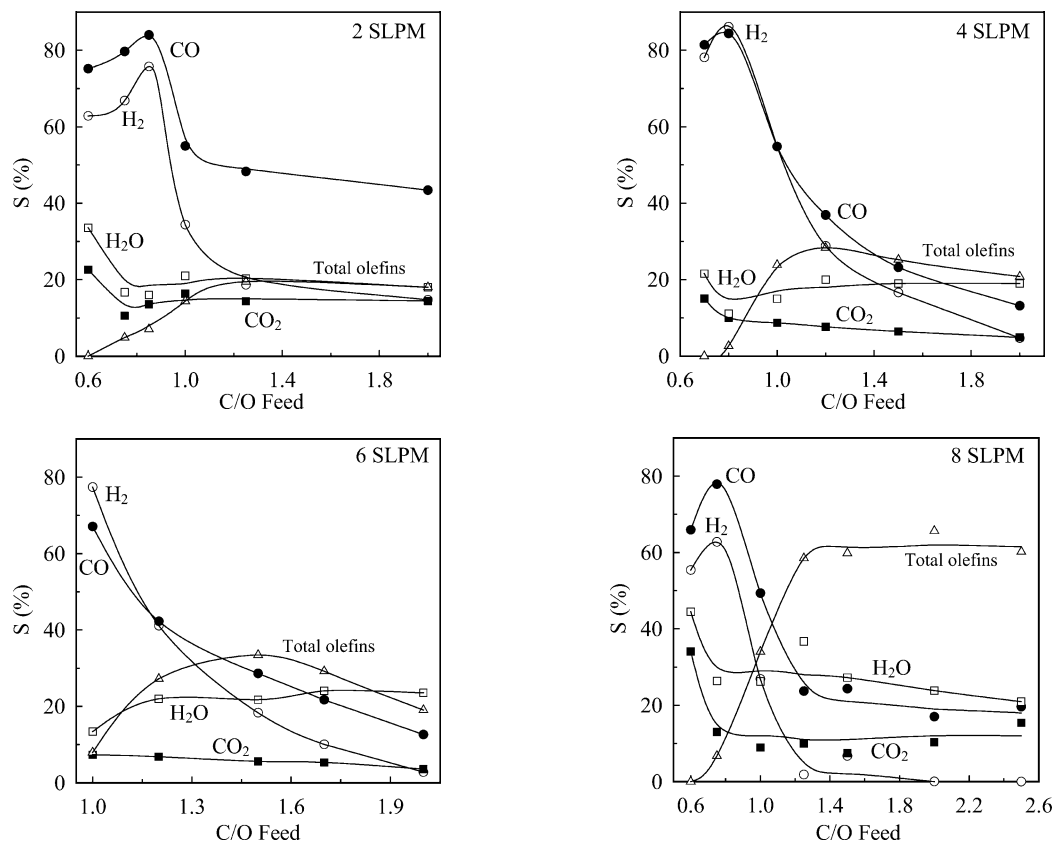


Fig. 3. Effect of n -decane/oxygen feed ratio on the products selectivities at 2, 4, 6, and 8 SLPM.

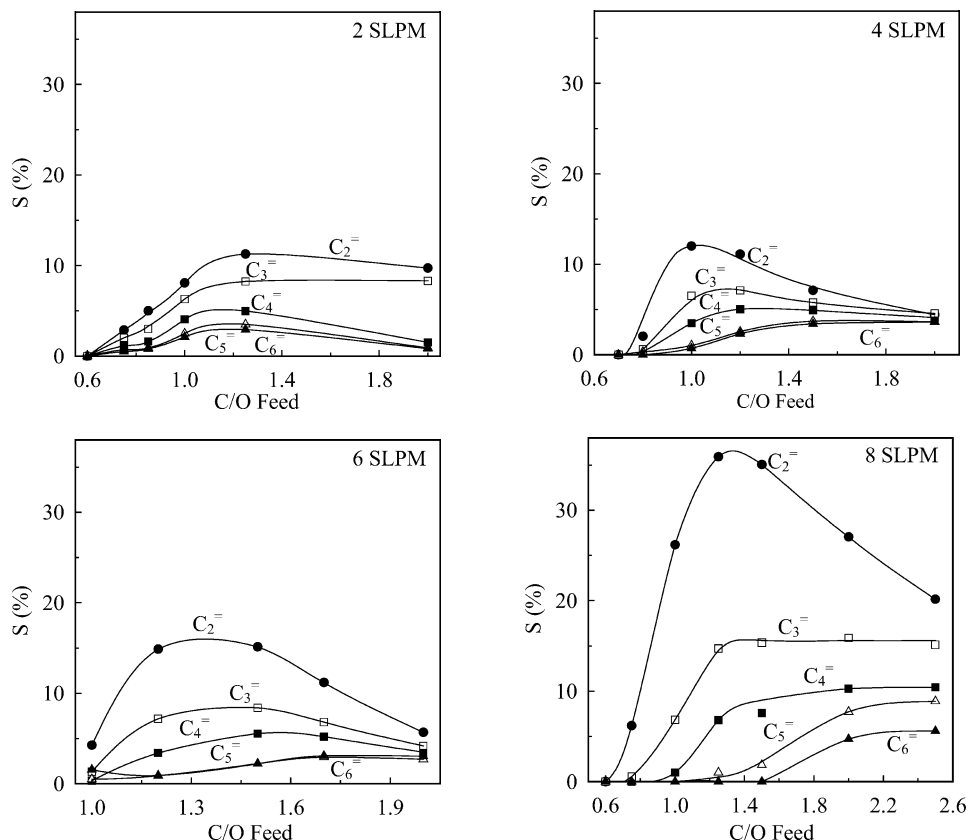


Fig. 4. Effect of *n*-decane/oxygen feed ratio on the ethylene, propylene, and α -olefin selectivities at 2, 4, 6, and 8 SLPM.

