Desulfurization of Liquid Fuel via Fractional Evaporation and Subsequent Hydrodesulfurization Upstream a Fuel Cell System

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Desulfurization of commercial liquid fuels for fuel cell application is a mandatory process step in a fuel cell system. A new three-step desulfurization process characterized by fractional evaporation and subsequent hydrodesulfurization (HDS) in vaporous phase at moderate conditions ($p = 0.4$ MPa, $T = 300$ °C) was experimentally investigated. The results indicate that the fractional distillation reduces the sulfur compounds, above all high boiling sulfur compounds with a low reactivity. The distillate could be desulfurized in gas-phase reaction down to 1 ppm despite moderate reaction conditions. The new process is well-suited for fuel cell application in small scale.

Introduction

The fuel cell technology promises to reduce both gaseous pollution and primary energy consumption. The polymer electrolyte membrane fuel cell (PEMFC) and the solid oxide fuel cell (SOFC) are favored for application in the foreseeable future. To prevent poisoning of catalysts, the fuel needs to be desulfurized down to 10 ppm (most commonly set) for autothermal reforming upstream a SOFC and less than 0.2 ppm[1,2] for the PEMFC stack. Well-established and new desulfurization processes were recently reviewed.[3,4] Additionally, extraction with ionic liquids,[5] separation via membranes,[6] and hydrodesulfurization (HDS) with hydrogen presaturator[7] are known from lab-scale development.

HDS is the most common desulfurization process in the petroleum refining industry by which the organic sulfur compounds are converted to hydrogen sulfide and the corresponding hydrocarbons. Usually, sulfided CoMo/Al$_2$O$_3$ or NiMo/Al$_2$O$_3$ catalysts are applied in a trickle-bed reactor at temperatures up to 380 °C and pressures up to 8 MPa.[8] The formed hydrogen sulfide (H$_2$S) is either removed by washing or, in smaller scale application, by a zinc oxide bed.

Selection of a desulfurization process for fuel cell application depends largely on the type and the content of the sulfur compounds in the feed and on the application of the fuel cell system. Processes with high system complexity or with large-volume vessels for adsorption are not likely to fulfill the requirements for small-scale applications. With regard to mobile fuel cell applications, systems have to be small, light, and insensitive to shaking and heeling, thus conventional HDS in a trickle bed is inapplicable.

Readily available petroleum products typically contain sulfur in mercaptans, aliphatic and cyclic sulfides, and thiophenes.[9−15] After being desulfurized by hydrotreating in the refinery, sulfur species with low reactivity remain. Song and co-workers[16] gave a reactivity ranking based on a literature review:

mercaptans, sulfides, disulfides > thiophene > alkylated thiophenes > benzothiophene > alkylated benzothiophenes > dibenzothiophenes and alkylated dibenzothiophenes

Type and amount of residual sulfur compounds in the fuel depend on the refinery feedstock, the boiling range of the fuel, and the desulfurization process applied in the petroleum refinery. Low boiling crude oil fractions contain mainly mercaptans, sulfides, disulfides, and thiophenes. These are sufficiently reactive to be removed in conventional low severity HDS process. Consequently, sulfur compounds with a low reactivity such as dibenzothiophenes remain completely in these fractions.

In recent years the sulfur contents in fuels were limited to lower values (Figure 1). However, sulfur limits for jet fuel A-1 are still to high, up to 3000 ppm (m/m), but the maximum sulfur content in most commercial jet fuels in the E.U. is below 500 ppm because of low sulfur content in refinery feedstock and of the HDS processes used. For fuel cells to be fuelled with liquid fuels as per Figure 1, an upstream desulfurization step is mandatory. For an international launch of fuel cell systems, for example, as auxiliary power units (APU) for trucks and passenger cars, much higher sulfur contents have to be taken into account. This work presents a new process for deep desulfurization for small-scale application based on gas-phase HDS with an upstream fractional evaporation.

