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Hydrodesulfurization of JP-8 fuel and its microchannel distillate using steam reformate

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Abstract

A field-deployable process for generation of clean desulfurized fuel from JP-8 feedstock is described. The process employs a compact hydrodesulfurization unit, operated in the vapor phase using steam reformate provided by an integrated steam reformer, as a replacement for hydrogen co-feed gas. The process includes a microchannel distillation unit upstream of the hydrodesulfurizer unit, which allows use of a lighter feed fraction to be processed in place of the full JP-8. The novel microchannel distillation concept is described and performance data for the unit, operating as a rectifier, are provided. Since the generated light fraction fuel from microchannel distillation contains fewer refractory sulfur components, the subsequent HDS process can readily achieve a significant sulfur reduction. The overall process can generate an ultra-clean JP-8 light fraction fuel with approximately 300 ppb sulfur residual. Hydrodesulfurization of full JP-8 fuel without the microchannel distillation unit was also studied. The effect of various operating parameters on the overall hydrodesulfurization performance, as well as the conversion of some individual sulfur components such as 2,3-dimethyl-benzothiophene, 2,3,5-trimethyl-benzothiophene and 2,3,7-trimethyl-benzothiophene, were investigated. Steam content in reformate at 30 mol% or less was found to improve HDS performance compared with dry reformate, despite a decrease in hydrogen partial pressure. However, at even higher concentrations of steam, hydrodesulfurization performance decreased.

Keywords: Hydrodesulfurization; Microchannel distillation; Steam reformate; JP-8 fuel

1. Introduction

The development of fuel cell power systems supplied by liquid hydrocarbon fuels such as jet fuel (JP-8) or diesel has continued to be challenged by the difficulty in cleanly reforming these fuels without catalyst deterioration. One of the major sources of catalyst deterioration and resulting low conversion activity has been the presence of sulfur in these fuels. Reformation of JP-8 to provide hydrogen for quiet, clean, and reliable 1–100 kW fuel cell power generation systems for field and other applications has been a focus of R&D activities by the U.S. Army's Tank Automotive Research, Development and Engineering Center (TARDEC). However, JP-8 logistics fuel may contain up to 3000 ppmw sulfur. Sulfur impurities, even at low concentrations, could result in significant poisoning of both reforming catalysts in the reformer [1–3] and electrode catalysts in the fuel cells [4,5] when their sulfur-tolerance limits are reached. A critical requirement to enable fuel cell system viability is efficient desulfurization of JP-8 fuel.

Various approaches to deal with sulfur have been investigated: (i) Develop sulfur-tolerant reforming catalysts that remain sufficiently active to provide the necessary catalytic activity despite the presence of sulfur in the fuel [6–9]. This generally requires operation at elevated temperatures which can lead to component corrosion or deterioration, and moreover this approach generally still requires recovery of H_2S post-reformer due to the extreme sulfur sensitivity of the fuel cell. (ii) Remove sulfur species from the liquid fuel using regenerable adsorbents [10,11]. Challenges associated with this approach include: the difficulty in removing the heavy, sterically hindered sulfur species from the fuel, especially in the presence of high concentrations of aromatic hydrocarbons; the relatively low capacity of most adsorbents prior to required regeneration; and the regeneration protocols required frequent result in the need for multiple beds and increased mechanical complexity. (iii) Remove sulfur via catalytic hydrodesulfurization (HDS) using

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pure H_2 [12–15]. This latter approach is practiced in refineries but has generally been considered impractical for operation in small-scale applications. Moreover, high-pressure hydrogen is required as an input to the HDS process, limiting field deployment.

This work challenges the assumption that HDS operation cannot be carried out efficiently and compactly at the several kW scale. In order to provide pressurized hydrogen, the HDS unit is integrated with a steam reformer, and steam reformate provides the high-pressure hydrogen source. A fraction of the total reformate is diverted to the HDS unit, with the remainder treated and provided to the fuel cell. The HDS unit operates in the gas phase, which is possible with JP-8 without carbon formation during vaporization and heating. This allows a lower operating pressure compared with three-phase flow encountered in the conventional HDS process with heavy fuels. A schematic of the process is provided in Fig. 1. The system also incorporates a small surge reservoir of desulfurized fuel to be used during fuel reformer startup, and to provide transient control between the HDS and reformer units.

An approach incorporating a microchannel distillation unit was developed to provide a variable light fraction of the JP-8 for subsequent HDS processing. This eliminated the most intractable heavy sulfur species, thereby reducing the burden on the HDS unit. The remaining heavier fraction could be used for vehicle propulsion. In this work, the light fraction sent to the HDS reactor comprised about 20 wt.% of the full JP-8. This 20% cut-off was somewhat arbitrarily selected and could be modified by changing the operating parameters of the microchannel distillation unit. Reasons for this 20% selection included: (i) minimizing sulfur species heavier than unsubstituted benzothiophene; (ii) minimizing impact of the decreased volatility of the returned fuel; (iii) minimizing concentration of various additives in the light fraction due to their unknown impact on either HDS or steam reforming.

The hydrodesulfurization step comprises a once-through pass of reformate along with the JP-8 light fraction. The light gas product from the HDS unit is combusted to provide process heat, either to preheat the feed entering the HDS unit or to generate heat to support the endothermic steam reforming reaction. An optional final polishing step was also initially envisioned, but as will be shown was not required to meet our targets. This method of desulfurizing JP-8 is only possible by integrating with a steam reformer unit, since pumping liquid feeds allow facile generation of pressurized hydrogen. Catalytic partial oxidation or autothermal reforming of JP-8 reforming would be unable to practically generate the necessary hydrogen partial pressure to sustain HDS operation.