causes the gas-phase stoichiometry to differ from the surface stoichiometry. The highest selectivities for H_2 (86%) and CO (84%) occurred at 4 SLPM. The combustion products increased as the feed ratio approached the combustion stoichiometry. The syngas selectivity dropped and the olefin selectivity increased as the feed became more fuel rich ($C/O > 1$). The olefin products consisted of almost exclusively α -olefins ranging from ethylene to 1-hexene, and the highest selectivity of 63% occurred at 8 SLPM.

Fig. 4 shows the selectivities to olefin products in detail. Ethylene had the highest selectivity with 36% at $1.2 < C/O < 1.5$ and 8 SLPM. The ethylene selectivity dropped at leaner or richer ratios. At higher C/O ratios, the yield to higher α -olefins increased and at lower ratios the yield to syngas increased. The highest selectivities for propylene (16%), 1-butene (10%), 1-pentene (9%), and 1-hexene (6%) were obtained at $C/O = 2.5$ and 8 SLPM.

In all experiments the total selectivity to all alkane products was $< 8\%$ (not shown). The alkane selectivities increased with the C/O feed ratio and became $\sim 0\%$ at $C/O < 1$. The alkane products were mostly methane ($> 95\%$) and small amounts of ethane and propane. In some instances traces of butane were observed.

3.2. *n*-Hexadecane

The difference of the reactivity between small and large molecules was explored by feeding *n*-hexadecane and air

to the Rh-monolith reactor at varying flow rates. The carbon/oxygen feed ratio was varied from 0.5 to 3 at total flow rates of 2, 4, 6, and 8 SLPM. These flow rates correspond to catalyst contact times of 24, 12, 8, and 6 ms, respectively, estimated at an average catalyst temperature of 800°C . The reactor pressure was kept at 1 atm and the feed temperature was 400°C , which is above the boiling point of *n*-hexadecane of 287°C . The combustion ratio for *n*-hexadecane is $C/O = 0.327$, while the syngas ratio is $C/O = 1$.

Fig. 5 shows that the fuel conversion was $> 95\%$ and the oxygen conversion was 100% at $C/O > 0.8$. The oxygen breakthrough increased as the flow rate increased. The catalyst back-face temperature follows the same trend as the fuel conversion, decreasing as the C/O feed ratio increases. As the flow rate increased, the range of C/O studied became narrower because low C/O ratios resulted in high catalyst temperatures and the maximum should not exceed 1200°C , to prevent Rh sublimation [13].

Fig. 6 shows that the optimum syngas selectivities of 82% to H_2 and 81% to CO were achieved at $C/O = 0.8$ and 4 SLPM. As the feed became more fuel rich, the syngas selectivity dropped and the olefins selectivity increased. The maximum olefin selectivity reached 84% at $C/O = 3$ and a flow rate of 4 SLPM.

Fig. 7 shows the olefins produced in detail. Ethylene and propylene showed the highest selectivities for olefins

