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14. ABSTRACT

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JP-8 catalytic cracking for compact fuel processors

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Abstract

In processing heavier hydrocarbons such as military logistic fuels (JP-4, JP-5, JP-8, and JP-100), kerosene, gasoline, and diesel to produce hydrogen for fuel cell use, several issues arise. First, these fuels have high sulfur content, which can poison and deactivate components of the reforming process and the fuel cell stack; second, these fuels may contain non-volatile residue (NVR), up to 1.5 vol.%, which could potentially accumulate in a fuel processor; and third is the high coking potential of heavy hydrocarbons. Catalytic cracking of a distillate fuel prior to reforming can resolve these issues. Cracking using an appropriate catalyst can convert the various heavy organosulfur species in the fuel to lighter sulfur species such as hydrogen sulfide (H_2S), facilitating subsequent sulfur adsorption on zinc oxide (ZnO). Cracking followed by separation of light cracked gas from heavies effectively eliminates non-volatile aromatic species. Catalytic cracking can also convert heavier hydrocarbons to lights (C_1–C_3) at high conversion, which reduces the potential for coke formation in the reforming process. In this study, two types of catalysts were compared for JP-8 cracking performance: commercially-available zeolite materials similar to catalysts formulated for fluidized catalytic cracking (FCC) processes, and a novel manganese/alumina catalyst, which was previously reported to provide high selectivity to lights and low coke yield. Experiments were designed to test each catalyst's effectiveness under the high space velocity conditions necessary for use in compact, lightweight fuel processor systems. Cracking conversion results, as well as sulfur and hydrocarbon distributions in the light cracked gas, are presented for the two catalysts to provide a performance comparison.

Keywords: Fuel cells; Reforming; Fuel processors; JP-8; Catalytic cracking

1. Introduction

Fuel cells have the potential to provide efficient mobile electric power generation for both military and civilian applications. Proton exchange membrane (PEMFC) and solid oxide fuel cell (SOFC) systems are currently being developed which may offer significant advantages over conventional internal combustion-powered generator sets, including greater thermal efficiency, greater power density, lower noise signature, and reduced maintenance [1]. However, both PEMFCs and SOFCs require a hydrogen-rich, low-sulfur fuel feed stream. Hydrogen is a difficult fuel to store and transport due to its high compression cost, high volatility, and low volumetric energy density. Reforming liquid hydrocarbon fuels can be a more practical source of hydrogen for fuel cell mobile electric power generator systems. A logistic fuel processor has been proposed and is being developed for generation of hydrogen from logistic fuels such as JP-8 and diesel in military applications [2].

Reforming heavy liquid fuels such as JP-8, diesel, and kerosene, presents several technical problems. First, liquid fuels contain significant amounts of sulfur, which is typically present as a range of organosulfur compounds. These organosulfur compounds are not easily removed from the fuel by adsorption, and can poison and deactivate catalysts, membranes, and fuel cell electrodes. Second, liquid fuels may contain non-volatile species, which can accumulate in fuel evaporator channels and foul reformer components. JP-8, for example, may contain up to 1.5 vol.% non-volatiles [3,4]. And third, heavy liquid fuels normally contain high-molecular weight aromatic compounds, which introduce a high potential for coke formation within heated reformer system components.

Catalytic cracking of a liquid fuel feed stream as a pretreatment step in a reforming process may offer partial or complete solutions to these problems. In a catalytic

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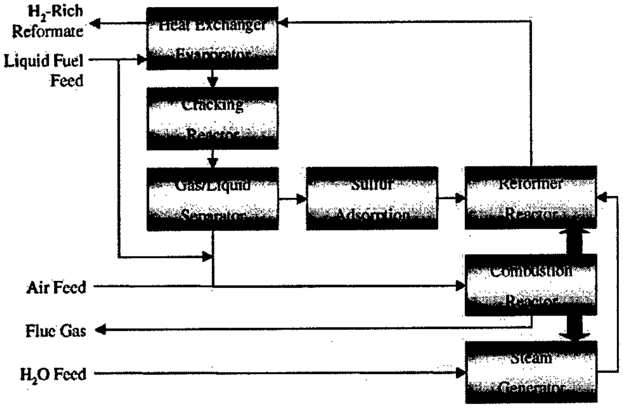

Fig. 1. Generalized flow diagram of a liquid fuel steam reforming system incorporating catalytic cracking with gas/liquid separation.

cracking process, heavy refractory organosulfur compounds are converted to lighter sulfur species, primarily hydrogen sulfide (H_2S) and methanethiol (CH_3SH), which are more easily removed by adsorption. Catalytic cracking followed by gas/liquid separation effectively removes non-volatile species from the process stream, protecting downstream reformer components. Catalytic cracking followed by gas/liquid separation can also selectively break down the aliphatic portion of the fuel feed, allowing for subsequent separation of the aromatics, which diminishes the potential for coking in the reforming reactor. Fig. 1 shows a generalized flow diagram of a liquid fuel steam reformer system incorporating catalytic cracking with gas/liquid separation.