The initial portion of this paper describes the demonstration of a first-of-a-kind microchannel distillation unit to produce a 20 wt.% light cut, followed by HDS to achieve sulfur levels in the product to below 1 ppmw S. Subsequent evaluation of the HDS capability with full JP-8, without a distillation step, is also described. Successful performance was also achieved, although sulfur levels were higher than for the case of HDS of the light cut fraction.

2. Experimental

2.1. Materials

Commercially available presulfided NiMo/Al_2O_3 catalyst DN-200 provided by Criterion Catalysts Inc. was used in this work. The catalyst was crushed to 40–80 mesh and pretreated with H_2 for 6 h at 343 °C and 250 psig, with a co-feed of JP-8 light distillate fuel. Simulated dry reformate (syngas) consisted of 74 mol% H_2, 14.1 mol% CO_2 and 11.9 mol% CO. Steam content in the wet reformate was 30 mol%. Full JP-8 fuel containing 1300 ppmw sulfur was provided by BP in Tacoma, WA.

2.2. Analysis of JP-8 fuel

Sulfur removal efficiency was evaluated by quantification of the sulfur concentration in the liquid product. Sulfur analysis of the JP-8 sample was carried out using an Agilent model 6890 gas chromatograph equipped with a sulfur chemiluminescent detector (SCD). The response factor for the SCD detector is essentially constant over a wide range of hydrocarbons, allowing the assumption that a single response factor could be used for the analysis. The detection limit for any individual sulfur component is approximately 50 ppb. The hydrocarbon

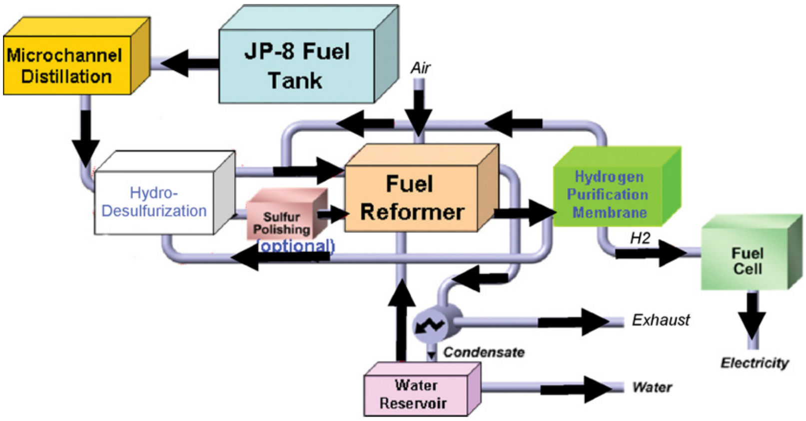

Fig. 1. Schematic of an integrated distillation–hydrodesulfurization-steam reforming process for powering fuel cells using JP-8 fuel.

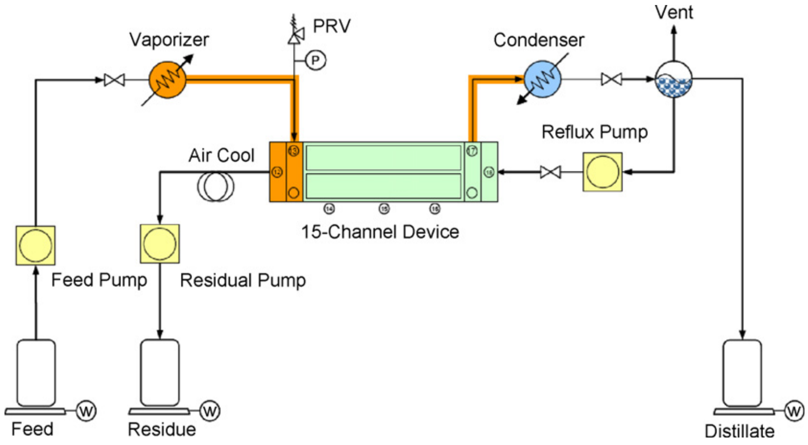

Fig. 2. Diagram of a microchannel distillation apparatus operating as a rectifier.

distribution was analyzed using a Hewlett Packard model 5890 chromatograph equipped with a FID detector and a DB5 column. Boiling point range curves were obtained based on the hydrocarbon GC data per ASTM D2887 test standard. Identification of individual sulfur components was based on the comparison of retention time of sulfur standards.

2.3. Microchannel distillation (MCD) operation

The microchannel distillation device was used as a rectifier section to separate a low-sulfur fraction from the full JP-8. A diagram of the microchannel distillation apparatus is shown in Fig. 2. JP-8 fuel was preheated to 230 °C and fed to the device at one end. The vapor product was removed from the other end and condensed as the distillate product. A portion of this condensate was refluxed back to the device as liquid feed. A heavy fraction liquid was removed from the feed end as the residual product. The microchannel distillation device was oriented in such a way that all internal vapor and liquid flowed horizontally. A parametric study was performed to find the best feed temperature, flow rate, and reflux ratio in order to optimize the process for product sulfur content and fuel recovery. A 100-h distillation run was operated using a 15-channel rectifier to produce a low-sulfur JP-8 fraction for subsequent extended HDS testing. The undecane (C_{11}) concentration in the distillate product was monitored to verify consistency of performance. The distillate stream was analyzed every 30 min. The average recovery of the distillate product from the JP-8 was set at 20 wt.%.

2.4. HDS testing

The HDS reaction was carried out in a fixed-bed reactor loaded with 100 cm^3 $NiMo/Al_2O_3$ catalyst. A flow distributor at the reactor inlet was added to minimize channeling of the feed flow. A 24-in. long profile thermocouple, located inside the reactor, contained 10 temperature detection points spaced at 1.5 in. intervals. This allowed monitoring of temperatures including reactor inlet, multiple points inside the catalyst bed, and reactor outlet, facilitating accurate thermal monitoring of the process. The overall catalyst bed length was about 4.6 in. A microchannel vaporizer with 60 channels was employed to allow the simultaneous vaporization of fuel and steam in one device. The HDS reaction was carried out with continuous operation under various process conditions (pressure: 100–280 psig; temperature: 360–400 °C; JP-8 fuel flow rate: 1.5–6 cm^3/min). The HDS liquid product was condensed and periodically separated from a cold trap followed by GC analysis. The gaseous effluent was not analyzed.

