Deep Desulfurization of Diesel Fuels by a Novel Integrated Approach

Final Technical Progress Report
for the period
September 1, 2000 – January 31, 2004

Xiaoliang Ma, Uday Turaga, Shingo Watanabe, Subramani Velu and Chunshan Song

Issued: May 2004

Award Number: DE-FG26-00NT40821

The Pennsylvania State University
The Energy Institute
C211 Coal Utilization Lab
University Park, PA 16802

DISCLAIMER

1. Abstract

The overall objective of this project is to explore a new desulfurization system concept, which consists of efficient separation of the refractory sulfur compounds from diesel fuel by selective adsorption, and effective hydrodesulfurization of the concentrated fraction of the refractory sulfur compounds in diesel fuels. Our approaches focused on 1) selecting and developing new adsorbents for selective adsorption of sulfur or sulfur compounds in commercial diesel fuel; 2) conducting the adsorption desulfurization of model fuels and real diesel fuels by the selective-adsorption-for-removing-sulfur (PSU-SARS) process over various developed adsorbents, and examining the adsorptive desulfurization performance of various adsorbents; 3) developing and evaluating the regeneration methods for various spent adsorbent; 4) developing new catalysts for hydrodesulfurization of the refractory sulfur existing in the commercial diesel fuel; 5) on the basis of the fundamental understanding of the adsorptive performance and regeneration natures of the adsorbents, further confirming and improving the conceptual design of the novel PSU-SARS process for deep desulfurization of diesel fuel

Three types of adsorbents, the metal-chloride-based adsorbents, the activated nickel-based adsorbents and the metal-sulfide-based adsorbents, have been developed for selective adsorption desulfurization of liquid hydrocarbons. All of three types of the adsorbents exhibit the significant selectivity for sulfur compounds, including alkyl dibenzothiophenes (DBTs), in diesel fuel. Adsorption desulfurization of real diesel fuels (regular diesel fuel (DF), S: 325 ppmw; low sulfur diesel fuel (LSD-I), S: 47 ppmw) over the nickel-based adsorbents (A-2 and A-5) has been conducted at different conditions by using a flowing system. The adsorption capacity of DF over A-2 corresponding to an outlet sulfur level of 30 ppmw is 2.8 mg-S/g-A. The adsorption capacity of LSD-I over A-5 corresponding to the break-through point at 5.0 ppmw sulfur level is 0.35 mg-S/g-A. The spent A-5 can be regenerated by using H_2 gas at a flowing rate of 40-50 ml/min, 500°C, and ambient pressure. Adsorption desulfurization of model diesel fuels over metal-sulfide-based adsorbents (A-6-1 and A-6-2) has been conducted at different

temperatures to examine the capacity and selectivity of the adsorbents. A regeneration method for the spent metal-sulfide-based adsorbents has been developed. The spent A-6-1 can be easily regenerated by washing the spent adsorbent with a polar solvent followed by heating the adsorbent bed to remove the remainder solvent. Almost all adsorption capacity of the fresh A-6-1 can be recovered after the regeneration. On the other hand, a MCM-41-supported HDS catalyst was developed for deep desulfurization of the refractory sulfur compounds. The results show that the developed MCM-41-supported catalyst demonstrates consistently higher activity for the HDS of the refractory dibenzothiophenic sulfur compounds than the commercial catalyst. On the basis of the fundamental understanding of the adsorptive performance and regeneration natures of the adsorbents, the conceptual design of the novel PSU-SARS process for deep desulfurization of diesel fuel is confirmed and improved further.

2. Table of Contents

3. List of Graphical

Introduction

Deep desulfurization of diesel fuels is receiving increasing attention in the research community worldwide due to increasingly stringent regulations and fuel specifications in many countries for environmental protection purpose. US Environmental Protection Agency has issued regulations that will require the refineries to reduce the sulfur content of highway diesel fuel from a current limit of 500 ppmw to 15 ppmw by 2006 [News-EPA, 2001]. The problem of deep removal of sulfur has become more serious due to the lower and lower limit of sulfur content in finished fuel products by regulatory specifications, and the higher and higher sulfur contents in the crude oils. A survey of the data on crude oil sulfur content and API gravity for the past two decades reveals a trend that U.S. refining crude slates continue towards higher sulfur contents and heavier feeds [Swain, 1998, 2002]. The average sulfur contents of all the crude oils refined in the five regions of the U.S. known as five Petroleum Administration for Defense Districts (PADDs) increased from 0.89 wt% in 1981 to 1.25 wt% in 1997, while the corresponding API gravity decreased from 33.74° in 1981 to 31.07° in 1997.

The production of ultra-low-sulfur fuel is motivated in part by the need for using the new emission-control technologies that are sensitive to sulfur. On the other hand, ultra-low-sulfur fuel is also needed for use with a fuel cell system [Song, 2003]. Fuel cell is one of the most promising and convenient energy conversion devices for generating electricity for both mobile vehicles and stationary power plants including residential applications. For the automotive fuel cells and military fuel cells, diesel fuel is ideal fuels due to its higher energy density, ready availability, and proven safety for transportation and storage. However, the commercial diesel fuel usually contains certain sulfur compounds. These sulfur compounds and H_2S produced from these sulfur compounds in the fuel processor are poisonous to both the catalysts used in fuel processor (such as reforming catalysts and water-gas-shift catalysts in hydrocarbon-based fuel cell system) and the electrode catalysts in fuel cell stacks. Thus, the sulfur concentration in diesel fuel needs to be reduced to less than 10 ppmw for SOFC and to less than 0.1 ppmw for PEMFC.

It is difficult to meet such an extremely demanding fuel sulfur requirement by using the conventional hydrotreating technology. Consequently, development of new deep desulfurization

processes for liquid hydrocarbon fuels becomes one of the major challenges to the refining industry and to the producers of ultra-low-sulfur fuels for fuel cell applications.