In this system, a liquid fuel feed is evaporated in a heat exchanger using heat recovered from the H_2-rich reformate product stream. Vaporized fuel is sent to a cracking reactor, and then to a gas/liquid separator, where the cracked light gas stream is separated from the liquid residue. Cracked light gas is desulfurized in an adsorber, then mixed with steam and reformed to H_2-rich product in a reformer reactor. The liquid residue from the gas/liquid separator may be mixed with fresh fuel feed as needed, then mixed with air feed and combusted in a combustion reactor to provide heat for reforming and steam generation. Heat and mass balances for this system require that the cracking reactor operate at high enough conversion so that only enough liquid residue for combustion is generated to meet the heat requirements of the reformer reactor and the steam generator.

Past studies of JP-8 catalytic cracking have focused on reactor systems operating at supercritical pressures and temperatures with moderate cracking conversions [5–7], conditions that are relevant to various aviation applications, such as endothermic cooling of high-altitude aircraft surfaces. Compact fuel processors for integration with fuel cells must operate at lower pressures, so that small, lightweight fuel pumps can be used. Also, compact fuel processors require high cracking conversion, so that overall heat balance can be maintained. In this study, JP-8 catalytic cracking conversion using two different catalyst types was measured at atmospheric pressure and at temperatures and space velocities appropriate for use in compact fuel processor systems. The effect of catalytic cracking conversion on the light gas composition, liquid residue composition, and sulfur mass distribution were also studied.

2. Experimental

2.1. Catalyst preparation

Two different types of cracking catalysts were studied: acidic zeolite catalysts, which are often used in fluidized catalytic cracking (FCC) processes, and a Mn/alumina formulation that has been reported in the literature to give high lights yield with low selectivity to coke [8]. ZSM-5 type (MFI) zeolite (Zeolyst CBV5524G, SiO_2/Al_2O_3 ratio of 50, NH_4^+ cation, 0.05 wt.% Na_2O, 425 m^2/g surface area) and Beta type (BEA) zeolite (Zeolyst CP814E, SiO_2/Al_2O_3 ratio of 25, NH_4^+ cation, 0.05 wt.% Na_2O, 680 m^2/g surface area) were obtained from the vendor as extrudate pellets. The extrudate pellets were ground and dry-sieved to 12–16 mesh particles, then activated by calcining in air at 450 °C for 4 h. Mn/alumina catalyst was prepared by wet impregnation of 8–14 mesh γ-alumina particles with a solution of manganese electrolytic metal in nitric acid, followed by drying at 90 °C for 30 min and calcining in air at 450 °C for 4 h. The final manganese metal loading was 11 wt.%, and the as-prepared Mn/γ-alumina catalyst pellets had specific surface area of 151 m^2/g.

Both packed bed and coated wall tubular cracking reactors were tested. Table 1 lists the properties and dimensions of the four tubular reactors studied. All reactor tubes were 30.5 cm long, and consisted of high-alumina ceramic tubes (McMaster-Carr Supply Co.). The densities of the packed beds were 0.98 and 0.58 g/cm^3 for the Mn/γ-alumina and mixed zeolites, respectively. Coated wall reactors were prepared by pretreating the tube inner surface with 10 wt.% nitric acid, then washcoating with a suspension containing 20 wt.% finely-ground BEA zeolite powder and 0.6 wt.% sodium silicate (Ludox AS-40, Aldrich). After washcoating, the tubes were dried at 200 °C for 30 min, and then calcined in air 400 °C for 16 h. The coated catalyst layers were activated by exchanging with 1 M NH_4NO_3 for 16 h, then drying at 90 °C for 30 min, followed by calcining in air at 450 °C for 4 h. The coating procedure used was adapted from a procedure reported previously for coating BEA zeolites on cordierite monoliths [9].

2.2. Apparatus

Fig. 2 is a diagram of the experimental apparatus used to test the performance of the tubular cracking reactors. JP-8 feed from a syringe pump with ±1% volumetric accuracy (Isco model LC-5000) was sent through a preheater that consisted of a 406 cm long, 0.318 cm o.d., 0.216 cm i.d. section

Table 1
Dimensions and properties of tubular cracking reactors used

Reactor	Type	Catalyst	o.d. (cm)	i.d. (cm)	$V_{reactor}$ (cm^3)
MnAl-PB	Packed bed	Mn/γ-alumina	0.635	0.478	5.47
MFI/BEA-PB	Packed bed	Mixed zeolites, 1:1 MFI:BEA	0.635	0.478	5.47
BEA-CW1	Coated wall, 1 channel	BEA zeolite	0.318	0.160	0.61
BEA-CW2	Coated wall, 2 channels	BEA zeolite	0.318	2 × 0.102	0.50