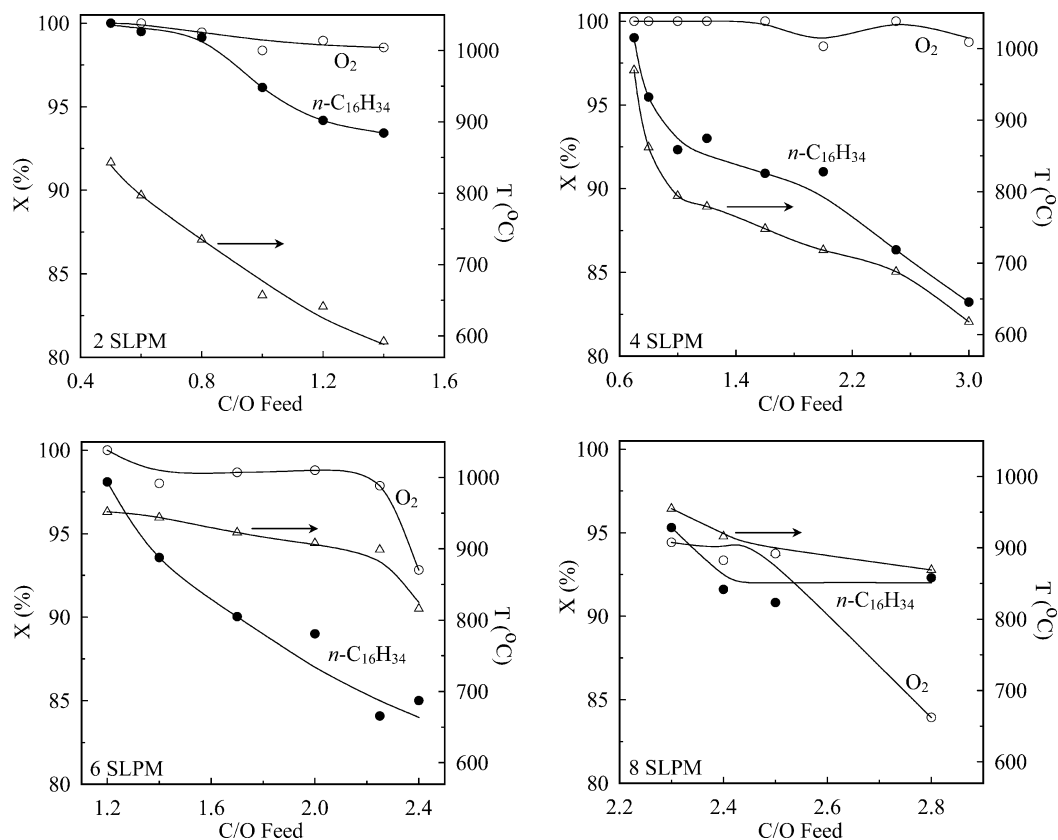


Fig. 5. Effect of n -hexadecane/oxygen feed ratio on the fuel and oxygen conversions and the catalyst back-face temperature at 2, 4, 6, and 8 SLPM.

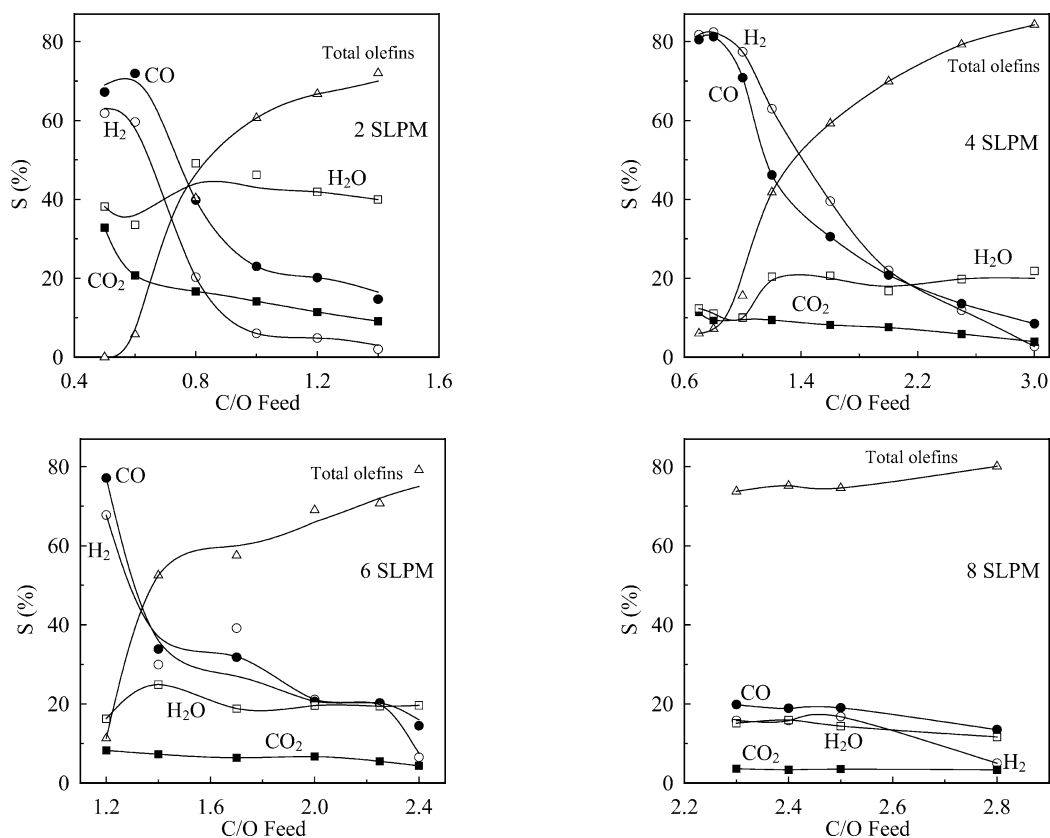


Fig. 6. Effect of n -hexadecane/oxygen feed ratio on the products selectivities at 2, 4, 6, and 8 SLPM.