In terms of technology availability, the sulfur content in diesel is difficult to be reduced to less than 15 ppmw by the current hydrotreating technology, because the remaining sulfur compounds in current diesel fuel with 500 ppmw S level are the refractory sulfur compounds [Ma et al. 1994, Whitehurst et al. 1998, Knudsen et al. 1999, Song 2000]. These refractory sulfur compounds are the alkyl dibenzothiophenes with one or two alkyl groups at 4- and/or 6-positions, which strongly inhibit hydrodesulfurization of the compounds [Ma et al, 1995, Ma et al, 1996a, Ma et al, 1996b]. A kinetic study shows that in order to reduce the sulfur content of the diesel fuel from 500 ppmw to less than 15 ppmw using the current hydrotreating technology, the reactor volume or the catalyst activity must be at least 3 times larger than those currently used in refineries [Ma et al, 1994]. If reducing the sulfur content of the diesel fuel from 500 ppmw to less than 0.1 ppmw using the current hydrotreating technology, the reactor volume or the catalyst activity must be about 7 times larger than those currently used in refineries [Ma et al, 1994]. As is well known, the increase in volume of the high-temperature and high-pressure reactor is very expensive. Consequently, it is difficult to meet such an extremely demanding fuel sulfur requirement by using the conventional hydrotreating technology. Consequently, development of new deep desulfurization processes for diesel fuel becomes one of the major challenges to the refining industry and to the producers of ultra-low-sulfur fuels for fuel cell applications.

The sulfur compounds in the current diesel corresponding to the S level of 500 ppmw account for only about 0.32wt % of the whole diesel. The conventional hydrotreating approaches will need to increase catalyst bed volume at high-temperature and high-pressure conditions for treating the whole (100 %) fuel in order to convert the fuel mass of less than 0.4 wt %.

In this research project, we took a different approach to explore a new desulfurization system concept, which consists of efficient separation of the refractory sulfur compounds and effective hydrodesulfurization of the concentrated fraction of the refractory sulfur compounds separated from diesel fuels. We believe that the proposed process can effectively reduce the

sulfur content in the commercial diesel fuel at low investment and operating cost to meet the needs for ultra-clean transportation fuels and even for fuel cell applications.

The major challenge to our proposed approaches is to develop adsorbents that can selectively adsorb sulfur compounds onto the surface of the solid adsorbent but leave the aromatic and olefinic hydrocarbons as well as the open-chain and cyclic paraffinic hydrocarbons untouched, or directly remove sulfur in the diesel fuel by selective adsorption. Figure 1 shows the known coordination geometris of thiophene in organometallic complexes. There are eight coordination configurations of thiophene in organometallic complexes [Sanchez-Delgado, 1994; Angelici, 1995; Hughes et al., 1986; Potrin et al., 1980]. Here, we are interested in the first two configurations, where thiophene coordinates directly with the metal through sulfur-metal interaction, $\eta^1 S$ or $S-\eta^3$-bonding. These configurations suggest that there are likely adsorbents that are able to adsorb the thiophenic compounds selectively through $\eta^1 S$ or $S-\mu^3$-bonding.

The key point in development of the regenerable adsorbent is that the interaction between the sulfur compounds and the adsorption sites on the adsorbent should be suitable. The too strong interaction will cause a difficulty in the subsequent regeneration process, while the too weak interaction will result in a low adsorption capacity and selectivity.

In this final report, we will describe our findings in this study and summarize our work in development of the regenerable adsorbents, and finally, give a conceptual design of the adsorptive desulfurization process.

5. Executive Summary

In this research project, our approaches focused on 1) selecting and developing new adsorbents for selective adsorption of sulfur or sulfur compounds in commercial diesel fuel. 2) conducting the adsorption desulfurization of model fuels and real diesel fuels by the selective-adsorption-for-removing-sulfur (PSU-SARS) process over various developed adsorbents, including metal-chloride-based adsorbents (A-1), the activated nickel-based adsorbents (A-2 and

A-5) and examining the adsorptive desulfurization performance of various adsorbents; 3) developing and evaluating the regeneration methods for various spent adsorbent; 4) on the basis of the fundamental understanding of the adsorptive performance and regeneration natures of the adsorbents, further confirming and improving the concept design of the novel PSU-SARS process for deep desulfurization of diesel fuel

- The metal-chloride-based adsorbents have been developed and tested for selective removing sulfur from diesel fuel. The adsorption capacity and selectivity of the adsorbents have been measured.

- The two nickel-based adsorbents have been developed for selective removing sulfur from diesel fuel. Adsorption desulfurization of a real diesel fuels (DF, S: 325 ppmw) over the different nickel-based adsorbents has been conducted at different conditions by using a flowing system. The adsorption capacity and selectivity of the adsorbents have been measured.

- Regeneration of the spent nickel-based adsorbent has been explored by using hydrogen gas, and the performance of the regenerated adsorbent has been examined in comparison with that of the fresh adsorbent.

- The metal-sulfide-based adsorbents have been developed for selective adsorption and separation of the sulfur compounds. Adsorption desulfurization of a model diesel fuel over metal-sulfide-based adsorbents has been conducted at different temperatures to examine the capacity and selectivity.

- Regeneration of the spent metal-sulfide-based adsorbent has been explored by washing the spent adsorbent with a polar solvent followed by heating the adsorbent bed. The performance of the regenerated adsorbent has been examined in comparison with that of the fresh adsorbent.

- On the basis of the fundamental understanding of the adsorptive performance and regeneration natures of the adsorbents, the concept design of the novel PSU-SARS process for deep desulfurization of diesel fuel is confirmed and improved further.

- Our work in this project results in a significant improvement of our knowledge in ultra-deep desulfurization of liquid hydrocarbon fuels for ultra-clean fuels and for fuel cell applications, as shown in our publications listed in this report, section 10.

.

6. Experimental

6.1. Flowing Adsorption Device

A four-channel flowing adsorption device was set up for both screening adsorbents and regenerating the spent adsorbents. The system includes HPLC pump, gas system, column, furnace, and sample collection system. The adsorption experiments can be run at temperature range from 20 to 400 ˚C and different LHSV. Pretreatment and regeneration of adsorbents can be conducted by using the same device at a temperature range from ambient temperature to 700 ˚C and a pressure range from ambient pressure to 100 kg/cm^2. The flowing rate of liquid phase and gas phase can be controlled. The loading of adsorbent sample can be changed from 1.0 to 20 ml.