of Silcosteel-treated stainless steel tubing (Restek Corp.), wound into a coil 3 cm in diameter, 28 cm long. This tube coil was clamped within a radiant tube heater, 5.1 cm i.d., 735 W maximum power (Omega). The exterior temperature of the preheater tube at the inlet end of the coil ($T_{\mathrm{Coil,In}}$) was monitored using a type-E thermocouple. Preheater power was controlled with a variable voltage power supply (Staco, 0–140 V), and was adjusted to maintain the tube exterior at the hot end of the coil ($T_{\mathrm{Coil,Ex}}$) at 610 ± 5 °C, which was monitored using a type-E thermocouple positioned near the tube. Preheated JP-8 flowed out of the tube coil, past a type-E thermocouple, which measured the reactor feed temperature (T_{Feed}), and into the reactor tube. The reactor tube was heated using an approximately 90 cm long piece of 28 AWG Ni/Cr heating wire wrapped tightly around the outside of the tube, with a sleeve of insulation covering over the tube and wire. Reactor heating power was controlled with a second variable voltage power supply. Flow exiting the reactor tube passed another type-E thermocouple which monitored the product stream temperature (T_{Product}), then through an air-cooled coil of Silcosteel tubing, 0.318 cm o.d., 0.216 cm i.d., 80 cm long, where any condensable products were condensed to liquid. Liquid residue was separated using a gas/liquid separator with <1 cm^3 hold-up volume, and collected in a removable glass screw-top vial connected to the bottom of the separator. Light gas product exited the top of the separator and passed a septum fitting sample port before being vented to a fume hood. Overall system pressure was monitored using a pressure transducer in the syringe pump, and was <10 psig throughout all experiments.

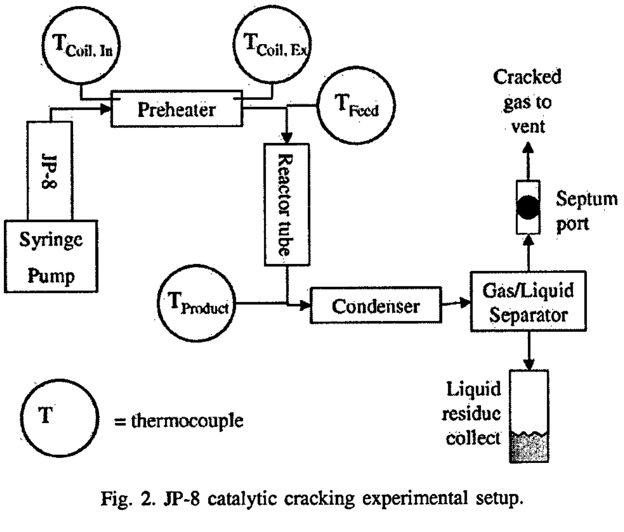

Fig. 2. JP-8 catalytic cracking experimental setup.

Steady-state cracking conversion was determined by first establishing a specified JP-8 feed rate (Q_{Feed}, cm^3/min) with the syringe pump, then bringing the preheater up to operating temperature, then heating the reactor tube to achieve a steady T_{Product} temperature. After allowing about 10 min for the system to stabilize, a tared collection vial was connected to the gas/liquid separator, and liquid residue was collected for a measured collection time Δt (minutes). The vial was then removed and reweighed to determine the mass of liquid residue (m_{Liquid}) collected. The cracking conversion was then calculated as:

$$\text{conversion (wt.\%)} = 100\left(1 - \frac{m_{\mathrm{Liquid}}}{Q_{\mathrm{Feed}}\,\Delta t d^{\mathrm{JP\text{-}8}}}\right) \qquad (1)$$

where $d^{\mathrm{JP\text{-}8}}$ is the density of the JP-8 feed, which was measured to be 0.792 ± 0.002 g/cm^3. During the run, two samples of the cracked gas were drawn through the septum port using a gas-tight syringe and analyzed using the gas chromatographic methods described below. The liquid residue sample was also analyzed by gas chromatography as described below.

2.3. Analytical methods

Hydrogen (H_2), methane (CH_4), ethylene (C_2H_4), ethane (C_2H_6), propylene (C_3H_6) and propane (C_3H_8) concentrations in the cracked light gas were all determined using a gas chromatographic method with thermal conductivity detection (TCD). The column used in the TCD method was a 30 m Carboxen 1010 PLOT (Supelco), with argon carrier gas. CH_4, C_4, and C_5 aliphatic hydrocarbons, benzene, toluene, and xylene (BTX, collectively), hydrogen sulfide, methanethiol, thiophene (C_4H_4S), and methylthiophenes (C_5H_6S) in the cracked light gas were determined using a pulsed flame photometric detector (PFPD, OI Analytical model 5380). The column used in this PFPD method was a 60 m SPB-1 SULFUR (Supelco) with He carrier gas. This PFPD method provided baseline separation of all sulfur species from hydrocarbons, allowing for sulfur/carbon molar detection selectivity >80 [10]. Both of the gas analytical methods were calibrated by determining the molar responses of pure analytes using multi-level calibration curves. For each sample analyzed, the results of the two methods were combined by normalizing analyte responses to the CH_4 response, which was present in every gas sample analyzed. The JP-8 feed and liquid residue samples were analyzed using a gas chromatographic method with a 5 m

Petrocol column (Supelco), He carrier gas, and FID detection. Catalyst sample specific surface areas were determined by N_2-BET analysis (Micromeritics model FlowSorb 2300).