3. Results

3.1. Generation of JP-8 light distillate by microchannel distillation

Fig. 3 shows the correlation between boiling point, GC retention time, and carbon number (*n*-alkanes) for the hydrocarbons present in JP-8. Selected sulfur species have been added to the figure based on their boiling points, along with estimated boiling points for JP-8 additives. The 20 wt.% cut-off at about 200 °C (nominally C_{11}) provides a separation of benzothiophene from its di-alkylated analogs and other higher

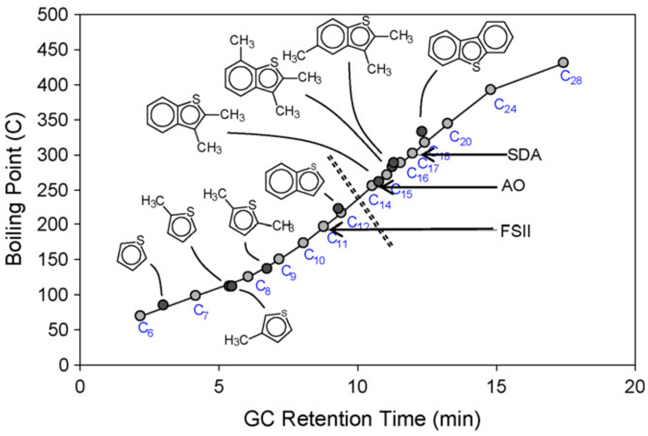

Fig. 3. Plot of GC retention time vs. boiling point for *n*-alkanes found in JP-8. Major sulfur species are overlaid based on boiling point. A 20 wt.% distillate cut at C_{11} separates benzothiophene from sterically hindered dibenzothiophenes. Boiling points of various additives (FSII = fuel system icing inhibitor; AO = antioxidant; SDA = static dissipater additive) are also shown.

molecular weight sulfur species. Most of the additives in JP-8 are retained in the heavier fraction.

3.1.1. The microchannel distillation concept

The approach for microchannel distillation of JP-8 is based on PNNL's patented Microwick technology [16–18]. Liquid hydrocarbon is pumped through thin wicks that have thicknesses in the range of 0.1–1.0 mm. Vapor flows counter-current to the liquid flow. The thinness of the wicks facilitates rapid heat and mass transfer between the vapor and liquid phases, resulting in intensification of the process. The microchannel distillation hardware is easily scalable through the addition of more channels.

Microtechnology achieves process intensification by targeting the rate-limiting step in either heat or mass transfer. In normal distillation processes and in almost all cases involving mass transfer between a gas and liquid phase, the rate-limiting step is diffusion in the liquid phase. In conventional distillation, the gas is typically bubbled through the liquid as it flows across trays or through structural packings. The pressure drop associated with bubbling a gas through a liquid and the energy lost in boiling a fluid at high temperature and condensing at a lower temperature makes conventional distillation a very energy-intensive process.

In the microtechnology approach, a liquid film is maintained by confining it to a wick or a porous material that is wetting for the liquid. Orders of magnitude reduction in hardware volume may be achieved by controlling this liquid-film thickness. This size reduction is possible because the time constant for diffusion in the liquid phase is a function of L^2/D_{ab}, where L is the liquid film thickness and D_{ab} is the binary diffusion coefficient. Thus a reduction in the film thickness by a factor of 10 results in a two-orders-of-magnitude reduction in the time required for the same level of diffusion to occur.

As shown in Fig. 4, a simple microchannel distillation column consists of a feed, a bottom product, and a distillate product. Heat is supplied at the reboiler and extracted where the distillate is removed. Liquid flows towards the reboiler via wicks, which are shown to be located on the device walls but could quite easily be located in the center of the device. Vapor is shown to flow towards the distillate exit in the center of the device.

3.1.2. Generation of JP-8 light distillate by microchannel distillation

Parametric studies were carried out to determine the optimal process conditions to produce a high-quality light fraction comprising approximately 20 wt.% of the full JP-8. These process variables included reflux ratio, feed temperature, and JP-8 feed flow rate. Final optimized conditions were: reflux ratio 4.3; inlet temperature 230 °C; JP-8 feed flow rate 2.5 g/min. The 15-channel microchannel device was operated as a rectifier for a 100-h continuous distillation. This process generated approximately 1 gallon of JP-8 distillate for subsequent HDS processing.

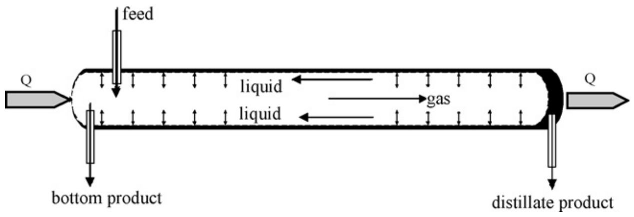

Fig. 4. Schematic of a microchannel distillation column.

Fig. 5 provides the sulfur component distribution in full JP-8 and the microchannel distillate, and Fig. 6 provides the distillation curves for both JP-8 and the light distillate. The JP-8 contains a range of sulfur species, from alkylated thiophenes to alkylated benzothiophenes, with a total sulfur content of 1300 ppmw. The major sulfur species are dimethyl- and trimethyl-benzothiophenes. Dibenzothiophene and other heavier sulfur species are present in negligible amounts. It can be seen that the alkyl-benzothiophenes and other heavy sulfur species are mostly removed from the JP-8 distillate product. The majority of sulfur components in the light distillate are benzothiophenes or alkyl-substituted thiophenes, with boiling points mostly below 200 °C. The total sulfur content was reduced to 329 ppmw from the original 1300 ppmw. The hydrocarbon distribution (not shown) for the light distillate showed very little product above C_{11}.