6.2. Feeds

Three model diesel fuels were made for examining the adsorption capacity and selectivity of the adsorbents. The model diesel I (MDF-I) contains 0.167 wt % of dibenzothiophene (DBT), 0.195 wt % of 4,6-DMDBT with a total sulfur level of 585 ppmw and total aromatics of 12 wt %. The model diesel II (MDF-II) contains 0.095 wt % of dibenzothiophene (DBT), 0.099 wt % of 4-MDBT, and 0.107 wt% of 4,6-DMDBT, corresponding the sulfur contents of 165, 160 and 162 ppmw, respectively. MDF-II also contains 10 wt% of n-butylbenzene for mimicking the aromatics in the real diesel. The saturates in MDF-II are n-hexadecane, n-dodecance and decalin. In addition, MDF-II also contains 2-methylnaphthalene with a molar concentration as the same

as each sulfur compound in MDF-II for analyzing selectivity. The model diesel III (MDF-III) contains 0.115 wt % of DBT, corresponding the sulfur content of 200 ppmw, using. The detailed compositions of MDF-I, MDF-II and MDF-III are listed in Tables 1, 2 and 3, respectively. All chemicals contained in the model diesels were purchased from Aldrich, and were utilized without further purification.

Three real diesel fuels were used in the adsorption experiments. One is a commercial regular diesel fuel (DF) from Conoco with 320 ppmw sulfur. The other diesel fuels are the low sulfur diesel fuel I (LSD-I) and low sulfur diesel II (LSD-II) with 47 and 9 ppmw sulfur, respectively. The composition and property of the first two fuels are listed in Table 4 and 5.

6.3. Adsorbents

Three different types of adsorbents were used the current study. The first type of adsorbent (A-1) is pallalium chloride supported on silica gel with 5.0 wt % loading of the metal chloride. The second type of the adsorbents (A-2 and A-5) is the nickel-based adsorbents with or without alumina support, A-2 is an activated nickel-based material with a surface area of 80-100 m^2/g. A-5 is a nickel-based material supported on alumina with a surface area of 156 m^2/g. The third type of adsorbents (A-6-1, A-6-2) is the metal-sulfide-based material supported on γ-alumina. A-6-1 and A-6-2 have surface area of 150 and 190 m^2/g, respectively.

6.4. Adsorption Experiments

All adsorption experiments of model diesel fuels and the real diesel fuels over the adsorbents were performed at the designed temperatures by using the flowing adsorption device under ambient pressure. The adsorbent was placed into a stainless steel column with an internal diameter of 4.6 mm and length of 150 mm. The adsorbent bed volume is 2.49 ml. The feed was pumped into the column and flowed up through the column at a flowing rate of 0.20 ml/min. The corresponding LHSV is $4.8h^{-1}$. The treated fuel flowed out from the top of the column and was collected for analysis. The flowing adsorption device which was designed for the adsorption experiments is shown in Figure 2.

6.5. Preparation of the MCM-41-supported Catalyst

Aluminosilicate MCM-41 of SiO_2/Al_2O_3 ratios 25, 50, and 100 were synthesized using sodium aluminate as the aluminum source based on a previously reported recipe [Reddy et al. 1996, 1998]. The only modification in the synthesis procedure was to impart the molecular sieve with additional pore wall stability. After filtration and washing off the surfactant from the synthesized MCM-41, the sample, approximately 5 g in weight, is mixed with ca. 25 ml deionized water and heating for another 12 h under hydrothermal conditions. The acidic and impregnated catalysts were obtained by procedures reported previously [Reddy et al. 1996, Song and Reddy 1999].

6.6. Hydrodesulfurization Experiments

A fixed-bed catalytic flow reactor was used to evaluate the developed catalysts in this study. Table 6 summarizes the flow reactor experimental conditions.

6.7. Sample Analysis

The quantitative analysis of sulfur compounds and aromatic hydrocarbons in the model diesel fuels and the treated model diesel fuels was conducted by using a HP5000 gas chromatograph with a capillary column, XTI-5 (Restek, 30 m long, 0. 25 mm i.d.) and a flame ionization detector (FID). The identification of sulfur compounds in the real diesel fuels was conduced by using another HP5000 gas chromatograph with the same capillary column and a pulsed flame photometric detector (PFPD). The total sulfur concentration of the real diesel fuels and the treated fuels was analyzed by using Antek 9000S Pyro-fluorescent Sulfur Analyzer.

7. Results and Discussion

7.1. Identification of Sulfur Compounds in Commercial Diesel Fuels

The GC-PFPD chromatograms of the three commercial diesel fuels are shown in Figure 3. The sulfur compounds in the regular diesel fuel with sulfur level of 320 ppmw are alkyl dibenzothiophenes (DBTs). The major sulfur compounds are alkyl DBTs with one or two alkyl group(s) at the 4- and/or 6-positions, such as 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT). No alkyl benzothiophenes were detected. The peak

for DBT was very small. In the low sulfur diesel I (LSD-I) with sulfur level of 47 ppmw, only the alkyl DBTs with one or two alkyl group(s) at the 4- and/or 6-position were detected, indicating that such sulfur compounds are the most difficult to be removed by the conventional HDS processes. No DBT and other methyl DBT except 4-MDBT were detected. In the LSD-II with a sulfur level of 9 ppmw, the major sulfur compounds are 4,6-DMDBT, and 4-ethyl-6-methyldibenzothiophene (4-E,6-MDBT). Even no any 4-MDBT was detected in the fuel. Other three peaks in a region of retention time from 37 to 38 min should be alkyl sulfur compounds with two methyl groups at the 4- and 6-positions. All the sulfur compounds remains in the last two LSDs are the refractory sulfur compounds, as the alkyl groups at 4 and/or 6-positions block the way of the sulfur to the active sites on the catalyst surface in the conventional HDS process [Ma et al., 1994; Whitehurst et al., 1998, Gates and Topsoe, 1997]. Thus, we need to pay more attention to these sulfur compounds in deep desulfurization by adsorption.

7.2. Adsorption Desulfurization over a Metal-chloride-Based Adsorbent

Desulfurization of the model diesel fuel by adsorption over a metal-chloride-based adsorbent (A-1) was performed at ambient temperature and pressure. The sulfur concentration of the outlet fuel as a function of treated fuel volume is shown in Figure 4. No sulfur was detected in the treated model diesel fuel (S < 1ppmw) when the elution volume was less than 4.5 ml, indicating the sulfur compounds, even 4,6-DMDBT, were removed by adsorption. After effluent volume of 4.5 ml, the sulfur concentration increases with the effluent volume increasing. When the effluent volume reached about 30 ml, the sulfur concentration of the outlet fuel was almost the same as that of the untreated model diesel fuel, implying the adsorbent is saturated by sulfur. The saturated adsorption capacity of the adsorbent A-1 was calculated on the basis of the break-through curves, being 2.27 mg/g (milligram of sulfur per gram of the adsorbent). The break-through capacity at sulfur level of 30 ppmw is about 0.9 mg/g.