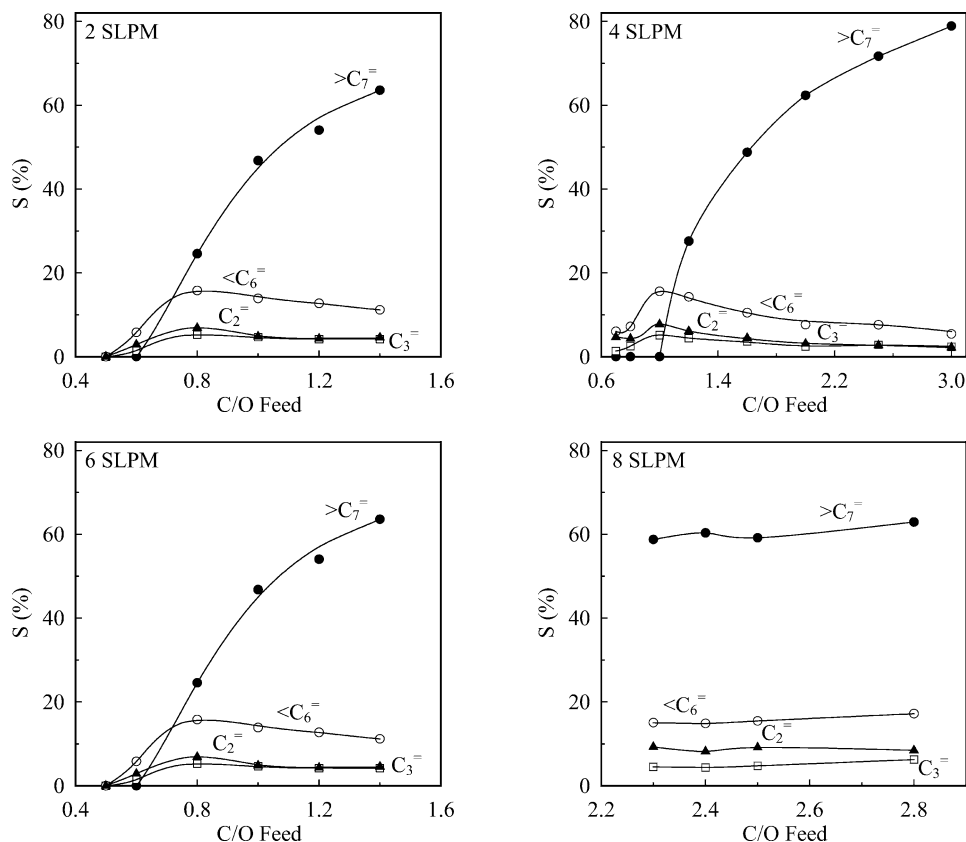


Fig. 7. Effect of *n*-hexadecane/oxygen feed ratio on the ethylene, propylene, and α -olefin selectivities at 2, 4, 6, and 8 SLPM.

with six or less carbon atoms. The selectivities were 8% to ethylene and 5% to propylene at C/O = 1 and 8 SLPM. Olefins with six or more carbon atoms had a combined selectivity of 78% at C/O = 2 and 4 SLPM. An analysis by GC mass spectrometer showed that the large olefin products consisted of α -olefins ranging from 1-C₈H₁₆ to 1-C₁₆H₃₂. Total internal olefins were < 0.5%, and branched alkanes were < 1%. Trends in the selectivities to alkanes (not shown) were similar to those observed with *n*-decane.

3.3. Quantification of diesel reforming

Analysis of results for diesel fuel is more complicated than for single molecule fuels. Diesel fuel is a mixture; separation of reactants and products is difficult, and calibration of GC responses of all possible reactants and products is not possible.

To estimate the conversion of diesel we assumed that all molecules > C₈ were diesel fuel reactants and that GC responses were the same for all molecules. This clearly gives a lower bound to the conversion, and the actual conversion may be higher than shown. In the range of C/O examined, the conversion to products less than C₈ is nearly quantitative, so the estimate is fairly accurate.

Selectivities to light olefins and alkanes < C₈ can also be determined accurately because there are no reactant species in this molecular weight range. For higher molecular weights

where reactants and products overlap, we suspect that most of the species are product olefins by analogy with decane and hexadecane results.

A more detailed analysis of conversions and product selectivities is possible by more extensive calibrations, but the estimates used here are accurate to $\pm 5\%$ error. This error was obtained from a calibrated GC mass spectrometry analysis.

3.4. Low sulfur diesel fuel

Although it is more difficult to quantify reaction parameters, such as conversion and selectivity for this mixture of higher hydrocarbons, we can estimate and make comments on the performance of the system. Most importantly, we have successfully demonstrated the use of a commercial diesel as a fuel for partial oxidation to produce syngas.

The runs with low sulfur diesel were done only at 2 SLPM, as higher flow rates gave back-face temperatures in excess of 1100 °C at C/O = 1. As with *n*-decane and *n*-hexadecane, the fuel was vaporized in the reactor between 300 and 350 °C and no flames were observed in the reaction chamber at C/O > 0.35. Flames were observed at C/O = 0.3. The combustion ratio for our mixture, which we assumed was C_{14.5}H₃₁, is 0.33, consistent with our observations.