3. Results and discussion

3.1. Preheater performance

Heat transfer in the preheater coil increased with increasing JP-8 flow rate as shown in Fig. 3. The temperature of the JP-8 entering the preheater coil from the syringe pump was $24 \pm 2\,°C$. At $Q_{\text{Feed}} = 0.5$ ml/min, T_{Feed} remained below 200 °C, which means that the fuel was only partly vaporized at this feed rate, given that the typical boiling range of JP-8 is from about 180–270 °C [4]. Increasing $T_{\text{Coil,Ex}}$ to greater than 620 °C caused pyrolytic cracking and coking to occur in the preheater tube coil, which would have confounded the experimental results. When $T_{\text{Coil,Ex}}$ was maintained less than 620 °C, cracking conversion in the preheater was less than 5 wt.%. Using reported properties of JP-8 [4] and the data in Fig. 3, the average inner heat transfer coefficient for the preheater tube coil was estimated to be 0.2, 1.5, 5.6, and 15 $W/m^2\,°C$ at Q_{Feed} of 0.5, 1.0, 2.0, and 4.0 cm^3/min, respectively. Better heat transfer in the preheater could have been achieved over the same range of flow rates by using smaller i.d. tubing; however, tests with JP-8 vaporization in tubes smaller than 0.2 cm i.d. showed that they are prone to plugging during minor system upsets such as flow rate changes. The 0.216 cm i.d. preheater tube coil was operated with $T_{\text{Coil,Ex}} = 610\,°C$ for more than 40 h without any measurable increase in back pressure. Heat transfer in the coil was observed to increase slightly during testing, so that at Q_{Feed} of 1.0 cm^3/min T_{Feed} was initially <260 °C, but after 30 h of use T_{Feed} had increased to >290 °C at the same flow rate.

3.2. Reactor performance

For practical application in compact fuel processor systems, catalytic cracking reactors must be small in size, and thermally efficient. Small cracking reactor size can be achieved if high fuel cracking conversion can be obtained while operating the reactor at high space velocities, while thermal efficiency requires that the reactor operate at as low a temperature as possible. JP-8 cracking conversion in the packed bed catalytic reactors MnAl-PB and MFI/BEA-PB is shown in Fig. 4. Conversion is plotted against mean reactor temperature to compensate for small increases in T_{Feed} during testing. The JP-8 feed rate is expressed as liquid hourly space velocity (LHSV), which is calculated as:

$$\text{LHSV}\,(\text{h}^{-1}) = \frac{60 Q_{\text{Feed}}}{V_{\text{Reactor}}} \tag{2}$$

where V_{Reactor} is the reactor tube internal volume (see Table 1). For both packed bed reactors, isothermal operation (i.e.,$T_{\text{Product}} \approx T_{\text{Feed}}$) at any space velocity yielded <10 wt.% conversion. As heating power to the reactor was increased, conversion increased sharply with increasing T_{Product}. At each space velocity and temperature, the MFI/BEA-PB reactor produced slightly greater conversion than the MnAl-PB reactor. The greater performance of the MFI/BEA-PB reactor could be due to greater activity of the mixed zeolites catalyst compared to the Mn/γ-alumina, or could be due to better heat transfer due to the slightly smaller particle size and more irregular particle shape of the zeolites.

Catalytic cracking of hydrocarbons is an endothermic process, and the endotherm of JP-8 catalytic cracking has been measured to be approximately 930 J/g at 80 vol.% conversion [6]. The performance of a catalytic cracking reactor can be limited by the catalyst activity, by the rate of heat transfer to the catalyst surface, or by rate of mass transfer

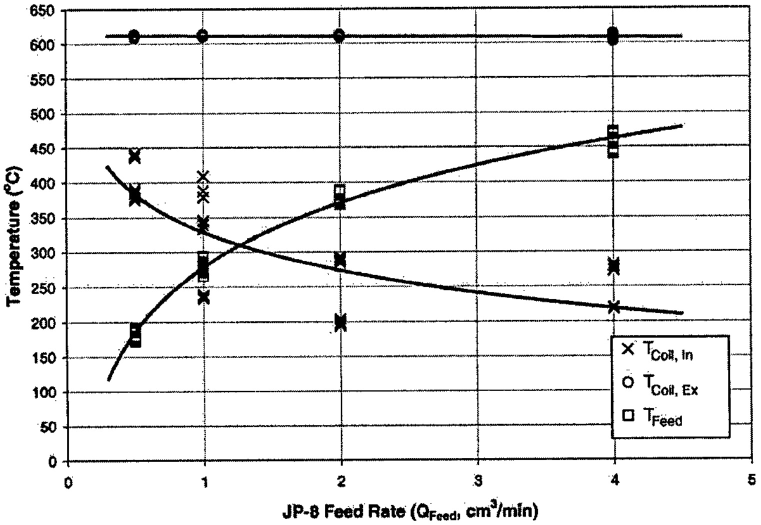

Fig. 3. JP-8 heating in the 406 cm long × 0.216 cm i.d. preheater tube coil.