Generation of JP-8 light distillate by batch distillation was also carried out to compare the separation efficiency with microchannel distillation. The cut-off temperature at the top of the distillation column was set at 190 °C to achieve 20% fuel recovery. The sulfur contents of the JP-8 distillate from these two distillation processes are shown in Table 1. Both total sulfur content and heavy sulfur content are slightly lower in the distillate obtained by microchannel distillation compared with the batch distillation.

3.2. Hydrodesulfurization of JP-8 distillate fraction

The unique attributes of this HDS approach include the direct utilization of reformate as an H_2 replacement, and operation of the HDS reaction in the gas phase at lower total pressure and higher reactor productivity than typical three-phase operation. Some aspects of the HDS reaction with the JP-8 light cut using steam reformate have previously been reported [19]. Those studies, employing a lab-scale reactor (1–2 g catalyst), showed steam to have an adverse effect on sulfur removal efficiency, but that $NiMo/Al_2O_3$ showed superior steam tolerance compared with $CoMo/Al_2O_3$. Hence, all subsequent work has focused exclusively on the use of $NiMo/Al_2O_3$.

Hydrodesulfurization of the microchannel distillate was continuously run for 30 h. The product sulfur concentration over this period is shown in Fig. 7. Steady-state operation was achieved within 1 h of operation. The product organic sulfur content was reduced to less than 0.5 ppmw. Fig. 8 provides a comparison of the sulfur traces between the starting feed and the HDS product. About 0.2 ppmw H_2S, dissolved in the liquid product can be seen in the chromatogram, however, this could be easily removed by

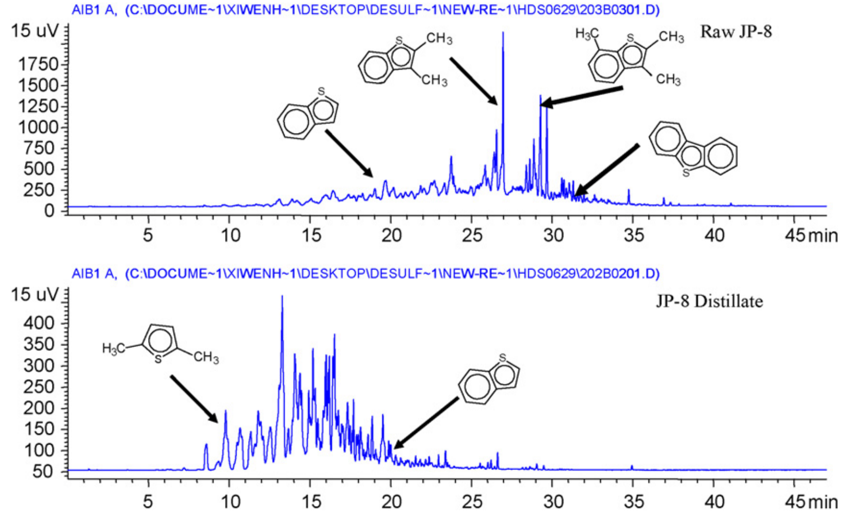

Fig. 5. GC-SCD chromatograms showing sulfur distribution of full JP-8 (upper) and light distillate fraction (lower) obtained after 100-h continuous microchannel distillation operation. *Note*: different vertical scales are used.

inert gas purge. The hydrocarbon distribution remained unchanged after 30 h of HDS reaction

Since steam reformate containing 30% steam was used as gas feed for the HDS reaction, the sulfur residual in the water phase were also analyzed. Only a small amount of organic sulfur was measured in the water phase. However, one new sulfur peak was observed adjacent to the H_2S peak in the chromatogram. This species was not identified, but probably corresponds to COS, which could have been generated from the reaction of H_2S with CO or CO_2. The total sulfur in the water phase was less than 1 ppmw.

Fig. 9 shows the reactor temperature profile under steady-state operating conditions. Temperatures at points A, B and C are catalyst bed temperatures. The reactor temperature profile shows a temperature gradient along the catalyst bed of less than 5 °C, indicating a quite uniform temperature of operation. The reactor set point was approximately 345 °C in the absence of feed. As seen in Fig. 9, the catalyst temperatures stabilized in the range of 365–370 °C, indicating the presence of an exothermic process with HDS operation. It was found that these temperatures were sufficient to achieve high sulfur removal efficiency, and further increases in temperature did not result in a significant improvement in HDS performance. Over the period of the run, there was no apparent catalyst deactivation (based on product quality), and neither was there any increase in pressure drop. The hydrocarbon distribution of the HDS product showed no evidence of any significant hydrocarbon cracking. It appears that a catalyst temperature of 370 °C caused no problems in operation.

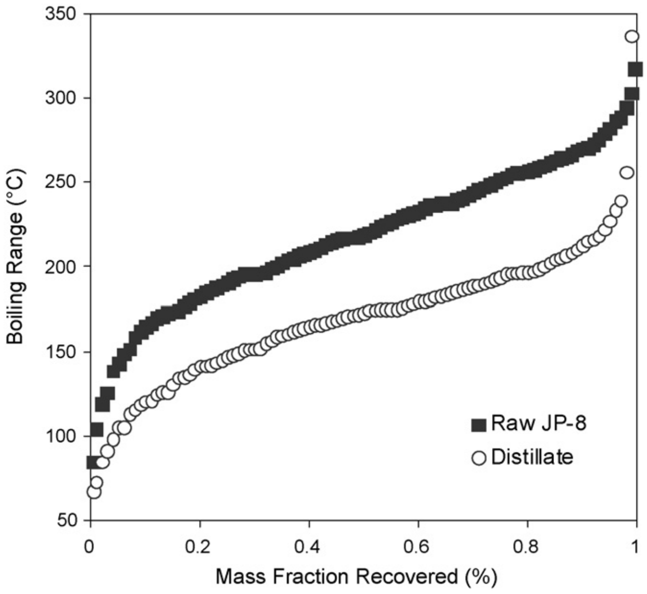

Fig. 6. Distillation curves for full JP-8 and light distillate obtained by microchannel distillation.