Process Description

Figure 2 shows the new three-step process for deep desulfurization. At first the feed is split into a vaporous low boiling part and a liquid high boiling part via fractional evaporation. Meanwhile this process principle was patented elsewhere.[17] The degree of evaporation depends on the boiling range and the sulfur content of the fuel and on the type of sulfur compounds within. The evaporation residue is either redirected to the storage tank or routed directly to other consumers of the system. These could be the heating of the reformer unit, an associated appliance in domestic use, or an

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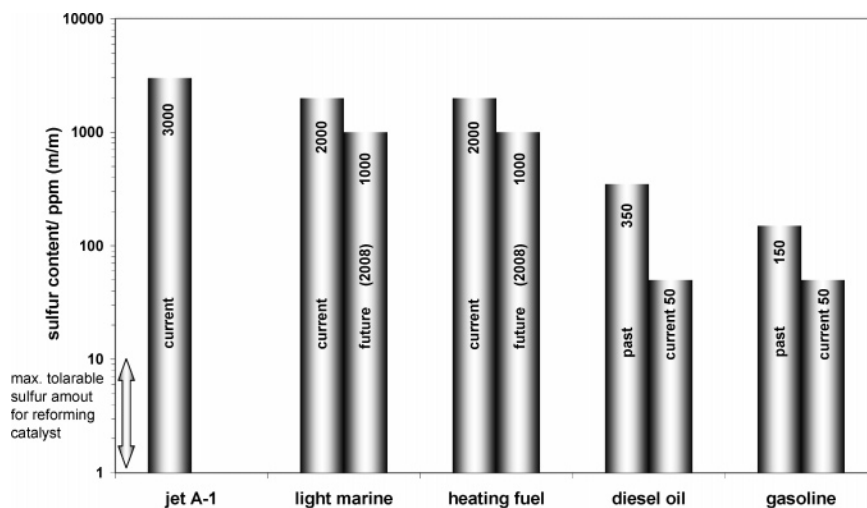* Corresponding author e-mail: Markus.Brune@ciw.uka.de.

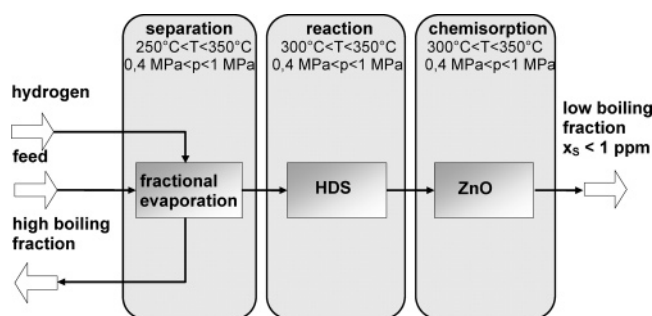**Figure 1.** Sulfur content in fuels; international (jet A-1) and European guidelines.

Figure 2. Three-step desulfurization process.

Table 1. Jet Fuel A-1 Data

distillation	jet fuel A-1 (A)	jet fuel A-1 (B)
initial boiling point (°C)	72	104
fuel recovered		
10% vol (°C)	162	159
20% vol (°C)	168	167
30% vol (°C)	174	174
40% vol (°C)	180	180
50% vol (°C)	186	187
60% vol (°C)	195	195
70% vol (°C)	205	205
80% vol (°C)	218	216
90% vol (°C)	233	230
end point (°C)	246	251
sulfur content/ ppm (w/w)	530	140
density/ (kg/m^3)	797.2	797.2

internal combustion engine in case the fuel cell serves as an APU in mobile application. The minimum evaporation ratio is limited by the fuel consumption ratio for the whole system in which the fuel cell is embedded.

The increase of the sulfur content in a tank caused by fractional evaporation can be calculated by simple mass balances. Considering values for the ratio of the fuel cell's and the main consumer's power of 4−6%, even an emptying of the tank down to 5% of its capacity increases the sulfur content of the remaining fuel by only about 15−20% at the most.

The vapors are fed to the reactor, where the fuel will be hydrotreated. Downstream, a conventional zinc oxide bed will remove the hydrogen sulfide with a high sulfur loading. The temperature remains the same in both the HDS and the ZnO process steps (see reaction conditions as given in Figure 2).