Figure 5 shows selectivity of the adsorbent for sulfur compounds and aromatic hydrocarbons, in which the mol concentration of DBT, 4,6-DMDBT, naphthalene (NA) and 2-methylnaphthalene (2-MNA) are shown as a function of the effluent volume. It is clear that the concentration of NA and 2-MNA in the outlet fuel is much higher than that of DBT and 4,6-

DMDBT before the saturation of the adsorbent by sulfur compounds, although the initial concentrations of the four compounds are almost the same in the model diesel fuel (~0.007 mol/l). The results indicate that the adsorbent has significant selectivity toward the sulfur compounds. By comparison of DBT and 4,6-DMDBT, the outlet concentration of the latter is slightly higher than the former during the whole adsorption process, implying that the methyl groups at 4 and 6 positions of DBT inhibit somewhat the interaction between sulfur atom in the sulfur compounds and adsorption sites by steric hindrance. This result indicates that the interaction between the sulfur in the sulfur compounds and the active sites play an important role. This is why A-1 shows a higher selectivity for the sulfur compounds. The result is also in agreement with the coordination adsorption through $\eta^1 S$ or $S\text{-}\mu^3$-bonding [Vecchi et al., 2003, Hughes et al., 1986; Potrin et al. 1980].

7.3. Adsorptive Desulfurization over the Nickel-based Adsorbents.

7.3.1. Adsorptive Desulfurization of a Model Diesel Fuel (MDF-II) over A-2

Adsorption desulfurization of a model diesel fuel (MDF-II) over A-2 was conducted at 27 and 150 ˚C, LHSV of 24 h^{-1}and under an ambient pressure. The break-through curves are shown in Figure 6. At 27 ˚C, 4-MDBT and 4,6-DMDBT break through at the beginning. The concentration of 4,6-DMDBT in the effluent is higher than that of 4-MDBT. DBT breaks through at the treated amount of ~ 34 g/g (gram of the treated MDF per gram of adsorbent. The amount of the treated MDF-II corresponding to saturate point for three sulfur compounds is similar, around 52 g/g. In comparison of the areas between break-through curve and the initial sulfur line for 4-MDBT and DBT, it is clear that about a half of number of the active sites that can adsorbent DBT can not adsorbent 4-MDBT or 4,6-DMDBT. The results indicate that at 27 ˚C, the methyl groups at 4 and 6-positions inhibit the interaction between the sulfur atom and the active site by blocking the way of the sulfur atom to the active sites. Interestedly, when increasing the adsorptive temperature to 150 ˚C, the break-through amount of the treated MDF-II for 4,6-DMDBT and 4-MDBT increased to 8 and 14.5 g/g, while the break-through amount for DBT decreases to 20 g/g. The results imply that the increase in the temperature moderates the effect of the methyl groups, probable by reducing steric hindrance via relaxing the methyl group and/or by increasing hydrogenolysis rate of C-S bond on the surface. On the other hand, the

9

increase in the temperature decreases the break-through amount for DBT, because the more active sites have been occupied by 4,6-DMDBT and 4-MDBT. Figure 7 shows the break-through curves for total sulfur at the two temperatures. It is clearly shown that the break-through amount of the treated MDF-II at 150˚C is greatly higher than that at the room temperature. The adsorptive capacity corresponding to a sulfur level of 30 ppmw is 0.4 and 7.3 mg/g for 27 ˚C and 150˚C, respectively. The saturate adsorptive capacity is about 12.9 and 14.0 mg/g for 27 ˚C and 150˚C, respectively.

7.3.2. Adsorptive Desulfurization of a Regular Diesel Fuel over A-2

Adsorption desulfurization of a regular diesel fuel (DF, S: 320 ppmw) over A-2 was conducted at 200˚C and ambient pressure. The flowing rate of DF was 0.2 ml/min with LHSV of 4.8 h^{-1}. The total sulfur concentration in the treated fuel as a function of amount of the treated DF is shown in Figure 8. The total sulfur concentration in the first collected fraction, corresponding to 0.3 g/g of the effluent amount, is 15 ppmw, and then, it increases slowly with increasing amount of the treated DF. The adsorption capacity of A-2 corresponding to sulfur level at 30 ppmw is 2.8 mg/g. In comparison with the break-through curves for the MDF, the capacity of A-2 for the real diesel fuel is lower that the model fuel. It indicates that the sulfur compounds in the real diesel fuel is more difficult to be removed than those in the MDF by the adsorptive desulfurization over A-2. We note that the sulfur concentration at outlet increases slowly, even when the sulfur concentration is higher than 30 ppmw. The adsorption capacity of Adsorbent-I corresponding to a sulfur level at 50 ppmw is about 4.5 mg-S/g-A.

The GC-PFPD chromatogram of the treated fuel corresponding to the treated DF amount of 9.9 and 15.9 g/g is shown in Figure 9. It is clear that all alkyl dibenzothiophenes without any alkyl group at both the 4- and 6-positions or with only one alkyl group at the 4- and 6-position have been removed. The results indicate that the two alkyl groups at the 4- and 6-positions, respectively, such as 4,6-DMDBT and 4-ethyl-6-methyldibenzothiophene (4-E,6-MDBT) are also two of the most refractory sulfur compounds in the adsorptive desulfurization of diesel fuel. It is probably because that the alkyl groups at the 4- and 6-positions block the way of the sulfur atom in DBTs to approach the adsorption sites, resulting in the lower adsorptive selectivity of

them. It is also noted that 4-E,6-MDBT is even more difficult to be removed than 4.6-DMDBT, probably because the size of the ethyl group at the 4-position is larger than that of the methyl group.

7.3.3. Adsorptive Desulfurization of a Low Sulfur Diesel Fuel over A-2 and A-5

Adsorption desulfurization of the low sulfur diesel fuel (LSD-I) over A-2 and A-5 was conducted at different temperatures and ambient pressure. The flowing rate of LSDF was also 0.2 ml/min with LHSV of 4.8 h^{-1}, except the run at 27°C over A-2, in which the flowing rate is 1.0 ml/min. The total sulfur concentration in the treated fuel as a function of the treated fuel amount is shown in Figure 10. As shown in Figure 3, all sulfur compounds in the low sulfur diesel are the refractory sulfur compounds. Figure 10 implies that such refractory sulfur compounds can be removed by A-2 and A-5.   However, it was found that A-2 and A-5 is difficult to remove sulfur to less than 1 ppmw although the total sulfur concentration in the feed is only 47 ppmw. This is because 1) the all sulfur compounds in LSD-I are the DBTs with one and/or two alkyl groups at the 4- and/or 6- positions of DBT; the coexisting aromatics and/or olefins might reduce the adsorptive performance of nickel-based adsorbents.