3.3. Hydrodesulfurization of full JP-8

3.3.1. Analysis of HDS product

As described above, the HDS treatment of the light cut JP-8 was successful in removing organic sulfur from the JP-8 light distillate cut to well below 1 ppmw, making any subsequent treatment by sulfur polishing unnecessary. Based on these results, it was of interest to determine how effective would be this HDS approach with full JP-8. The incentive would be to eliminate microchannel distillation, despite its effectiveness, in order to simplify the process by removing one unit operation.

Table 1
Sulfur content (in ppmw) of microchannel distillate and 190 °C batch distillate

	Microchannel distillate	Batch 190 °C distillate
Total sulfur	328.7 ± 3	331.9 ± 3
Heavy sulfur[a]	16.6 ± 0.5	17.3 ± 0.5

[a] Heavy sulfur is defined here as those sulfur species that have a retention time greater than 25 min on the SCD-GC. These include 2,3-dimethylbenzothiophenes and other heavy sulfur compounds.

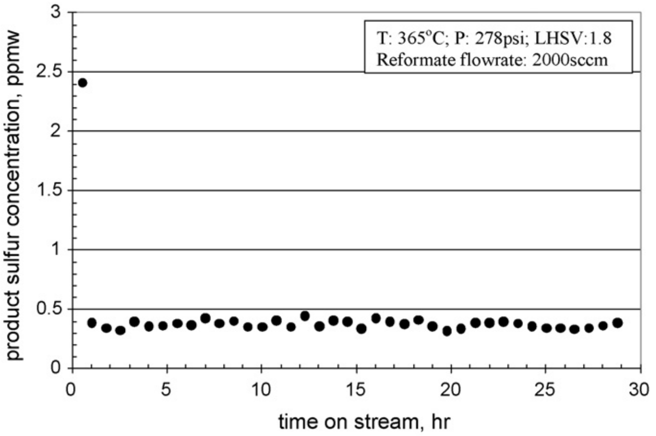

Fig. 7. Product sulfur concentration vs. time on stream for HDS of JP-8 light distillate.

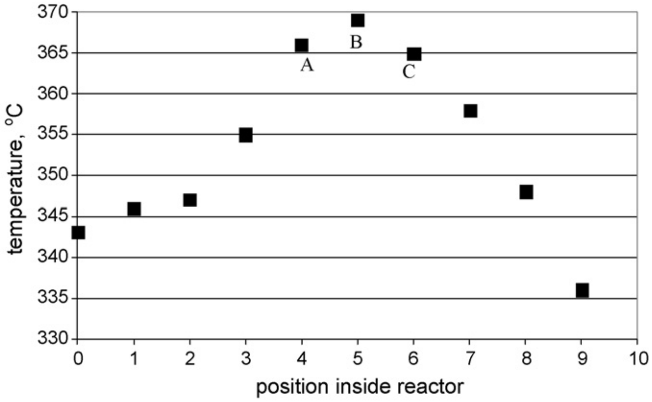

Fig. 9. HDS reactor temperature profile under steady-state operation with JP-8 light distillate fuel. Points A, B, and C correspond to front, middle, and end of the catalyst bed, respectively.

The same ranges of operating parameters were selected for the full JP-8 hydrodesulfurization tests.

For full JP-8 fuel (containing 1300 ppmw sulfur), major sulfur components include 2,3-dimethyl-BT (2,3-DMBT), 2,3,5-trimethyl-BT (2,3,5-TMBT) and 2,3,7-trimethyl-BT (2,3,7-TMBT). The concentrations of these components are provided in Table 2. All have some steric hindrance around the sulfur atom as a result of the adjacent methyl group in the 2-position, but the combination of methyl groups in the 2 and 7 positions can provide additional steric hindrance. Fig. 10 shows a typical HDS result with full JP-8 fuel using the NiMo/Al_2O_3 catalyst. The sulfur concentration in HDS product was reduced from an initial 1300 ppmw to a final 4.6 ppmw. The HDS reaction successfully removed the majority of the sulfur components, with only a few species remaining, the 2,3,7-TMBT being the most prominent.

3.3.2. Effect of temperature on sulfur removal efficiency

The temperature dependence of hydrodesulfurization performance was investigated over the range of 350–410 °C at various space velocities. The relationship between temperature and product sulfur content, shown in Fig. 11, demonstrates that higher temperatures and longer residence times result in improved HDS performance with the full JP-8 feed. At 1.5 cm^3/min JP-8 flow (LHSV = 0.9) and 408 °C, the residual sulfur in the fuel could be reduced to below 1 ppmw. The favorable effect of increasing temperature is especially pronounced at the elevated LHSV, whereas at low LHSV, temperature plays a less important role.

Table 3 shows the effect of temperature on the conversion of some specific sulfur components. The results demonstrate that 2,3-DMBT and 2,3,5-TMBT can be completely converted even at the lowest reaction temperature. However, for 2,3,7-TMBT, conversion is strongly dependent on reaction temperature. Therefore, the temperature effect on the HDS performance is strongly dependent on the molecular structure of the organo-sulfur species.