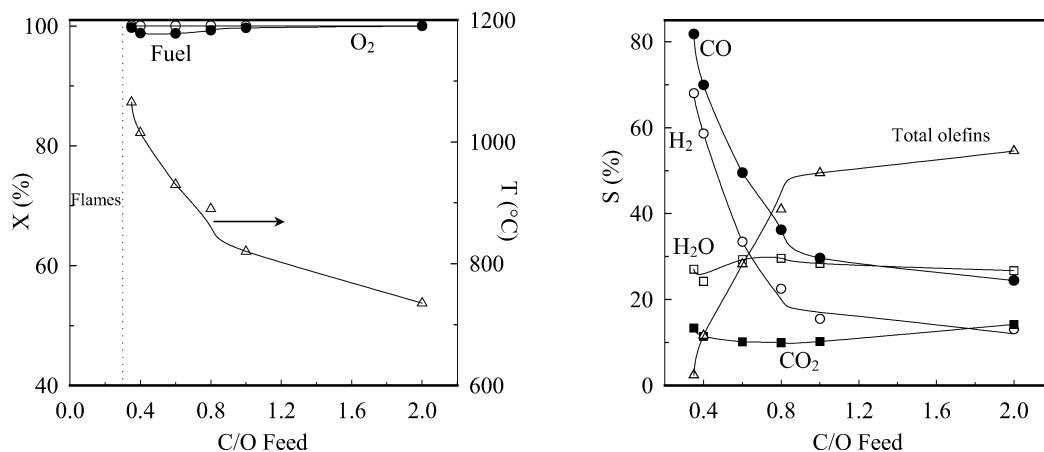


Fig. 8. Effect of the feed ratio on the partial oxidation of diesel fuel at 2 SLPM.

The reaction ignited when the back-face temperature reached ~ 260 °C and the temperature proceeded to rise quickly over ~ 1 min, reaching an equilibrium temperature after ~ 10 min. Analysis of the lower molecular weight products, $< C_6$, indicated that at least 98% of the reactant material has been converted to products with 6 or fewer carbons for all C/O ratios. The dominant products at C/O ratios near 1 were CO and H_2 , with small amounts of ethylene and CO_2 .

The product trends, shown in Fig. 8, are similar to those observed for *n*-decane and *n*-hexadecane. The back-face temperature is higher at lower C/O, and this corresponds to higher H_2 production. Similarly, higher C/O resulted in the production of more ethylene and propylene. Maximum H_2 production was achieved at C/O = 0.35, although this will certainly vary with different diesel fuels due to varying compositions and the ill-defined meaning of C/O in a mixture. It is surprising that the maximum H_2 production occurs at a C/O ratio close to the combustion ratio. The explanation for it is yet to be determined. However, we speculate that it is related to the fuel mixture containing alkanes, alkenes, and aromatic compounds, each having a specific reactivity. This topic is being pursued with known mixtures to determine relative reactivities.

4. Discussion

This is a complicated process in terms of reactions, reactor configuration, range of operation, and products. More detailed experiments are required to decide definitively how each of these variables affects the process, because we have only considered the variation of composition and total flow rate with fixed geometry and sufficient preheat to vaporize the fuels. In this discussion we will consider some of these subjects, but we can only speculate on detailed mechanisms that may be operative.

4.1. Range of operation

We first note that this process is operable over a surprisingly wide range of composition. We have operated stably from C/O = 0.5 to 3.0 without any evident deterioration in performance over at least several hours. The lower limit was determined by the maximum temperatures that the catalyst can withstand without Rh loss, and we seldom used C/O < 0.5 for that reason. The upper C/O limit was determined by the low reactor temperatures and the resultant low conversion. We generally did not continue experiments when the conversion of alkane was < 50%.

In these experiments we used air rather than pure O_2 to reduce the possibility of flames and explosions. For applications such as automotive fuel, reforming air is obviously the most relevant, but for olefins production pure O_2 may be required. In experiments such as these it may be possible to operate in pure O_2 or with less dilution, at least over a narrow range of composition and preheat.

The critical variable in determining the range of operation is the reactor temperature. It appears that these experiments are possible only with autothermal, nearly adiabatic operation, because with dilution in a furnace the temperatures will never be high enough to avoid coke formation, and high temperatures in the reactor before the catalyst will cause homogeneous combustion and soot formation. For the size of the monolith used here (1.8-cm diameter and 1-cm long) and with heat shields and insulation around the catalyst tube, the measured temperature at the exit of the catalyst is within 100 °C of the calculated adiabatic temperature. It is essential to preheat the reactants before they enter the catalyst to completely vaporize the fuel, so minimum preheat temperatures are from 250 to 400 °C, depending on the fuel boiling point; higher preheat obviously increases the reactor temperature. The temperature profiles within the catalyst are not well characterized. For methane to syngas the maximum temperature within the catalyst can be as much as 300 °C higher than the exit temperature [14], while for ethane oxidative dehydrogenation to ethylene the maximum temperature is seldom more than 100 °C above the exit temperature [15].

Since the present experiments make both syngas and olefins, we anticipate temperature maxima within the catalyst to be between 100 and 300 °C above the measured exit temperatures.

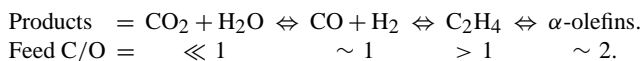
It is surprising that carbon formation before and within the catalyst does not shut down the process because graphite is thermodynamically stable for the feed compositions used at all temperatures if $C/O > 1$, and graphite is predicted at equilibrium at lower temperatures for $C/O < 1$. We sometimes found that the catalyst extinguished because of carbon formation, but this was almost always due to inadequate preheat that allowed liquid fuels to contact the catalyst; at 8 SLPM the feed contains ~ 5 g of carbon per minute, so even traces of carbon would plug the catalyst or accumulate downstream.