In examining effect of the temperature, we found that for A-2 the operating temperature at 200 ˚C is much better than that at 27 ˚C for the desulfurization performance. Figure 11 shows the GC-PFPD chromatograms of the low sulfur diesel fuel (LSD-I) and the treated fuels over A-2 at 200 ˚C, LHSV: 4.8 h^{-1}, indicating that the adsorptive selectivity decreases in the order of 4-MDBT, 4,6-DMDBT and 4-E,6-MDBT. 4-E,6-MDBT is more difficult to be removed than 4,6-DMDBT probable because the larger size of the ethyl group than that of the methyl group at the 4-position results in higher steric hindrance.   In comparison of A-2 and A-5 at 200 ˚C, the break-through curve for A-2 is clearly above the break-through curve of A-5. The adsorption capacity of A-5 corresponding to the break-through point at 5.0 ppmw sulfur level is 0.35 mg/g, while the adsorption capacity of A-2 at the same break-through sulfur level is only 0.05 mg/g. It indicates that A-5 exhibits the better desulfurization performance than A-2. It is probably because A-5 has higher surface area than that of A-2.

7.3.4. Regeneration of the Spent A-5 and Performance of the Regenerated A-5

The regeneration of the spent A-5 was conducted in the device by using H_2 gas at a flow rate of 40-50 ml/min, 500˚C, and ambient pressure for 3.5 h. The 1st regenerated A-5 was from the regeneration of the spent A-5 and the 2nd regenerated A-5 was from the regeneration of the spent 1st regenerated A-5. The break-through curves of LSD over the 1st and 2nd regenerated A-5s are also shown in Figure 10. The adsorption performance of the 1st regenerated A-5 is not good as that of the fresh one, but the adsorption performance of the 2nd regenerated A-5 is similar to or en slightly better than that of the fresh one. The adsorption capacity of the 2nd regenerated adsorbents corresponding to the break-through point at 5.0 ppmw sulfur level is about 0.36 mg/g, indicating that all of the adsorption capacity for the fresh A-5 can be recovered by the regeneration procedure using hydrogen.

7.4. Adsorptive Desulfurization of Model Diesel (MD-4) over Metal-sulfide-based Adsorbents

7.4.1. Adsorption Capacity

Adsorption desulfurization of MD-4 over A-6-1 and A-6-2 was conducted at 50 and 150 ˚C under ambient pressure. The flowing rate of MD-4 was 0.20 ml/min with the LHSV of 4.8 h^{-1}. The total sulfur concentration at the outlet as a function of amount of the treated MD-4 is shown in Figure 12. At 50 ˚C, when amount of the effluent is less than 3 g/g, the total sulfur concentration at outlet is less than 10 ppmw. After 3 g/g of the effluent amount, the total sulfur concentration increases quickly with increasing effluent amount. Both A-6-1 and A-6-2 were saturated when the effluent amount reached about 5.5 g/g. A-6-1 shows slightly better performance than A-6-2. The adsorption capacity corresponding the saturation point is 2.13 and 2.08 mg/g, respectively.

The adsorption performance of both A-6-1 and A-6-2 at 150 ˚C is poorer than those at 50˚C. The adsorption capacity at 150 ˚C is 1.47 and 1.44 mg/g, respectively for A-6-1 and A-6-2. This indicates that lower temperature is better for the adsorptive desulfurization over the metal-sulfide-based adsorbents, in contrast to the nickel-based adsorbents, indicating that the desulfurization is through a selective adsorption instead of the surface reaction.

7.4.2. Adsorption Selectivity

Figure 13 presents the molar concentration of the sulfur compounds, and 2-methylnaphthalene as a function of amount of the treated MD-4 in the desulfurization over A-6-1 at 50˚C. By comparing various sulfur compounds, almost no DBT is detected in the treated MD-4 when the effluent amount is less than 3.8 g/g. However, 4-MDBT and 4,6-DMDBT break through point is at around 0.4 g/g, and then, their concentration increases with increasing amount of the treated MD-4. The molar concentration of the sulfur compounds in MD-4 is the same, while the molar concentration of the sulfur compounds at outlet before the saturation point increases significantly in the order of DBT < 4-MDBT < 4,6-DMDBT. This result indicates clearly that the alkyl groups at 4- and 6-positions inhibit the interaction between the sulfur compounds and the adsorption site on the adsorbent. 2-Methylnaphthalene has the same molar concentration as DBT, 4-MDBT and 4,6-DMDBT in the initial fuel. The break-through point of 2-methylnaphthalene is at ~ 0.4 g/g. The molar concentration of 2-methylnaphthalene at the outlet, as shown in Figure 13, is much higher than those of DBT, 4-MDBT and 4,6-DMDBT. The adsorbent was saturated by 2-methylnaphthalene when the effluent amount increased to 1.6 g/g. The results imply that A-6-1 has significant adsorption selectivity for the sulfur compounds. As shown in Figure 13, A-6-2 exhibits the selectivity similar to that of A-6-1.

7.4.3. Regeneration of the Spent A-6-1 and Performance of the Regenerated A-6-1

The regeneration of the spent A-6-1 was accomplished by washing the adsorbent with a polar solvent followed by heating the adsorbent to remove the solvent. A polar solvent was pumped through the adsorbent bed at 60 ˚C and LHSV of 24 h^{-1}. The sulfur concentration in the eluate as a function of the eluate amount is shown in Figure 14. It was found that the first collected fraction contains almost all sulfur compounds adsorbed on the adsorbent, while the second fraction only contains less than 4 ppmw of sulfur. The results indicate that the adsorbed sulfur compounds can be easily washed out by the solvent. Each gram of the spent A-6-1 only needs about 2 gram of the solvent to wash out the sulfur compounds. Figure 15 shows that sulfur compound in the eluate is DBT, confirming further that no surface reaction takes place in the

adsorption. As most of sulfur compounds in diesel fuel have the boiling point higher than that of DBT (331°C), the sulfur compounds washed out from the adsorbent bed will be easy to be separated by a simple evaporator from the solvent, which has a boiling point less than 150 °C.