Several advantages of this process scheme are obvious. The fractional evaporation drastically reduces the sulfur content in the part of the fuel fed to the HDS reactor. Especially the high boiling, low reactive sulfur compounds (e.g., alkylated benzothiophenes and alkylated dibenzothiophenes) are kept out of the desulfurization unit. In addition, the amount of polycyclic aromatic hydrocarbons will be reduced in the HDS feed. Thus, their hydrogenation at low temperatures[18] and in case of using a CoMo catalyst as well as coke formation in the downstream reforming step can be limited.[19] The resulting low hydrogen consumption and reduced hydrogen recycle allow low energy consumption and low investment of a fuel cell system. Due to the gasphase reaction, the system is compared to, for example, trickle-bed HDS insensitive to shaking and heeling.

Experimental Section

Two samples of commercial A-1 jet fuel were analyzed. The data are recorded in Table 1. One sample (A) was purchased at the domestic airport in Baden-Baden, Germany. The other one (B) was kindly supplied by the Institut für Thermische Strömungsmaschinen, Universität Karlsruhe.

To determine the sulfur content, sulfur compounds were separated by gas chromatography and quantitatively measured with a pulsed flame photometric detector (PFPD) Varian 3400 cx, using a 105 m fused silica capillary column with dimethylsiloxane as stationary phase (Restek Corp.). For quantitative sulfur analysis, benzothiophene (BT) was added serving as an internal standard.

Aromatic hydrocarbons were identified and measured with high-performance liquid chromatography (HPLC) using an Agilent Technologies HP 1100 system with a refraction index detector (RID) and a Hypersil APS 5 μm (200 × 4.6 mm) column.

The fractional evaporation was done in an isothermally operated coiled tube heat exchanger. For the HDS reaction a commercially available CoMo alumina catalyst (Südchemie C-49, 3 mm extrusions) was used. The original catalyst was ground to smaller diameter (0.8−1.0 mm). The diameter of the stainless steal reactor was 19 mm, and the embedded catalyst bed volume was 113 cm^3. All experimental results shown were obtained at a constant pressure of 0.4 MPa (pressure limit for a PEMFC application) and at a constant reaction temperature of 300 °C. The residence time was up to 40 s.
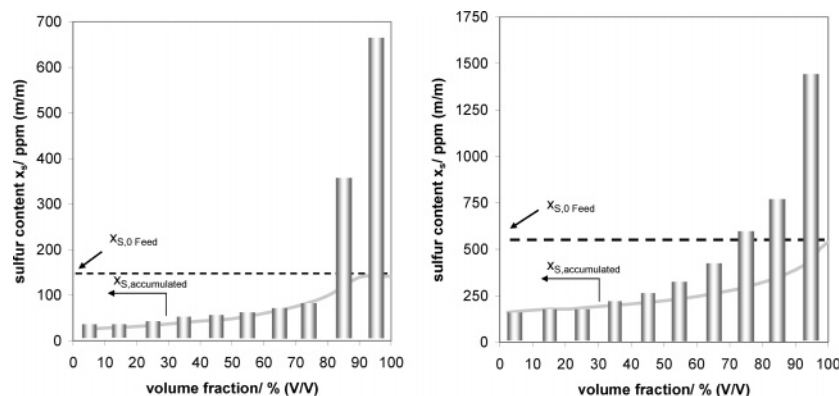
Figure 3. (a) Sulfur distribution in jet fuel A-1 (A) fractions. (b) Sulfur distribution in jet fuel A-1 (B) fractions.

To separate the hydrogen sulfide downstream HDS, the liquid samples taken for sulfur detection were stripped with nitrogen before analyzing.

Results and Discussion

Engler Distillation and Sulfur Distribution. Boiling curves were acquired according to the ASTM D86 rule. The initial boiling temperature of sample A was 72 °C and was 104 °C for sample B. The boiling curves of the two jet fuel samples were rather similar with a maximum deviation of less than 2% in the boiling range between 10 and 90%. As expected, for both samples the sulfur content increases drastically with the boiling temperature range of the fraction. Up to an evaporation ratio (α) of approximately 75%, the sulfur content of the accumulated fuel fractions could be reduced to approximately 50% of the feed value for each sample. Additionally, sulfur compounds with low reactivity for HDS, remain mainly in the high boiling fractions. Thus, a preliminary desulfurization can be realized by fractional evaporation (see Figure 3).

