

Microchannel Distillation of JP-8 Jet Fuel for Sulfur Content Reduction

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Abstract

In microchannel based distillation processes, thin vapor and liquid films are contacted in small channels where mass transfer is diffusion-limited. The microchannel architecture enables improvements in distillation processes. A shorter height equivalent of a theoretical plate (HETP) and therefore a more compact distillation unit can be achieved. A microchannel distillation unit was used to produce a light fraction of JP-8 fuel with reduced sulfur content for use as feed to produce fuel-cell grade hydrogen. The HETP of the microchannel unit is discussed, as well as the effects of process conditions such as feed temperature, flow rate, and reflux ratio.

Introduction

Pacific Northwest National Laboratory (PNNL) has created a family of microchannel devices for gas-liquid processing, including phase separation, partial condensation, absorption, desorption, and distillation.^[1-4] For many of these unit operations, the primary resistance to mass transfer occurs due to diffusion in the liquid phase. Thus, intensification of mass transfer can be exerted through control of the liquid film thickness. In PNNL's devices, this thickness is controlled through the use of wicks. Diffusion occurs from an adjacent vapor channel. The wicks offer the additional advantage of orientation and gravitational independence since the fluid flow is controlled through capillary forces. The results of these attributes are devices that are highly suitable for portable applications or applications where energy savings or higher separations are desirable. In the area of distillation PNNL has demonstrated a number of devices, starting initially with a column in total reflux and moving to reactive distillation. Current work includes distillation to obtain a light cut of JP8 followed by hydrodesulfurization, as well as catalytic distillation of C4 hydrocarbons. The goal of the former project is to provide 5-10 kW power for a fuel cell used in silent watch that does not use batteries and allows the military to use a single fuel. The latter project targets industrial energy savings, with one potential application hydrogenation of C3 and C4 acetylene byproducts from ethylene production. In this paper, the distillation unit for the sulfur removal from JP-8 jet fuel and the test results are discussed.

Raw JP-8 fuel contains light sulfur compounds such as thiols and sulfides as well as heterocyclic sulfurs of increasing boiling point such as thiophene, benzothiophene, dibenzothiophene, and their alkyl substituted derivatives. The JP-8 microchannel distillation is the first step in sulfur reduction in the overall fuel preparation process as shown in Figure 1. The removal of the heavy sulfur species by distillation allows the subsequent hydrodesulfurization step to operate at favorable conditions with high efficiency.