In order to remove the solvent remained in the column, after the solvent washing, the adsorbent bed was heated to 300 °C and kept at 300 °C under a nitrogen flow at 20 ml/min for 1 h, and then, the column was cooled to 50 °C for the subsequent adsorptive desulfurization. The model diesel was pumped through the column again to test the performance of the regenerated A-6-1. The break-through curves of MD-5 over the fresh and regenerated A-6-1s are shown in Figure 16. It is clear that the two break-through curves for the first regenerated and second regenerated A-6-1 coincide well with the fresh one, indicating that adsorption performance of the regenerated A-6-1 is similar to that of the fresh one.

7.5. Relevance of Selective Adsorption to Fuel processing for Fuel Cells

Conventional hydrodesulfurization process requires the use of H_2 at elevated pressures, which may not be applicable for on-board or on-site desulfurization for fuel cell applications. There are alternative desulfurization processes being developed for refinery operations [Hydrocarbon Processing, 1999; Irvine, 1998; Phillips Petroleum 2001; Gislason, 2002]. The selective adsorption process explored in this work can also be applied for removal of sulfur from diesel fuels on-site or on-board for fuel cell systems. It is advantageous to use the selective adsorption for sulfur removal from liquid hydrocarbon fuels for fuel cells, since this approach can be used at ambient temperatures without using hydrogen. The proposed selective adsorption may be applied as organic sulfur trap for sulfur removal from fuels before the reformer for fuel cells on-board or on-site, and it may be applied in a periodically replaceable form such as a cartridge. Further improvement in adsorption capacity is desired, and more work is in progress towards this direction in our laboratory.

7.6. MCM-41-supported catalysts for Deep HDS

7.6.1. HDS of 4,6-DMDBT and Real Feedstocks over the MCM-41-supported catalysts

Figure 17 shows the conversion of 4,6-DMDBT over different catalysts in *n*-tridecane (*n*-C_{13}) and petroleum-derived jet fuel (JP-8P). There is little significant difference between

activities of the commercial and MCM-41-supported catalysts when the active phase content (CoO-MoO$_3$) is comparable. Doubling the CoO and MoO$_3$ active phase content to 5.8 and 27.0 wt.%, respectively, increases the catalytic activity of the MCM-41 supported catalysts (designated Co-Mo/MCM-41 High) substantially. This increase in catalytic activity is particularly significant—more than twice that of the commercial catalysts—for the 4,6-DMDBT-spiked JP-8P.

Song and Reddy (1996) found a similar effect of active phase loading on results for the HDS of dibenzothiophene (DBT) in a batch reactor. Further, γ-alumina-supported catalysts with twice the normal metal loadings did not show a corresponding increase in DBT HDS activity. In the case of MCM-41-supported catalysts with active phase content similar to that in commercial γ-alumina supported catalysts, the surface area of MCM-41 (~900 m^2/g) is too high in comparison to that of γ-alumina (~250m^2/g) for creation of these large cylindrical molybdenum sulfide stacks. Preliminary temperature-programmed reduction results (see Figure 18) provide additional evidence for this. Molybdenum oxide is so finely dispersed on MCM-41 that strong metal-support interactions increase its reduction temperature to a broad zone starting from 520°C in contrast to sharp reduction temperatures of about 535°C for MoO$_3$ supported on γ–alumina and MCM-41 with double active phase loading. Therefore, an effective utilization of the high surface area of MCM-41 demands that the active phase content be increased—doubled in the present study.

The time on stream results—shown in Figure 19 show that the MCM-41-supported catalysts are as stable as commercial catalysts for real feedstocks. That the catalyst supported on MCM-41 not subjected to the recrystallization step rapidly loses activity demonstrates the importance of uniform mesopores, surface area, and presumably acid properties for deep HDS activity.

7.6.2. Effect of SiO$_2$/Al$_2$O$_3$ Ratio in MCM-41 on Deep HDS

Several researchers have reported that MCM-41 has little acidity for industrial use [Corma et al. 1995; Corma 1997; Zhao et al. 1996]. However, recent reports have definitively established that MCM-41 can be as acidic as Y-zeolite and the extent of acidity is a function of

the synthesis procedure and quality [Reddy and Song, 1998]. Based on the catalytic activity data obtained in this study it now seems plausible to synthesize MCM-41 with acidity just enough to isomerize refractory 4,6-DMDBT to the more reactive 2,8- or 3,7-DMDBT without causing undesirable cracking as often happens for zeolite Y-supported HDS catalysts [Isoda et al.1996].

Figure 20 documents the clear relationship between support acidity and the deep HDS activity as measured by the conversion of 4,6-DMDBT. The conversion of 4,6-DMDBT increases by more than 75% when the SiO_2/Al_2O_3 ratio changes from 100 (least acidic) to 25 (most acidic). Increasing acidity beyond that obtained in a catalyst with SiO_2/Al_2O_3 of 50 has limited practical benefits. The profound effect that acidity plays on deep HDS of 4,6-DMDBT is reflected in the product selectivity and distribution, which is presented in Figure 21.

The most acidic MCM-41-supported catalyst achieves deep HDS of 4,6-DMDBT primarily through the hydrogenolysis and cracking routes. 4,6-Dimethyldibenzo-thiophene is first desulfurized by hydrogenolysis and the biphenyl analog is then subsequently cracked to toluene. It is probable that the high acidity of the support might be isomerizing 4,6-DMDBT to more reactive isomers which can be desulfurized much easily. Although the 4,6-DMDBT conversion is high, the high toluene content in the product implies extensive cracking which could potentially cause volume and cetane number loss should this catalyst be used for HDS of middle distillate fuel feedstocks.

The catalyst with SiO_2/Al_2O_3 ratio of 50 has been found to be the most effective catalyst with optimal acidity. The catalyst seems to be achieving deep HDS through the hydrogenolysis route primarily as reflected in equal amounts of dimethylbiphenyl and toluene. The fairly significant amount of dimethyldicyclohexyl suggests that the second important route this catalyst is promoting is hydrogenation. This predominance of the otherwise difficult hydrogenolysis pathway suggests that it is being preceded by isomerization of 4,6-DMDBT to a more reactive PASC variant whose HDS does not require prior hydrogenation.