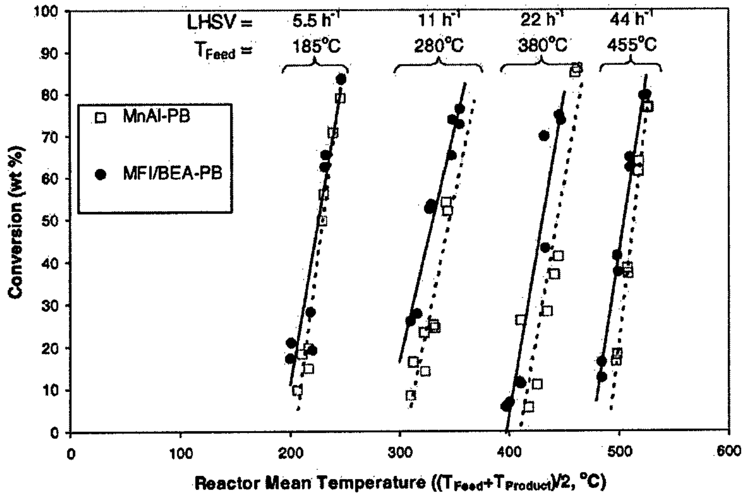

Fig. 4. Effects of reactor temperature and space velocity on cracking conversion in packed bed reactors.

of reactants and products to and from the catalyst surface. Flow conditions in these experiments were chosen to provide low pressures to simulate conditions using the small, lightweight fuel pumps required in compact fuel processors. These flow conditions, however, also yield low Reynolds numbers, and limited heat and mass transfer rates. Heat transfer to the catalyst surface should be improved by coating the catalyst material directly on the inner wall of the heated tube, rather than using a packed bed of catalyst particles. Improved heat transfer using thin layers of catalysts coated on reactor walls has been reported for endothermic processes such as methane steam reforming [11] and ethane dehydrogenation [12]. Fig. 5 shows the results obtained using reactors BEA-CW1 and BEA-CW2 at LHSV = 100 h^{-1}. Both coated tubes had outer diameters of 0.318 cm, but BEA-CW1 had a single inner channel 0.160 cm in diameter, while BEA-CW2 had two parallel inner channels each 0.102 cm in diameter. Comparison of Figs. 4 and 5 shows that BEA-CW1 produced 80 wt.% conversion at <500 °C mean temperature, while both packed bed reactors required a mean temperature of >520 °C to give the same conversion at less than half the space velocity. BEA-CW2 produced 80 wt.% conversion at <380 °C mean reactor temperature ($T_{\mathrm{Feed}} = 253\,°\mathrm{C}$, $T_{\mathrm{Product}} = 500\,°\mathrm{C}$) and 100 h^{-1} LHSV. These results demonstrate that high JP-8 cracking conversion at high space velocity can be achieved at low pressures and moderate reactor temperatures using coated wall catalytic reactors.

3.3. Characterization of the gas and liquid product streams

JP-8 catalytic cracking using the two packed bed reactors produced a light gas product containing H_2 and hydrocarbon compounds as shown in Fig. 6. The primary products were C_2H_4 and CH_4. H_2 concentration was 9–10 mol% at all conversions. Initially, the MFI/BEA-PB reactor with fresh zeolite catalysts produced C_3H_8 concentrations exceeding

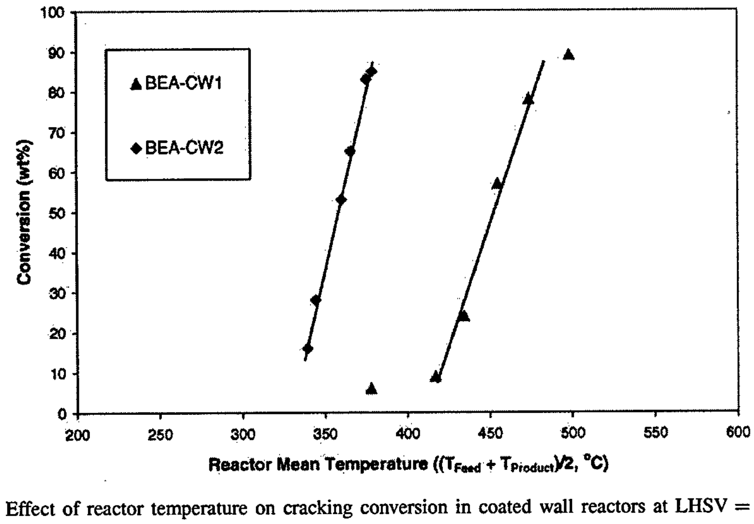

Fig. 5. Effect of reactor temperature on cracking conversion in coated wall reactors at LHSV = 100 h^{-1}.