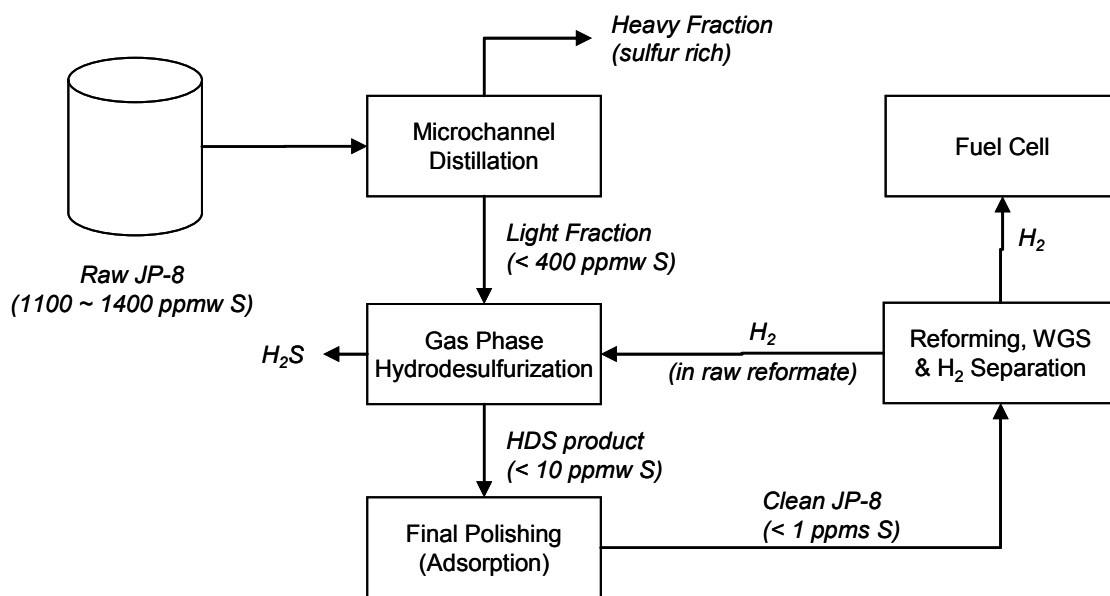


Figure 1. Overall process flow diagram for fuel cell grade hydrogen production from JP-8 fuel.

Experimental

A microchannel distillation device based on PNNL's patented "sheet architecture" [5-9] was used as a rectifying section to separate a low sulfur fraction from raw JP-8 jet fuel. JP-8 fuel was vaporized 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 the direction of all its internal vapor and liquid flows was horizontal.

The sulfur content in the raw fuel and product streams was analyzed on an Agilent 6890 GC equipped with a sulfur chemiluminescence detector. A 30m J&W DB-5 column programmed to operate from 50°C to 250°C provided separation of the various sulfur components. Hydrocarbon distribution of the process streams was analyzed by a HP 5890 GC with a FID detector. Boiling range curves were obtained based on the hydrocarbon GC data per ASTM D2887 test standard. Raw JP-8 fuel was obtained from a BP refinery facility in Tacoma, WA.

A parametric study was performed to find the optimal feed temperature, flow rate, and reflux ratio in order to produce a JP-8 light fraction of 350 ppmw or lower sulfur content with a distillate recovery of approximately 20 wt%. A 100-hr distillation run was also carried out to produce low-sulfur JP-8 fractions and test the reliability of the microchannel distillation operation.

Results and Discussion

The relative volatility of the various n-alkanes and sulfur species in raw JP-8 was established qualitatively according to their boiling points and the retention times on a nonpolar GC column, as is shown in Figure 2. In order to remove all of the alky substituted benzothiophenes and other heavier sulfur compounds, the desired light fraction of JP-8 should contain no hydrocarbons heavier than n-C₁₄. Because the most abundant n-alkanes in the JP-8 are n-C₁₀ to n-C₁₄, such low sulfur light cut can be obtained with good recovery. The above is the basis for the feasibility of distillation separation of JP-8 fuel into low-sulfur fractions.