The hydrogenoloysis pathway also dominates the HDS of 4,6-DMDBT on MCM-41-supported catalysts with low metal loading but same SiO_2/Al_2O_3 content. The similar

dimethylbiphenyl to dimethylcyclohexylbenzene molar ratios for both the low- and high-metal content catalysts implies that the level of molybdenum sulfide stacking is important for activity but has little role to play in selectivity. The product and pathway selectivity are instead extensively influenced by support acidity (i.e., the SiO_2/Al_2O_3 ratios) in the MCM-41-supported catalysts.

As the SiO_2/Al_2O_3 ratio increases to 100, the preferred pathway moves towards hydrogenation with little cracking. The selectivity of this catalyst is only somewhat better than that of the commercial hydrotreating catalyst. The commercial hydrotreating catalyst converts 4,6-DMDBT through the hydrogenation pathway.

Evidently the preferred pathway for the HDS of PASCs is hydrogenation followed by sulfur extrusion unless support acidity circumvents this route by isomerizing the PASC to a more reactive variant in which case sulfur extrusion becomes easier than hydrogenation especially at the HDS temperatures of 350°C where hydrogenation is known to be limited by thermodynamics [Cooper and Donnis, 1996].

7.7. A New Integrated Deep Desulfurization Process

On the basis of the present study, we propose a novel process in a future refinery for deep desulfurization of liquid hydrocarbons, which combines a selective adsorption process of the sulfur compounds and a hydrodesulfurization process of the concentrated sulfur fraction, as shown in Figure 22. The sulfur compounds in fuels are first adsorbed on the adsorbent in an adsorber and the hydrocarbon fraction with ultra-low-sulfur content is obtained from the top of the adsorber. The sulfur compounds adsorbed on the surface of the adsorbent are recovered by solvent elution. The spent adsorbent is regenerated via solvent elution followed by removal of the solvent. The eluate (solution of the sulfur compounds in the solvent) is sent to an evaporator to recycle the solvent and to obtain a concentrated sulfur fraction, which account for less than 1 wt % of the whole fuel. The concentrated sulfur fraction is then sent to a small HDS reactor for hydrodesulfurization. The hydrodesulfurized product is then blended with the hydrocarbon fraction from the adsorber. The concentrated sulfur fraction also can be used directly as a chemical feedstock.

The proposed new process illustrated in Figure 22 is different from IRVAD process [Hydrocarbon Processing, May 1999; Irvine, 1998], S Zorb process [Phillips Petroleum 2001; Gislason, 2002] and RTI's TreND process [Turk and Gupta, 2001] with respect to adsorption mechanism, adsorbent, and regeneration method. There are several potential advantages of the proposed process: 1) The process is efficient for ultra-deep desulfurization of liquid hydrocarbon fuel. 2) The adsorption process is operated at ambient temperature and ambient pressure, which does not need any H_2. 3) The HDS following the adsorption separation only deals with the sulfur fraction, which leads to low hydrogen consumption, low energy consumption, low investment and low operating cost. 4) Due to the separation of aromatics and olefins from the sulfur compounds by adsorption and the high concentration of sulfur compounds, the HDS reactor can be much smaller. The process of HDS can be more efficient as the coexisting polycyclic aromatics in the fuel are strong inhibitors for HDS of the refractory sulfur compounds.

8. Conclusions

In this research project, we explored a new approach for deep desulfurization by selective adsorption using a solid adsorbent at ambient temperatures without using hydrogen. we have developed and tested three types of adsorbents, metal chlorides (A-1), activated nickel-based adsorbents (A-2 and A-5) and the metal-sulfide-based adsorbents (A-6), and explored the adsorptive desulfurization of model diesel fuels and commercial diesel fuels over various adsorbents. The regeneration of the spent adsorbents has been studied. On the basis of the present study, we proposed a novel process in a future refinery for deep desulfurization of liquid hydrocarbon fuels. On the basis of our experimental results, the following conclusions can be made:

- The major sulfur compounds in the commercial regular diesel fuel (DF, 325 ppmw) are the alkyl sulfur compounds that have at least one alkyl group at the 4- or 6-position. The major sulfur compounds in the low S diesel fuel (LSD, 9 ppmw) are the alkyl sulfur compounds with two alkyl groups at the 4- or 6-positions, respectively, indicating these sulfur compounds are the most difficult to be removed by the conventional HDS process.

- Alkyl DBTs, even 4,6-DMDBT, in MDF-I can be removed efficiently by selective adsorption over a palladium chloride supported on silica gel at ambient temperature, ambient pressure without using hydrogen gas. The adsorbent shows higher selectivity for sulfur compounds in the presence of a large amount of aromatics (10 wt%). The adsorption capacity of A-1 for MDF-I corresponding to the outlet sulfur level of 30 ppmw is 0.9 mg/g.

- All alkyl DBTs, including DBT, 4-MDBT and 4,6-DMDBT, in diesel fuels can be removed efficiently by selective adsorption over the activated nickel-based adsorbent (A-2) at 200 °C, ambient pressure without using hydrogen gas. The adsorptive capacity of A-2 corresponding to outlet sulfur level of 30 ppmw is 7.3 mg/g for MDF-II at 150°C, and 2.8 mg/g for the real diesel fuel (DF) at 200°C.

- Methyl groups at the 4- and 6-positions have significantly steric hindrance for the adsorption of alkyl DBTs on the activated nickel-based adsorbents, which results in the lower adsorption selectivity of the alkyl DBTs with alkyl groups at the 4- and/or 6-positions than those without alkyl groups at the 4- and 6-positions.

- Increase in the temperature can moderate the effect of the methyl groups on the adsorptive selectivity, probable by reducing steric hindrance via relaxing the methyl group and/or by increasing hydrogenolysis rate of C-S bond on the surface.

- Increase in the temperature is significantly in favor of the desulfurization performance of nickel-based adsorbents for both cases, model diesel fuel and real diesel fuel. In comparison of effect of temperature on desulfurization of the low sulfur diesel fuel over Adsorbent-I, the operating temperature at 200 °C is much better than that at 27 °C.