There was definitely some carbon on the used catalysts in all situations. This could be observed visually as black carbon that filled the channels of the foam which formed at high C/O . As expected, carbon tended to form more around the edges of the catalyst where the temperature was lower. If coking were suspected, the catalyst was regenerated by operating at lower C/O ratios to remove it. Also, by switching from a reacting mixture to pure air an exotherm in temperature of up to 100 °C could be measured. Further experiments are planned to use the exotherm by burning off carbon to quantify the amount of carbon on the catalyst and the amounts of CO and CO₂ formed, both in steady-state and in transient experiments.

We have speculated that the absence of coking is caused by the water formed in the process that removes carbon by steam reforming to CO. Oxygen is present in the early region of the catalyst, so any carbon on the surface should be oxidized off. The presence of monolayer amounts of carbon later in the catalyst is probably important for slightly deactivating the Rh surfaces and thus preventing further reactions such as reaction of olefins to form acetylenes and aromatics that would certainly lead to additional coke formation.

4.2. Products observed

These results show systematic trends with respect to product selectivities as functions of feed composition and fuel type. For all fuels the selectivity goes from mostly CO₂ to CO to small olefins to large olefins as C/O increases. Thus the reactions switch from combustion to reforming to dehydrogenation with increasing C/O ,



This switch is determined by the amount of oxygen in the feed and the reactor temperature, both of which strongly affect the selectivities as discussed later.

In previous experiments we have observed similar results with CH₄ [2,16], C₂H₆ to C₄H₁₀ alkanes [16–18], and *n*-hexane, cyclohexane, and isooctane [6,11]. In Fig. 9

the present results are compared with previous experiments with *n*-hexane [6]. Results for *n*-hexane were only obtained at 2.5 SLPM, and they are compared with *n*-decane and *n*-hexadecane at 4 SLPM, so flow rates are similar but not identical. The *n*-hexane experiments were also obtained using a liquid vaporizer before mixing (preheating to ~ 100 °C) rather than a fuel injector, so slight variations could be caused by these differences.

The conversion generally increases as the molecular weight of the fuel increases. While for CH₄ the conversion is typically from 85 to 95% (depending on C/O and preheat), for the higher hydrocarbons the conversion is always $> 99\%$ even beyond the syngas ratio, $C/O = 1$. Similarly, the O₂ conversion is higher for higher hydrocarbons. This appears to be qualitatively explained by the higher reactivities of larger hydrocarbons. The C–H bond energy is 104 kcal/mol for CH₄, while the C–C bond energy is 80 kcal/mol for linear alkanes.

The CO and H₂ selectivities (Fig. 9) are somewhat higher for *n*-hexane than for *n*-decane and *n*-hexadecane, with some of this difference caused by the large amounts of olefins produced from higher alkanes. Note that CO₂ is nearly the same for all fuels. It is $\sim 10\%$ and almost independent of C/O .

The selectivities to olefins also increased with the molecular weight of the alkane as shown in Fig. 9. None are observed with methane but up to $\sim 5\%$ with hexane, $\sim 60\%$ with decane, and $\sim 80\%$ with hexadecane. Methane clearly can form olefins only by coupling, while the higher alkanes form olefins by cracking reactions. The larger the alkane, the more fragment olefins are possible.

Increasing C/O also causes a transition in selectivities from ethylene to higher alkenes as shown in Fig. 9. This seems reasonable in terms of the temperature and the series reactions by which larger molecules decompose into smaller ones. All higher olefins are α -olefins with double bonds only at one end of the hydrocarbon chains.

There are almost no small alkanes formed in these experiments. The total alkane selectivity was $< 8\%$ for all fuels, and this is predominately CH₄, which is typically more than 95% of all alkanes observed. There are also almost no branched isomers of alkanes or olefins, indicating little isomerization even though temperatures are > 800 °C.

4.3. Rates and mechanisms

These results suggest that only a few dominant reaction pathways operate in these experiments. The detailed chemistry of homogeneous combustion and pyrolysis for these alkanes is well known from diesel combustion and naphtha steam-reforming applications. The detailed surface chemistry of methane and ethane partial oxidation on Rh and Pt surfaces is also fairly well established, although the kinetics of surface reactions of higher alkanes have not yet been established.