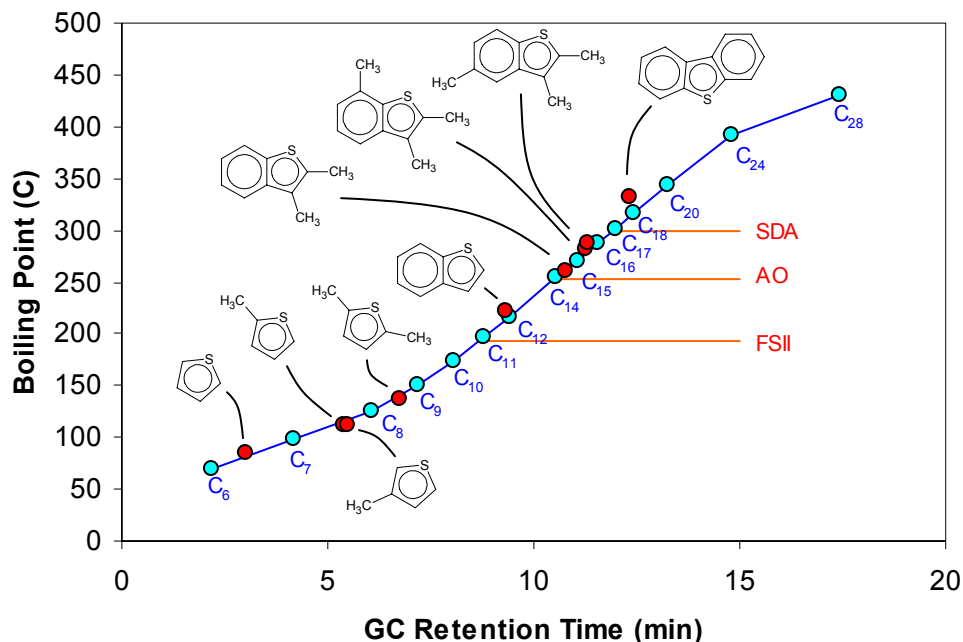


Figure 2. Boiling point and GC retention times of selected normal alkanes, sulfur species, and JP-8 fuel additives (SDA: static dissipation agent, AO: antioxidation additive, FSII: fuel system icing inhibitor).

The parametric study on effect of process conditions on JP-8 distillation was carried out first. The reflux ratio was adjusted from 1 to 10 and the effect of reflux ratio on the total sulfur content of distillation product streams is shown in Figure 3. The sulfur content in the distillate decreased, as expected, when higher reflux ratio was used.

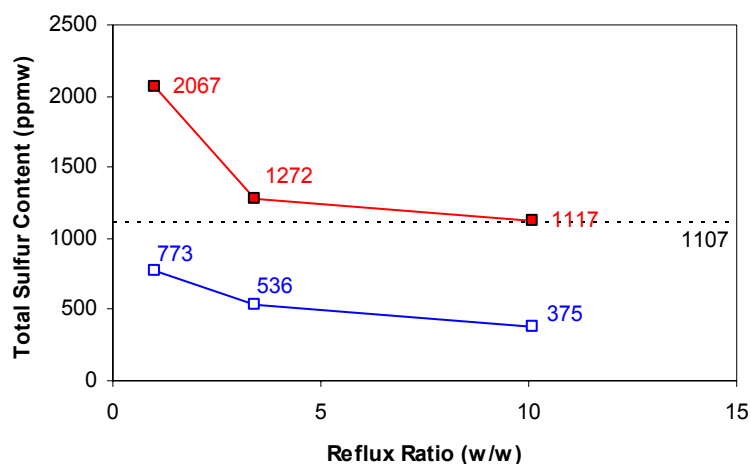


Figure 3. Effect of reflux ratio on the total sulfur content in the distillation products with JP-8 feed temperature at 300°C and feed flow rate at 1.59 g/min (blue: distillate, red: residual, dash line: raw JP-8).

Next, the JP-8 feed vapor temperature was optimized. The effect of feed temperature is shown in Figure 4. The lowest sulfur concentration in the distillate product was obtained when the feed temperature was 230°C. The dew point of JP-8 vapor at 1 atm was estimated to be between 218 to 231°C based on flash calculations using ChemCAD software with both literature JP-8 composition^[10] and pseudo composition based on measured ASTM D2887 boiling curves. Therefore at a feed temperature lower than 230°C the JP-8 stream was likely a two-phase flow. Because the feed flow distribution features on the current microchannel device was optimized for vapor flow, a two-phase feed flow likely caused partial flooding near the feed point, which degraded separation efficiency.

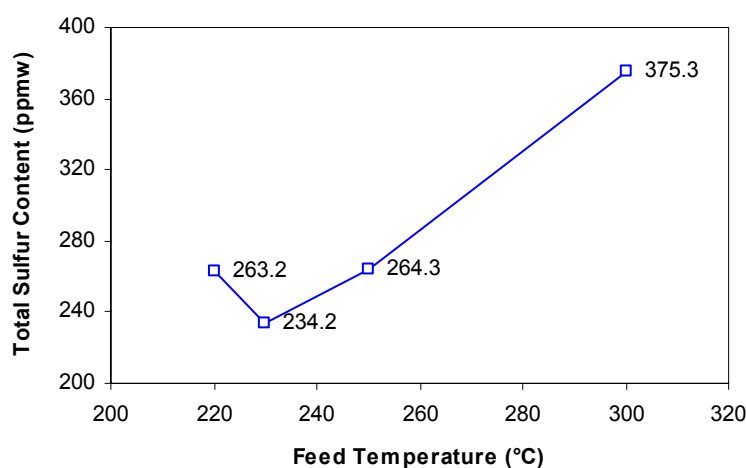


Figure 4. Effect of JP-8 feed temperature on the total sulfur content in the distillate product with JP-8 feed flow rate at 1.59 g/min and reflux ratio of 11.