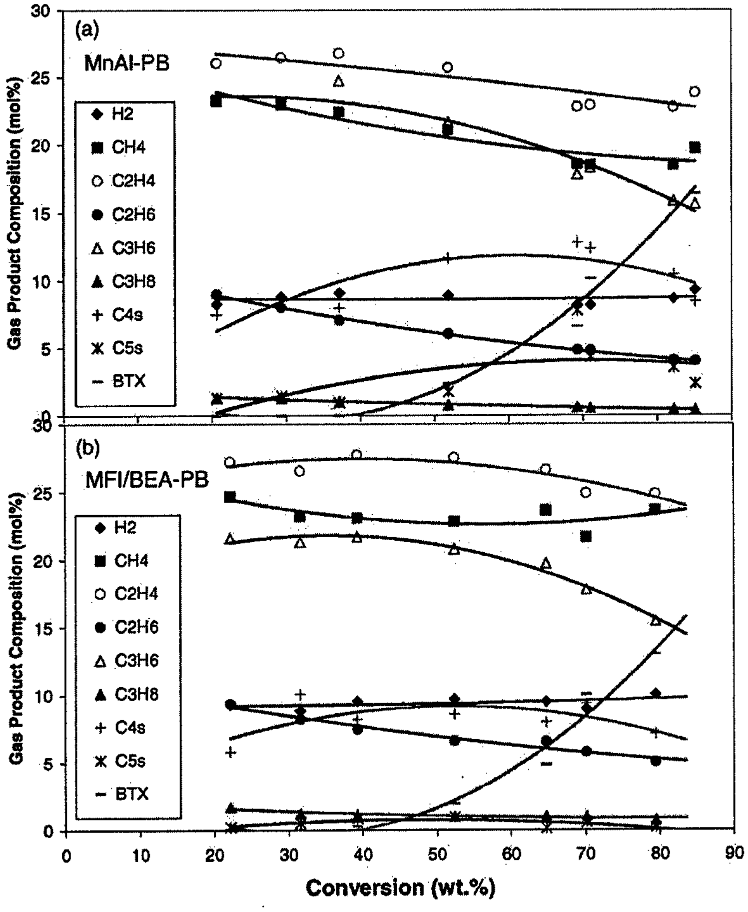

Fig. 6. Hydrogen and hydrocarbon compounds in gas product from JP-8 catalytic cracking using packed bed reactors (a) MnAl-PB and (b) MFI/BEA-PB.

20 mol%. With use, the propane concentration dropped until after 5 h at operating temperature the propane concentration was less than 3%. The data shown in Fig. 6b was all from the MFI/BEA-PB reactor after at least 5 h of aging. Acidic zeolite catalysts are used in FCC processes to improve the yields of branched and cyclic hydrocarbon products by selectively cracking long-chain normal alkanes to light alkanes such as propane, thus increasing fuel octane number [13]. However, in the FCC process, the catalyst is cyclically regenerated by burning off accumulated carbon. It is apparent that when the MFI catalyst is used continuously without regeneration, as in the present application, the selectivity of the catalyst changes. Decreasing selectivity toward normal alkane products with increasing coke yield during cracking of isooctane on a USY zeolite catalyst has been observed previously [14]. Mn/γ-alumina catalyst formulations have been reported to give high selectivities to light hydrocarbons in oil cracking [8]. Comparison of Fig. 6a and b shows that the MnAl-PB reactor actually produced lower amounts of CH_4 and higher amounts of C_4 and C_5 products than the MFI/BEA-PB reactor at high conversions. At conversions greater than 50 wt.%, the gas product contained significant amounts of benzene, toluene, and xylenes (BTX). At 80 wt.% conversion, the ratio of these three products was approximately 15:10:1 benzene:toluene:xylenes.

JP-8 typically contains about 18 vol.% aromatics, with a specified maximum of 25 vol.% [3]. Aromatics present in JP-8 are mostly alkyl-substituted naphthalenes and higher molecular weight polycyclic aromatics. As JP-8 cracking proceeds to higher conversions, the larger aromatic compounds are converted to the more stable light aromatics, which accumulate and, because of their higher vapor pressures at the operating temperature of the gas/liquid separator, are only partially trapped as liquid residue. Steam reforming of benzene, toluene, and other aromatic compounds has been studied using a variety of catalysts and conditions [15–17]. Benzene and toluene have been shown to have lower tendency to coke formation than higher molecular weight aromatics [15], and the kinetics of benzene steam reforming are more favorable than methane steam reforming [16].

Sulfur species in the light gas product was predominantly H_2S, with small amounts of CH_3SH, thiophene, and methylthiophenes. Fig. 7 shows thiophene and the methylthiophenes grouped as "thiophenes." Sulfur species were determined as mol% concentrations by the GC-PFPD procedure described above, then converted to mass units

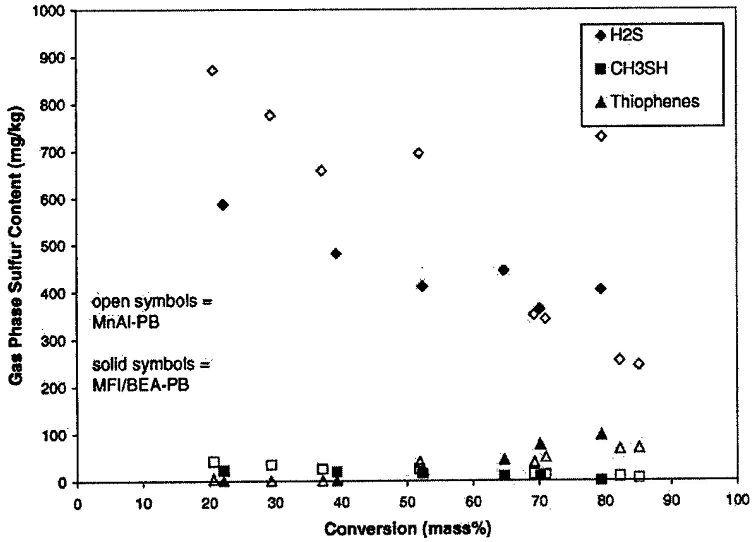

Fig. 7. Sulfur species concentrations in the light gas produced by JP-8 catalytic cracking using the packed bed reactors MnAl-PB and MFI/BEA-PB.