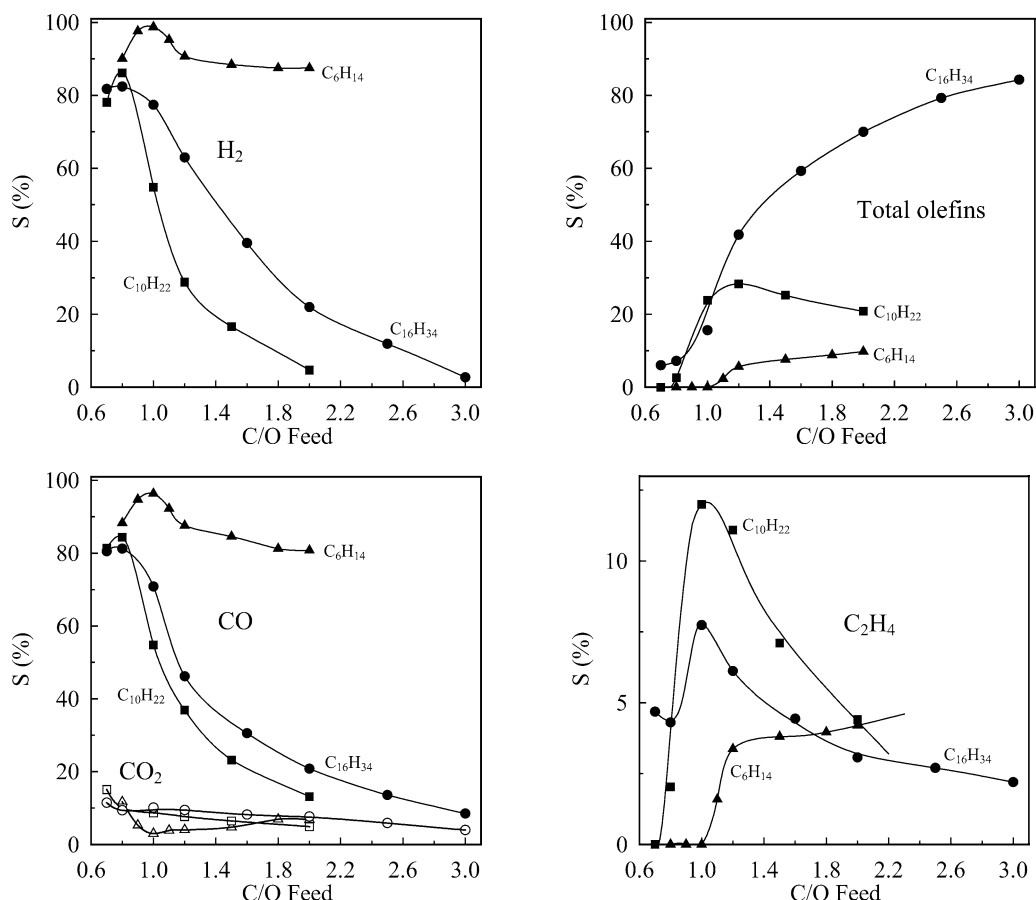


Fig. 9. Comparison of the product distribution from *n*-hexane (2.5 SLPM), *n*-decane (4 SLPM), and *n*-hexadecane (4 SLPM).

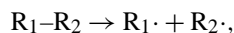
The exact roles of surface and homogeneous reaction steps are unclear in these experiments, and surface and homogeneous reactions are probably tightly coupled in this catalyst geometry because of the small channel sizes. While methane partial oxidation is known to be $> 90\%$ on the surface, ethane oxidative dehydrogenation occurs through both surface and homogeneous routes [15]. By analogy with CH_4 and C_2H_6 partial oxidation [2,4], we suggest that most CO and CO_2 is formed by surface reactions on the Rh surface and that most olefins are formed by homogeneous pyrolysis reactions.

Reaction could also be occurring before, within, or after the catalyst. Preheat of 250°C for *n*-decane and 400°C for *n*-hexadecane should cause negligible reaction in the residence time of ~ 20 ms in the preheat-mixing zone. However, the gases are heated to considerably higher temperatures before entering the porous catalyst by thermal diffusion of heat from the hot catalyst face, and homogeneous reaction could occur in the region within several millimeters of the catalyst. Most reaction almost certainly occurs within the catalyst because temperatures are highest and heat conduction between gas and surface assures highest gas temperature.

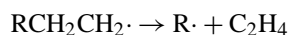
A basic picture assumes that reaction is initiated at the surface near the entrance of the catalyst where oxygen concentration and surface coverage are high. Since the temper-

ature is highest in this zone, oxidation reactions go rapidly to completion and consume all O_2 within the first millimeter of entering the catalyst, presumably generating mostly CO, CO_2 , H_2 , and H_2O . Once all O_2 is reacted, pyrolysis reactions should dominate, producing mostly olefins. These reactions could be homogeneous or on the surface, and it is difficult to determine the roles of surface and homogeneous reactions from product distributions.

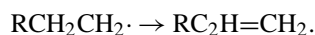
The pathway that appears to explain olefins is that of initiation by pyrolysis of the parent alkane to produce two alkyl radicals,



with the fragments $\text{R}_1\cdot$ and $\text{R}_2\cdot$ determined by the statistical probability of C–C bond scission, accounting for the higher bond strengths associated with methyl and ethyl. Next a radical can decompose by β scission to yield ethylene and a smaller radical,

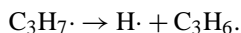
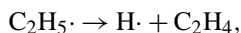


or by β hydrogen elimination to yield a larger stable olefin

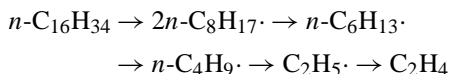


This process can continue with the radical eliminating ethylene molecules until it finally forms the ethyl or propyl

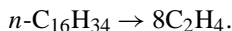
radical, which can only dehydrogenate to form ethylene or propylene,



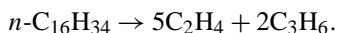
Thus the overall process is a series of reactions such as



whose overall stoichiometry is

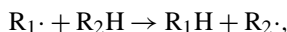


If the hexadecane molecule dissociated initially to produce radicals with an odd number of carbon atoms, the overall reaction would give five ethylene and two propylene molecules,



This may account for the $\text{C}_2\text{H}_4/\text{C}_3\text{H}_6$ ratio observed. If C/O is increased, the temperature is lower, and β hydrogen elimination becomes more important, yielding a larger olefin from the alkyl fragment.