Gas-Phase HDS of A-1 Jet Fuel Fraction. The HDS experiments were conducted on-line with the evaporation operated at a constant evaporation ratio of 0.8. In general, (i) reaction temperature (T_R), (ii) residence time (τ) (reactor volume divided by volume flow of gaseous phase), (iii) reaction total pressure (p_R) and hydrogen partial pressure (p_{H2}), and (iv) specific hydrogen supply ratio ($X_{H2} = {}^V\Phi_{H2}/{}^V\Phi_{jet\,A-1}$) (volume flow of hydrogen divided by volume flow of evaporated fuel in liquid state) will influence the HDS performance. For a constant reaction temperature of T_R = 300 °C, the influences of residence time and of specific hydrogen supply are shown in Figures 4 and 5, respectively. The results indicate that the required low sulfur content to 1 ppm is achievable, and the process is well-feasible for SOFC application with a tolerated sulfur content of 10 ppm.

The sulfur-selective chromatograms shown in Figure 6 reveal that alkylated C2- and C3-benzothiophenes remain in the liquid evaporation residue to a large extent. These are so-called refractory sulfur compounds that are difficult to remove by the HDS process.[14] No dibenzothiophenes were detected as their boiling temperature is beyond the boiling range of A-1 jet fuel. As expected, the distillate with a total sulfur content of 90 ppm (m/m) exhibits a broad variety of sulfurous compounds. In the HDS product, the partly evaporated C2- and the C3-benzothiophenes remain nearly unconverted (for the sake of visibility of the sulfur distribution, a sample with a residual sulfur content of 8 ppm (m/m)
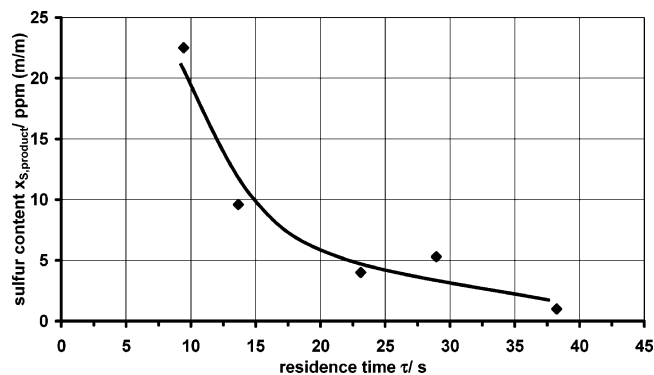

Figure 4. Effect of residence time on sulfur content of the HDS product. Conditions: $x_{S,Feed}$ = 530 ppmw, evaporation ratio α = 0.8, p = 0.4 MPa, T_{HDS} = 300 °C, ${}^V\Phi_{distillate,liquid}$ = 0.2–0.48 L/h, X_{H2} = 50, T_{evap} = 265 °C.
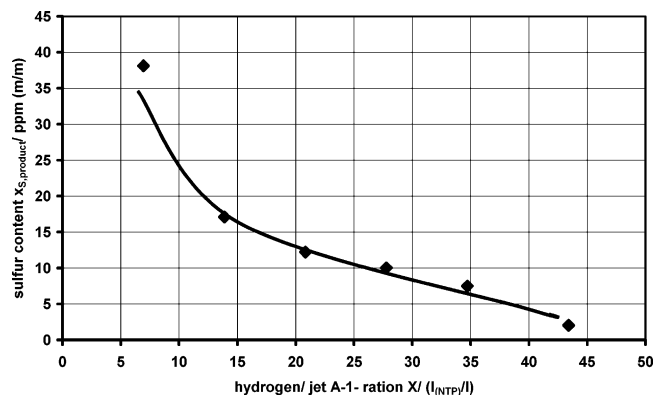

Figure 5. Effect of hydrogen supply ratio X_{H2} on sulfur content of the HDS product. Conditions: $x_{S,Feed}$ = 140 ppmw, p = 0.4 MPa, ${}^V\Phi_{Jet\,A-1,liquid}$ = 0.5 L/h, T_{HDS} = 300 °C, ${}^V\Phi_{distillate}$ = 0.4 L/h, τ = 22.6 s, T_{evap} = 265 °C.

is shown). Lower boiling sulfur compounds were nearly completely converted. In agreement with the results obtained by Waller,[14] especially C2-benzothiphenes behaved very stable at lower temperatures for hydrogenation.