3.3.3. Effect of pressure on sulfur removal efficiency

Successful integration of HDS with a steam-reforming process requires compatible operating pressure for both processes. Pressures above 300 psi are undesirable for reforming due to thermodynamic limitations on the product equilibrium (excessive methane formation). It was therefore

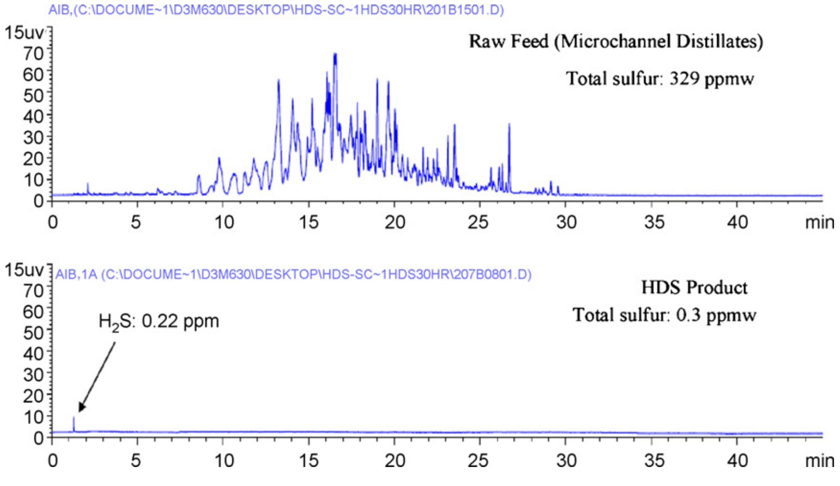

Fig. 8. GC-SCD traces of JP-8 light distillate and the hydrodesulfurized product.

Table 2
Concentration of identifiable sulfur species in JP-8

Sulfur compound	[S] (ppmw)	% of total sulfur
Benzothiophene (BT)	14.0 ± 0.1	1.1
2,3-Dimethyl-BT	58.5 ± 0.1	4.8
2,3,7-Trimethyl-BT	44.6 ± 0.1	3.6
2,3,5-Trimethyl-BT	33.0 ± 0.1	2.7
Dibenzothiophene (DBT)	3.5 ± 0.1	0.3

Total sulfur: 1300 ppmw.

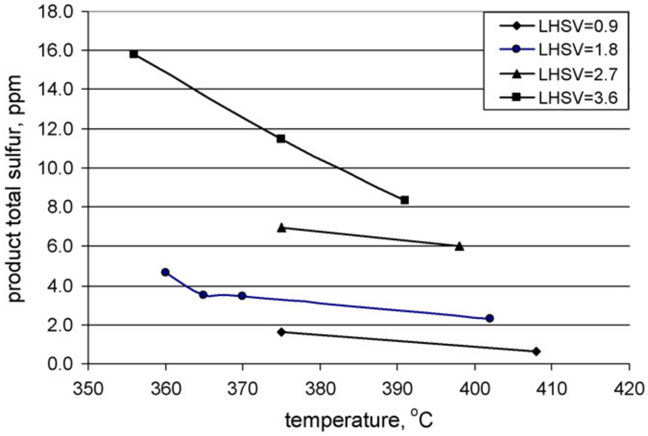

Fig. 11. Effect of temperature and space velocity on product sulfur from HDS of full JP-8.

necessary to evaluate the effects of operating pressure on HDS performance with full JP-8 over the pressure range 100–280 psi.

Fig. 12 shows the effect of total reaction pressure on residual sulfur content in the HDS product. Under these conditions, the H_2 partial pressure was proportional to the total pressure. The corresponding total and hydrogen partial pressures (in parenthesis) in psi were: 285 (146.4), 270 (138.7), 200 (102.7), and 100 (51.4). It can be seen that an increase in operating pressure leads to a decrease in residual sulfur content. However, diminishing returns are found at the highest pressures of operation.

The effectiveness of the NiMo/Al_2O_3 catalyst in hydrodesulfurizing different dimethyl- and trimethyl-substituted benzothiophenes as a function of total reaction pressure is shown in Fig. 13. The results show that the conversions of 2,3-DMBT and 2,3,5-TMBT are independent of total reaction pressure over the range investigated, and almost 100% conversion can be achieved even at a total pressure of only 100 psi. However, the conversion of 2,3,7-TMBT is strongly related to the reaction total pressure.

3.3.4. Effect of steam content on sulfur removal efficiency

Fig. 14 shows the effect of steam content on the HDS performance with full JP-8 at 365 °C. For reformate with up to 30 vol% steam in the gas feed, HDS performance was similar to or slightly better than performance with dry syngas. However, as the steam concentration was increased to 50 vol%, the desulfurization effectiveness declined, indicating that at a certain point steam began to act as a poison for the HDS reaction. The improved HDS performance with 30 vol% steam occurring despite a lower partial pressure of hydrogen being available. Although the water gas shift reaction could be occurring to raise somewhat the partial pressure of H_2, the maximum possible H_2 partial pressure with water gas shift is still well below that available with the dry syngas (156 psi vs. 200 psi). This favorable effect of H_2O at moderate concentration might be due to the increased catalyst bed temperature with addition of steam and resulting water gas shift activity (the catalyst bed temperature increased approximately 15 °C with steam present, as shown in Fig. 15), or possibly due to a reduction in CO content of the syngas through a combination of steam dilution and water gas shift.