The flow rate effect on distillate sulfur content was studied at a near optimal feed temperature of 240°C and a moderate reflux ratio of 4. The results are shown in Figure 5. At

higher flow rate, there was a slight increase in the distillate sulfur content. This is consistent with our previous observation that the HETP of a prototype microchannel device increased with increasing flow rate for acetone-methanol system under total reflux conditions. ^[11]

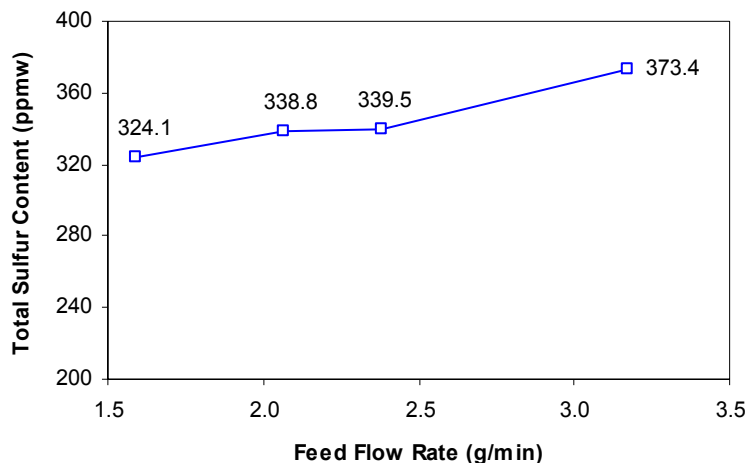


Figure 5. Effect of JP-8 feed flow rate on the total sulfur content in the distillate product with JP-8 feed temperature at 240°C and reflux ratio of 4.

A 100-hr continuous distillation run was successfully carried out at reflux ratio 4.3, feed temperature 230°C, and feed flow rate 2.5 g/min. These conditions were chosen based on the above parametric study. The distillate product sulfur content was 329 ppmw, which can be compared to the 1107 ppmw of sulfur in the raw JP-8. The distillate product yield was 19 wt%. The sulfur and hydrocarbon distributions of the raw JP-8 and the distillate product are given in Figure 6 and 7, respectively. It can be seen that methyl benzothiophenes and heavier sulfur species as well as n-tetradecane and heavier alkanes were both significantly reduced in the JP-8 distillate product as desired.

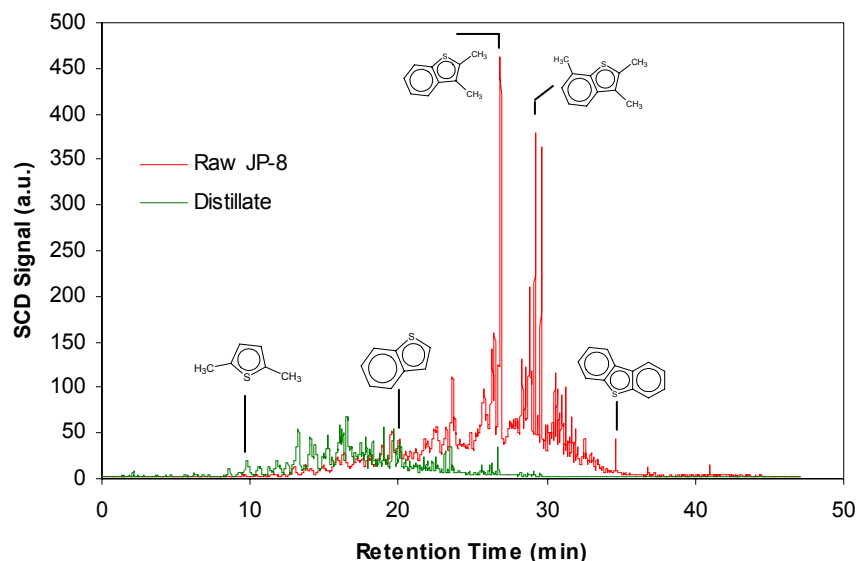


Figure 6. Sulfur distribution of the raw JP-8 and the distillate product from 100-hr microchannel distillation run.