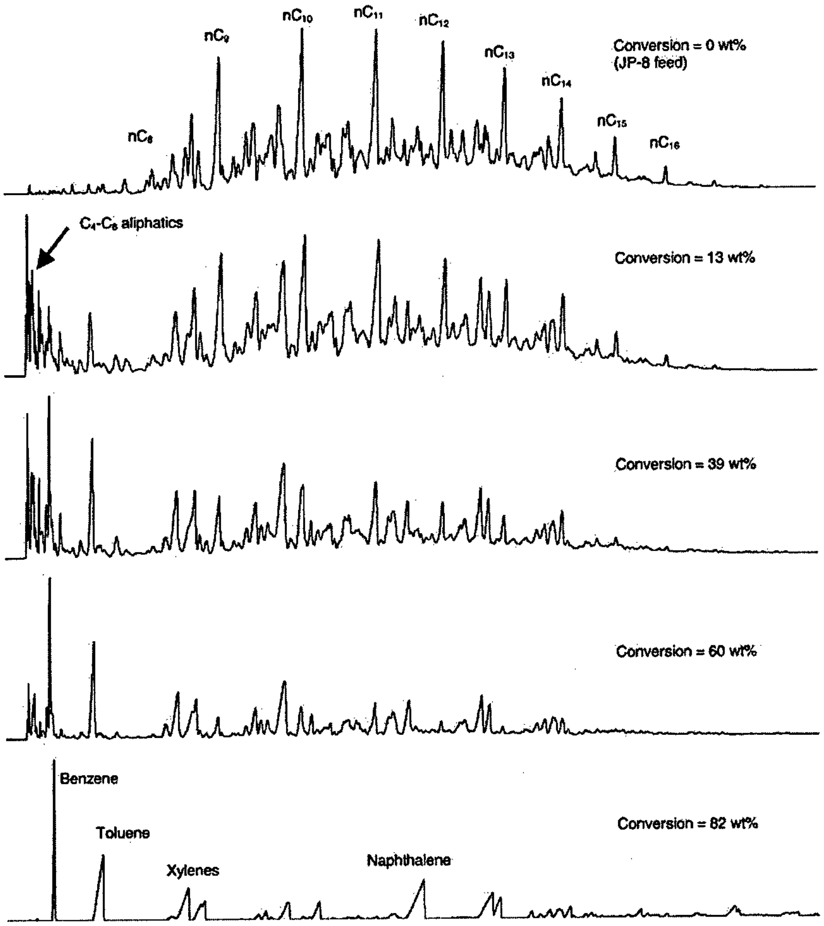

Fig. 8. GC-FID chromatograms of liquid residue from JP-8 catalytic cracking on Mn/γ-alumina catalyst.

(mg/kg) using the gas product average molecular weight, to simplify process design calculations. At low cracking conversions, the thiophenes are not detected in the gas product. As conversion increases, CH_3SH concentration decreases, and the thiophenes increase, with either catalyst. At lower conversions, the Mn/γ-alumina catalyst produced significantly more H_2S than the mixed zeolites, possibly due to better hydrogen transfer activity. Sulfur/carbon species cracking selectivity is highest at low conversions, so that sulfur is concentrated in the light gas product relative to the feed. H_2S and thiophene concentrations were lower in the gas product from the Mn/γ-alumina catalyst than from the zeolites catalyst at high conversions, probably owing to adsorption of the sulfur species by manganese oxides.

Fig. 8 shows GC-FID chromatograms of liquid residue samples from JP-8 catalytic cracking on Mn/γ-alumina catalyst at various conversion levels. At conversions from 13 to 60 wt.%, C_4–C_6 hydrocarbons are present in the liquid, but at 82 wt.% conversion, these intermediate species have been converted to light gas products, and the liquid is composed mostly of the BTX aromatic compounds and higher molecular weight aromatics. In general, the stabilities of hydrocarbons in cracking processes run in the order aromatics > normal saturated alkanes > normal alkenes > branched saturated alkanes > branched alkenes. As Fig. 8 shows, some normal alkanes can be seen to persist at cracking conversions as high as 60 wt.%, although by 82 wt.% conversion, even these compounds have been converted to light gas. Although the aromatic species remaining at 82 wt.% conversion are highly stable in the cracking process, they can be rapidly converted to CO_2 and H_2O in the high-temperature oxidizing environment of a combustion process to liberate heat for steam generation and reforming.

4. Conclusions

Catalytic cracking as a pre-treatment step in a liquid fuel reforming process can alleviate problems caused by the presence of sulfur compounds, non-volatiles, and coke precursors in the fuel feed. JP-8 catalytic cracking in packed bed and coated wall reactors was studied at temperatures, pressures, and space velocities relevant to applications in compact fuel processor systems. Two different catalyst formulations, manganese supported on γ-alumina, and mixed MFI and BEA acidic zeolites, were compared in tubular packed bed reactors, and found to give similar cracking conversions at atmospheric pressure over a range of temperatures and space velocities. Greater than 80 wt.% cracking conversion could be achieved with either catalyst at LHSV $= 5.5\,h^{-1}$ at mean reactor temperature <250 °C, while at LHSV $= 44\,h^{-1}$ mean reactor temperature of >520 °C was required. Tubular reactors with BEA zeolite catalyst coated on the tube inner wall achieved 80 wt.% conversion at $100\,h^{-1}$ liquid space velocity with reactor temperature <380 °C.