As per the aromatic hydrocarbons, their conversion is very low at these moderate hydrogenation conditions (Figure 7). This finding can be correlated with results of prior experiments for liquid-phase HDS.[18] In their investigation, a maximum of the conversion was detected in the temperature range of 340–360 °C. These experiments were conducted at a pressure of 4 MPa, and the hydrogen-to-oil ratio was 200 m³/m³. The conversion of the aromatic hydrocarbons does not contribute to the hydrogen consumption in the HDS. The content of the
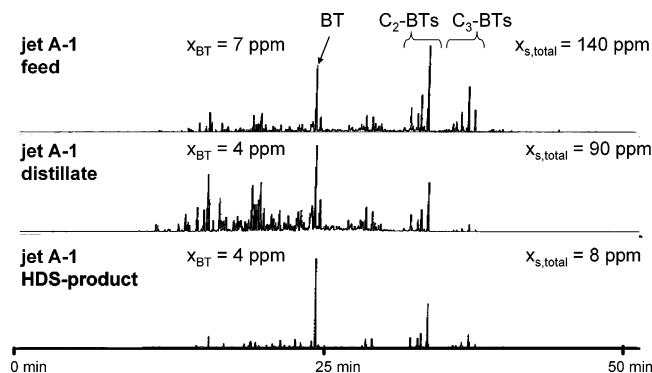
Figure 6. Chromatograms of the feed, the distillate, and the desulfurization product.
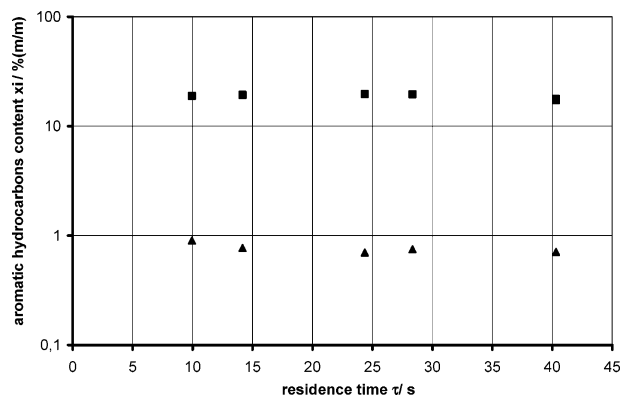

Figure 7. Behavior of the monocyclic (■) $x_{mah,Feed} = 21.3\%$ and the bicyclic (▲) $x_{bah,Feed} = 1.6\%$ aromatic hydrocarbons in the HDS. Conditions: $x_{S,Feed} = 530$ ppmw, evaporation ration $\alpha = 0.8$, $p = 0.4$ MPa, $T_{HDS} = 300$ °C, $^V\Phi_{distillate,liquid} = 0.2-0.8$ L/h, $X_{H2} = 50$.

bicyclic aromatic hydrocarbons however was reduced by about 50% through the fractional evaporation. The distribution of the aromatic hydrocarbons remains nearly constant.

Conclusions

A new, three-step process for deep desulfurization for fuel cell application via fractional evaporation and HDS in vapor phase under moderate conditions ($T = 300$ °C, $p = 0.4$ bar) was investigated. Two commercially available jet fuels were used as feedstocks. The experiments proved the advantage of the fractional evaporation: the sulfur content was reduced drastically; in addition, high boiling sulfur compounds with a very low reactivity are removed. Due to prior fractional evaporation, the HDS sulfur content in the product of approximately 1 ppm (m/m) can be realized with a low hydrogen pressure.

C2- and C3-benzothiophenes were identified as the sulfur compounds in jet fuel A-1 with the lowest reactivity. In addition, bicyclic aromatic hydrocarbons were reduced by fractional distillation, but their conversion in HDS was negligible. This might result in lower coke formation at downstream process steps and lower hydrogen consumption during HDS.

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