We suggest that bimolecular hydrogen abstraction reactions,



where a radical reacts with a parent alkane to form an alkane and an alkyl radical of the parent should not be important because it would produce smaller alkanes and also internal olefins when the alkyl eliminates a hydrogen atom. Since we observe very little branched alkanes or olefins, bimolecular alkyl transfer reactions must also be unimportant.

4.4. Issues in diesel reforming

As discussed previously, the characterization of products and conversion of a logistic fuel is more complex than with a single fuel component. In addition to these complexities, there are other issues in reforming that arise because of the nature of diesel fuel.

First, the stoichiometry (the C/O ratio) is not precisely described for a mixture with varying carbon atoms and variable C/H ratio. Thus, we attempted to describe C/O by assuming an average molecule containing 14.5 carbon atoms and 31 hydrogen atoms. This is probably a good approximation for this fuel because it was well characterized, but actual fuels can have variable compositions. Since H_2 and CO have maxima for C/O near 1, this maximum could be broadened and lowered or shifted with a fuel mixture because some components are above and below the optimum stoichiometry for H_2 production.

Second, the reactivities of different molecules may be quite different. Linear, branched, and cyclic alkanes should not react identically. Aromatic and polyaromatic molecules

should have different reactivities than aliphatics. Differences may also occur between pyrolysis and in oxidation reactions and between homogeneous and surface processes. Pyrolysis rates are probably well predicted by C–C and C–H bond strengths because breaking these bonds to form radicals is the initiation step in homogeneous reactions and probably for surface reactions. These reactivities are probably correlated with autoignition temperatures, which vary by as much as 100 °C between fuel components.

Oxidation reactions may have a different order of reactivities than pyrolysis reactions because they depend on reactions with O_2 , OH, O, O_2H , and related alkyl species where reactivities do not correlate with bond strength but are more sensitive to molecular geometry and electronic structure. Even less is known regarding the relative surface reactivities of these components and their variation with size and structure. Adsorption and decomposition are probably quite different on Rh than on the alumina support because the Rh should have much greater capability to adsorb O_2 which promotes surface oxidation channels. On alumina, decomposition might therefore be expected to have a greater tendency to form coke.

We note that a fundamental possible complication with partial oxidation of fuel mixtures is that reactivities are not simply an average over all reactant molecules because the most reactive component in a mixture will consume all O_2 very quickly. This will leave pyrolysis in an O_2 -free environment as the only reaction channel for less reactive components. For example, if aromatics are less reactive than aliphatics, the aromatics can only undergo pyrolysis reactions. This would probably not be desired because aromatics, being hydrogen deficient compared to aliphatics, must inevitably pyrolyze to coke and soot.

The fuel we used in these experiments is a high grade of diesel fuel that contains low sulfur (10 ppm), aromatics (8%), and olefins (2%) compared to a conventional diesel fuel. All of these components could cause problems in high concentrations, so experiments like those reported here must be done to determine how large fractions of these components affect performance.

Fuel vaporization is also different for mixtures because boiling points vary. Diesel fuel boils from 100 to 300 °C, so fractional distillation will occur if evaporation is slow. The highest boiling fraction is probably highest in polyaromatics that should have the greatest tendency to decompose to coke before evaporating. We believe that the evaporative mixing system we use produces a rather rapid vaporization and thus avoids excessive distillation to leave a residue. The relative amounts of evaporation in the drops from the fuel injector and at the wall will vary with the drop size, air and fuel temperature, and with the distance between injector and wall. Obviously, parameters such as surface temperature, heat flux to the surface, fuel delivery rate, and mixing concentration profiles should have large influences on vaporization and mixing. We have demonstrated the

operability of this system, but we have not yet examined these variables systematically.

Although a complete quantitative analysis was beyond the scope of this study, we have successfully demonstrated the partial oxidation of low sulfur diesel to produce a hydrogen-rich mixture. Additional study is required to characterize the reactivity and product distribution in detail. In the future we shall examine the effects of composition, including aromatic components, and C/O on the partial oxidation of model mixtures that represent diesel fuel, but are analytically tractable.

5. Summary

These experiments show that it is possible to oxidize higher alkanes to syngas and to olefins by partial oxidation in air at contact times of 5 to 25 ms. The process is fairly robust in that the catalyst can be operated successfully over a wide range of C/O as long as the fuel is vaporized and mixed with air and the catalyst is kept sufficiently hot.

The process appears to be fairly insensitive to catalyst form and loading, although it can certainly be “tuned” beyond results shown here by changing catalyst material or form. Thus, even higher yields of syngas or of light or large olefins should be obtainable by suitable modifications.

The simple qualitative mechanism we propose involving unimolecular series reactions appears to explain the switch from syngas to ethylene to α -olefins with increasing C/O, and it explains the predominance of α -olefins and the absence of alkane or branched products. Further experiments and modeling will be necessary to quantify this picture and predict performance with other alkanes and other fuels and fuel mixtures.

It is possible to operate the reactor in the presence of water, either by adding it with a separate fuel injector or

with an emulsion. This enables the water–gas shift in the short contact time reactor to produce high H₂/CO ratios, which are required in fuel cell applications. Experiments to generate hydrogen in high concentrations from diesel fuel and gasoline are in progress.

Acknowledgments

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