The main components of the light gas product formed in JP-8 catalytic cracking in packed bed reactors were determined to be CH_4, C_2H_4, and C_3H_6. The H_2 concentration was 8–10 mol% at any conversion. At conversions >50 wt.%, the gas product contained significant amounts of light aromatics, primarily benzene, with lesser amounts of toluene, and traces of xylenes. At high conversions, the manganese/γ-alumina catalyst produced greater amounts of C_4 and C_5 products than the zeolites. Sulfur in the light cracked gas product from either catalyst was mostly H_2S. CH_3SH concentration decreased, while thiophenes increased, with increasing conversion. The condensed liquid residue at >80 wt.% conversion was composed of benzene, toluene, xylenes, and higher molecular weight aromatics.

These results show the effects of catalytic cracking as a pre-treatment step in a JP-8 reforming process. The light sulfur species present in the cracked gas product can be removed by adsorption more effectively than the heavy refractory sulfur compounds present in the JP-8 feed. Any non-volatile species present in the feed are either converted to lighter products in the cracking process, or can be removed by gas/liquid separation after cracking, thus protecting downstream components from fouling. Also, the heavy aromatic species that are responsible for the high coking potential of JP-8 are cracked to lighter species at high conversion. The light product gas can be mixed with steam and subsequently reformed to a hydrogen-rich fuel cell feed stream, with significantly lower potential for coke formation in the reformer reactor than if JP-8 were to be reformed directly. The ability to achieve high cracking conversions at high space velocities, low pressures, and moderate temperatures, demonstrates that catalytic cracking can be a practical pre-treatment operation within a compact fuel reformer/fuel cell system for mobile electric power generation.

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References

[1] C. Song, Fuel processing for low-temperature and high-temperature fuel cells: challenges, and opportunities for sustainable development in the 21st century, Catal. Today 77 (2002) 17–49.
[2] A.H. Shaaban, T. Anderl, Logistics fuel processor, AFRL Technology Horizons, document ML-02-03, June 2002, p. 31, also available at http://www.afrlhorizons.com/Briefs/Jun02/ML0203.html.
[3] T. Edwards, W. Harrison, M. Lourdes, Properties and logistics of Air Force fuel: JP-8, Am. Inst. Aeronautics Astronautics, Report 2001–0498.

[4] Handbook of Aviation Fuel Properties, Coordinating Research Council Inc., Report No. 530, 1983.

[5] E.J. Szetela, J.A. TeVelde, External fuel vaporization study: phase II final report, NASA Contractor Report 165513, November 1981.

[6] D.R. Sobel, L.J. Spadaccini, Development of endothermic potential of JP-8, US Air Force Materiel Command Report WL-TR-2059, January 1994.

[7] J.S. Ervin, T.A. Ward, T.F. Williams, J. Bento, Surface deposition within treated and untreated stainless steel tubes resulting from thermal-oxidative and pyrolytic degradation of jet fuel, Energy Fuels 17 (2003) 577–586.

[8] P.-O.F. Andersson, M. Pirjamali, S.G. Jaras, M. Boutonnet-Kizling, Cracking catalyst additives for sulfur removal from FCC gasoline, Catal. Today 53 (1999) 565–573.

[9] A.E.W. Beers, T.A. Nijhuis, F. Kapteijn, European Commission Project No. GRD1 CT1999 10596: Intelligent Column Internals for Reactive Separations, Deliverable No. 25, Workpackage 6, December 2000.

[10] N. Kirshen, The determination of sulfur gases in natural gas with pulsed flame photometric detector (PFPD), Varian GC Application Note Number 60, http://www.varianinc.com.

[11] R. Charlesworth, A. Gough, C. Ramshaw, Combustion and steam reforming of methane on thin layer catalysts for use in catalytic plate reactors, in: Proceedings of the Fourth UK/National Conference on Heat Transfer, Institution of Mechanical Engineers, September 1995, pp. 85–89.

[12] K. Venkataraman, J.M. Redenius, L.D. Schmidt, Millisecond catalytic wall reactors: dehydrogenation of ethane, Chem. Eng. Sci. 57 (2002) 2335–2343.

[13] H.F. Rase, Handbook of Commercial Catalysts: Heterogeneous Catalysis, CRC Press LLC, 2000.

[14] M.-F. Reyniers, H. Beirnaert, G.B. Marin, Influence of coke formation on the conversion of hydrocarbons. I. Alkanes on a USY-zeolite, Appl. Catal. A 202 (2000) 49–63.

[15] R. Coll, J. Salvado, X. Farriol, D. Montane, Steam reforming model compounds of gasification tars: conversion at different operating conditions and tendency towards coke formation, Fuel Proc. Technol. 74 (2001) 19–31.

[16] X. Wang, R.J. Gorte, A study of steam reforming of hydrocarbon fuels on Pd/ceria, Appl. Catal. A 224 (2002) 209–218.

[17] D. Duprez, Selective steam reforming of aromatic compounds on metal catalysts, Appl. Catal. A 82 (1992) 111–157.