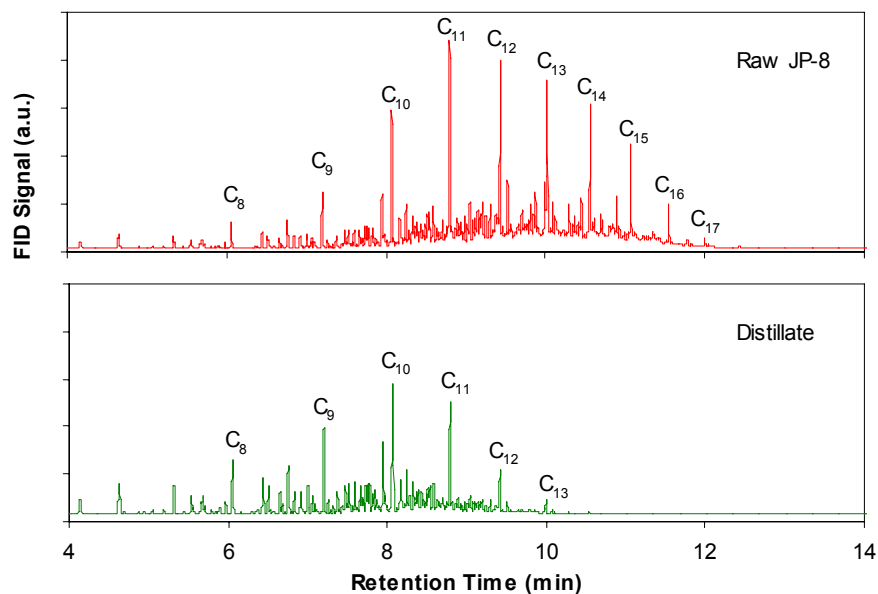


Figure 7. Hydrocarbon distribution of the raw JP-8 and the distillate product from 100-hr microchannel distillation run.

The HETP of the microchannel device, operated as a rectifying section in this case, was estimated based on the separation performance of n-alkane species present in the JP-8 fuel. Vapor-liquid phase equilibrium of JP-8 was approximated by ChemCAD simulation based on ASTM D2887 simulated distillation curves from GC data. The composition of JP-8 and its fractions were approximated by 38 pseudo components of increasing normal boiling points from 75 to 280°C. A ChemCAD model was created to simulate a conventional distillation column with vapor feed to the bottom and no reboiler. The model performed tray-to-tray

calculation using the inside-out algorithm. The fraction of components lighter than n-tetradecane in the distillate product was calculated at different combinations of reflux ratio and number of stages. This simulation result was compared with the composition of actual microchannel distillation product obtained at the experimental reflux ratio. An estimate of the number of theoretical plates was obtained this way for the microchannel device, which gives an HETP of 1.8 cm. Compared to the typically 30 cm or higher HETP of commercially available random and structured packings^[12-13], the HETP of our microchannel device was more than 10 times smaller.

Summary

We have demonstrated that low-sulfur fractions can be separated from JP-8 jet fuel using a PNNL-patented microchannel distillation device with high efficiency. The HETP achieved when using the device as a rectifying section, 1.76 cm, was an order of magnitude lower than commercial packed columns. The unique flow control based on wicks and capillary forces enabled the microchannel device to operate in a horizontal orientation. The operation stability of the microchannel distillation device was proved by a 100-hr JP-8 distillation test. Overall, the small footprint of our microchannel device combined with its high separation efficiency make it suitable for the development of compact and rugged units for military applications. The microchannel distillation technology is also promising for other separation applications where cost advantages can be derived from the high efficiency, robustness, and scalability of the microchannel architecture.

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