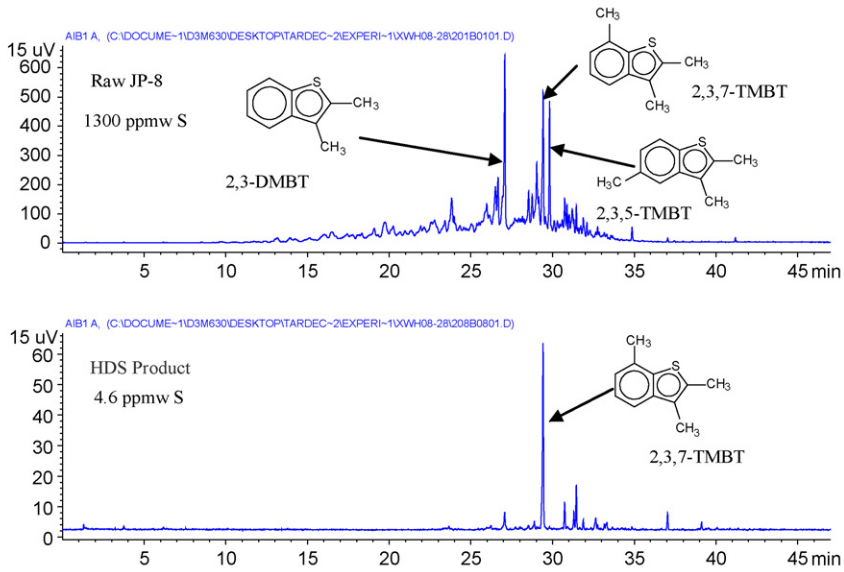

Fig. 10. Sulfur SCD traces of full JP-8 before and after HDS reaction using 100 cm^3 NiMo/Al_2O_3 catalyst at 365 °C. Feedrates: dry syngas (74% H_2) = 2000 sccm; $H_2O(l) = 0.5\ cm^3/min$; JP-8(l) = 3 cm^3/min.

Table 3
Effect of temperature on conversion of specific sulfur species present in JP-8 as a function of flow rate

Temperature (°C)	2,3-DMBT conversion (%)	2,3,7-TMBT conversion (%)	2,3,5-TMBT conversion (%)
$3\ cm^3/min$			
350	99.9	92.3	100.
365	99.9	95.2	100.
380	100.	96.3	100.
402	100.	96.9	100.
$4.5\ cm^3/min$			
356	99.2	84.8	100.
375	99.6	89.5	100.
391	99.9	91.5	100.

Conversions are estimated to be accurate within ±0.1%.

4. Discussion

It has been shown that hydrodesulfurization of a light cut of JP-8 fuel using a conventional $NiMo/Al_2O_3$ catalyst and steam reformate in place of hydrogen gas is effective for the removal of organic sulfur species to well below 1 ppmw. The operating conditions for the HDS unit are compatible with an integrated compact steam-reforming process which produces syngas from the purified JP-8 light cut stream. A small microchannel distillation unit (15 channels) operating in rectifier mode generates the light cut fraction. The microchannel system is readily scalable, and also tunable in terms of controlling the fraction of light cut extracted from the full JP-8 fuel.

The concept of utilizing a light fraction of JP-8 in order to facilitate desulfurization is not novel, although it does not appear to have been described in conjunction with hydrodesulfurization for fuel cell application. Velu et al. [20] described the use of a special fractionator to separate 70% of the JP-8 as a light fraction, for subsequent desulfurization by adsorption. The heavier remainder of about 30% of the JP-8, which contained approximately 50% of the total sulfur, could be burned to provide heat for a compact fuel processor. Subsequent adsorption using $Ni/SiO_2–Al_2O_3$ removed sulfur in the light fraction to approximately 30 ppmw. The HDS process described in this paper reduced the sulfur species from the full JP-8 to below 5 ppmw, compared with <0.5 ppmw with the light distillate fraction. This clearly demonstrates the benefit of generating a light fraction of JP-8 fuel for subsequent desulfurization, and the competitiveness of a compact steam reformation–hydrodesulfurization approach for sulfur removal.

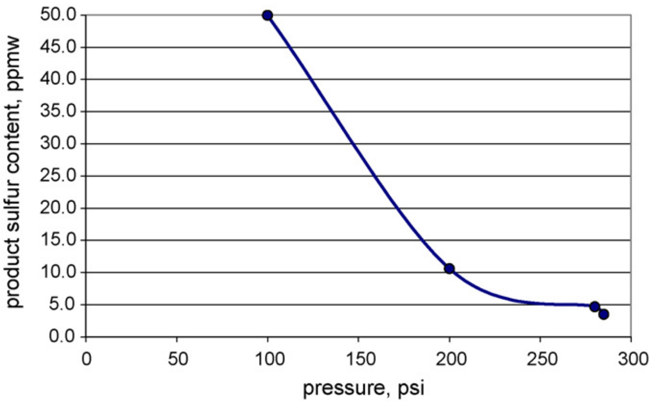

Fig. 12. Effect of total reaction pressure on HDS of full JP-8 using $100\ cm^3$ $NiMo/Al_2O_3$ catalyst at 365 °C. Feedrates: dry syngas (74% H_2) = 2000 sccm; $H_2O(l) = 0.5\ cm^3/min$; $JP\text{-}8(l) = 3\ cm^3/min$.

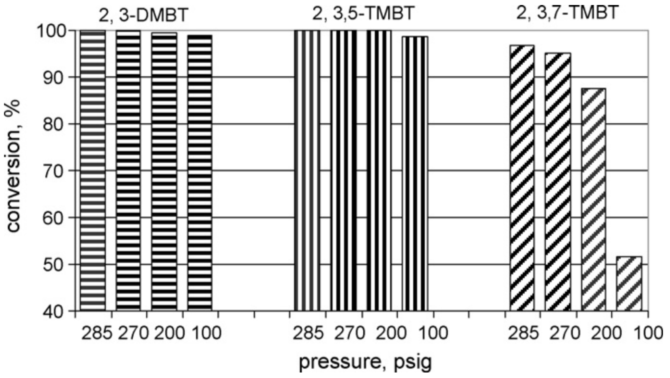

Fig. 13. Effect of total reaction pressure on the HDS conversion of various methyl-substituted benzothiophenes. Reaction conditions are the same as in Fig. 12.

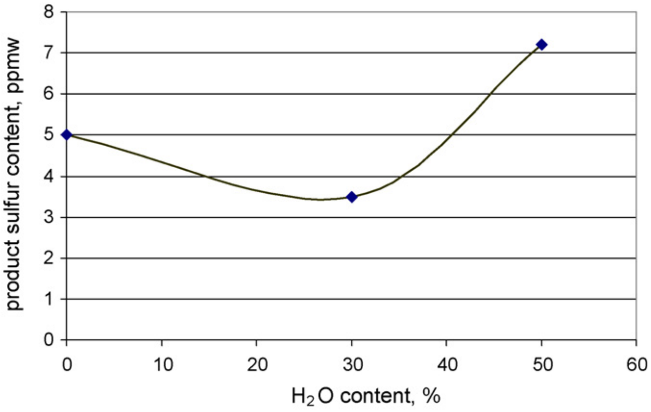

Fig. 14. Effect of steam content on hydrodesulfurization of full JP-8 using $100\ cm^3$ $NiMo/Al_2O_3$ catalyst at 365 °C and 270 psig. Feedrates: dry syngas (74% H_2) = 2000 sccm; $JP\text{-}8(l) = 3\ cm^3/min$ (1.8 LHSV); $H_2O(l)$ variable.

The use of wet syngas (steam reformate) in place of hydrogen has been demonstrated to be effective for HDS of both full JP-8

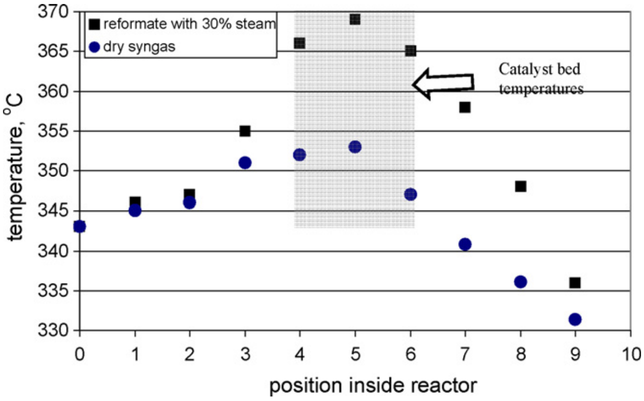

Fig. 15. Catalyst bed temperature profiles with/without steam addition.

fuel and its light distillate fraction. Improved HDS performance was observed with increases in hydrogen partial pressure. However, the surprising result of improved HDS performance with reformate containing 30 vol% H_2O deserves some comment, as hydrogen partial pressure is reduced with the addition of steam. The increase in catalyst bed temperature following the addition of steam seems most likely to be explained by the occurrence of the mildly exothermic water gas shift reaction. Hydrodesulfurization has been shown to occur using hydrogen internally generated from CO and H_2O via the water gas shift reaction over Mo-based [21] and $NiMo/Al_2O_3$ catalysts [22,23]. It was shown in this work that an increase in reaction temperature can lead to improved HDS activity. This affect is counteracted by a lower hydrogen partial pressure due to the addition of steam, even if water gas shift is occurring to full equilibrium. This seems to implicate either the benefits of in situ generated H_2 [21], or the role of the remaining CO present in the syngas as having an adverse influence on HDS performance. Both water gas shift activity and possible formation of COS (from the reaction of CO with H_2S) implicate CO as a potential competitor for reaction sites. Addition of steam to reduce CO concentration via water gas shift could help explain the improvement in performance at steam concentrations around 25–30 vol%, adding to the temperature effect noted above. At higher H_2O concentrations, decreased performance implies inhibition by H_2O, consistent with other reports [21,24].

The demonstrated system comprises a catalyst bed volume of 100 cm^3, and at standard conditions of 360 °C, 270 psig total pressure, and LHSV of 1.8 it is capable of providing purified fuel for a steam reformer to support a 0.5 kW power output. In a separate program, an integrated steam reforming–HDS system for full JP-8 has been successfully demonstrated with a 10 kW scale HDS unit and a 1 kW scale steam reformer, in which the entire output of the reformer was supplied to the HDS unit. It is projected that approximately 8–10% of the reformate generated by a 10 kW steam reformer would be required to supply the HDS unit, with the reminder being supplied to the fuel cell.

This paper has focused primarily on describing a steam reformate-based process to generate low-sulfur fuel from JP-8, to support field-based fuel cell power generation for military applications. There are a number of areas of scientific inquiry that were not addressed in this work but deserve further examination. These include but are not limited to the role and extent of the water gas shift reaction in HDS with $NiMo/Al_2O_3$ catalysts; the degree of feed hydrogenation that occurs in parallel with the HDS reaction; the effect of nitrogen-containing molecules in the feed; quantification of the role of CO on HDS performance; and examination of the possible role of steam in retarding carbon formation, especially at or above the temperatures employed in this study. There also remains room for development of improved catalysts to reduce the severity of the operating conditions or to reduce reactor volume.

5. Conclusions

A low-sulfur JP-8 light fraction was generated using a microchannel distillation device operating as a rectifier. The light fraction was 20 wt.% of the total JP-8 fuel, providing a nominal cut-off at about 200 °C. The microchannel device was operated in a 100-h JP-8 distillation test, providing feedstock for the hydrodesulfurization unit. HDS of this light JP-8 distillate, employing a $NiMo/Al_2O_3$ catalyst using steam reformate provided a sulfur reduction from an initial 329 ppmw down to less than 0.5 ppmw.

Subsequent HDS testing without the distillation step, i.e. with full JP-8 fuel, resulted in a reduction under similar operating test conditions from an initial 1300 ppmw S to a final concentration of 4.6 ppmw. By increasing temperature and residence time, residual sulfur levels below 1 ppmw could be achieved. Steam present in the reformate at less than 30 vol% improved HDS performance, possibly the result of a reduction in CO content via dilution and through the water gas shift reaction, which may also have provided a temperature increase within the catalyst bed leading to higher activity.

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