- The activated nickel-based adsorbent with alumina supporter (A-5) shows better performance than that (A-2) without alumina supporter for the adsorptive desulfurization of the low sulfur diesel fuel, probably because A-5 has higher surface area than that of A-

2. The adsorption capacity of A-5 for LSD-I (S: 47ppmw) corresponding to the break-through point at 5.0 ppmw sulfur level is 0.35 mg/g, while the adsorption capacity of A-2 at the same break-through sulfur level is only 0.05 mg/g.

- The spent A-5 can be regenerated by using H_2 gas at a flow rate of 40-50 ml/min, 500°C, and ambient pressure for 3.5 h. The regenerated A-5 shows an adsorption capacity similar to the fresh one.

- The metal-sulfide-based adsorbents (A-6-1 and A-6-2) have been developed for adsorptive desulfurization. A-6-1 and A-6-2 show high adsorption selectivity for the sulfur compounds, but their adsorption capacities are much lower than those of A-2 and A-5.

- In contrast to A-2 and A-5, low temperature favors the desulfurization performance over A-6-1 and A-6-2.

- The spent A-6 type of adsorbents can be easily regenerated by washing the spent adsorbent with a polar solvent followed by heating the adsorbent bed to remove the solvent. Almost all adsorption capacity of the fresh A-6-1 can be recovered after regeneration.

- Although the adsorption capacity of the current developed metal-sulfide-based adsorbents is significantly lower than that of the nickel-based adsorbents, but they have shown some significant advantages:
    1. Adsorptive desulfurization is performed at ambient temperature and pressure.
    2. Adsorptive desulfurization process and regeneration process do not need to use hydrogen.
    3. The spent adsorbent can be easy to be regenerated without using hydrogen.
    4. The solvent can be easy to be separated from sulfur fraction for recycle due to its low boiling point.

- The results obtained from the development of the MCM-41-suported catalysts for deep HDS of the refractory sulfur compounds show that
    1. The MCM-41-supported catalyst have advantages in comparison to a commercial γ-alumina-supported catalyst for deep HDS of refractory sulfur compounds.
    2. The important role played by MCM-41's acidity towards deep HDS iss clarified.
    3. The importance of the mesopores and their stability for effective deep HDS is identified

- There are several potential advantages of the proposed PSU-SARS process:
    1. The process is efficient for ultra-deep desulfurization of diesel fuel.
    2. The adsorption process is operated at ambient temperature and ambient pressure, which does not need any H_2 gas.
    3. The spent adsorbent can be regenerated easily.
    4. The HDS following the adsorption separation only deals with the sulfur fraction, which leads to low hydrogen consumption, low energy consumption, low investment and low operating cost.
    5. Due to the separation of aromatics and olefins from the sulfur compounds by adsorption and the high concentration of sulfur compounds, the HDS reactor can be much smaller in size. The HDS process can be more efficient as the coexisting polycyclic aromatics, which are strong inhibitors for deep HDS of the refractory sulfur compounds, have been removed substantially from the sulfur fraction.

9. References

Angelici, R. J. 1995, Bull. Soc. Chim. Beld. 104, 268.

Cooper, B. H. and B. B. L. Donnis, 1996, Applied Catalysis A: General, 137, 203.

Corma, A., A. Martínez, V. Martínez-Soria and J. B. Montón, 1995, Journal of Catalysis, 153, 25.

Corma, A., 1997, Chemical Reviews, 97, 2373.

Gislason, J. 2002, Phillips sulfur-removal process nears commercialization, Oil Gas J. 99, 74.

Hughes, D. L.; Richards, R. L.; Shortman, C. 1986, J. Chem. Soc. Chem. Comm 1731.

Hydrocarbon Processing, May 1999, p. 39.

Irvine, R. L. 1998, U.S. Pat. No. 5,730,860.

Isoda, T., S. Nagao, Y. Korai and I. Mochida, 1996, Preprints, Division of Petroleum Chemistry, American Chemical Society, 40, 563.

Knudsen, K. G; B. H. Cooper, H. Topsoe, 1999, Appl. Catal. A-Gen. 189, 205-215.

Ma, X.; Sakanishi, K.; Mochida, I. 1994, Ind. Eng. Chem. Res. 33, 218-222.

Ma, X.; Sakanishi, K.; Isoda, T.; Mochida, I.; 1995, Energy & Fuels 9, 33-37.

Ma, X.; Sakanishi, K.; Mochida, I.;, 1996a, Ind. Eng. Chem. Res., 35, 2487-2494.

Ma, X.; Sakanishi, K.; Isoda, T.; Mochida, I. 1996b, in Hydrotreating Technology for Pollution Control, M. L. Occelli, R. Chianelli, eds. Marcel Dekker, pp. 183-195.

News-EPA, 2001. Government Developments-EPA. *Oil Gas J.* Jan 1, p.7.

Phillips Petroleum December 2001, http://www.fuelstechnology.com/szorbdiesel.htm.

Potrin, C.; Bregalt, J. M.; Manoli, J. M. 1980, J. Chem. Soc. Chem. Comm. 664.

Sanchez-Delgado, R. A. 1994, J. Mol. Catal. 86, 287.

Song, C. 2000, in Chemistry of Diesel Fuels, Song, C.; Hsu, C. S.; Mochida, I. eds. Taylor and Francis, New York, pp. 1-60.

Song, C. 2003, An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel, Catal. Today, 86, 211-263.

Swain, E.J. 1998, US refining crude slates continue towards heavier feeds, higher sulfur contents, Oil Gas J. 96, 43.

Swain, E.J. 2002, Crudes processed in the US refineries continue to decline in quality, Oil Gas J. 100, 40.

Reddy, K. M. and C. Song, 1996, Catalysis Letters, 36, 103.

Reddy, K.M. and C. Song, 1998, Studies in Surface Science and Catalysis, 117: 291.

Song, C. and K. M. Reddy, 1999, Applied Catalysis A: General, 176(1), 1 .

Turk, B. S.; Gupta, R. P. 2001, Am. Chem. Soc. Div. Fuel Chem. Prepr. 46, 392-393

Vecchi, P. A.; Ellern, A.; Angelici, R. J. 2003, J. Am. Chem. Soc. 125, 2064.

Whitehurst, D. D.; Isoda, T.; Mochida, I. 1998, Adv. Cat. 42, 345-471.

Zhao, X. S.; Lu, G.Q.; Millar, G.J. and Li, X. S. 1996, Catalysis Letters, 38(1-2), 33.

10. List of Publications

1. Chunshan Song, An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel, Catal. Today, **2003**, 86, 211-263.
2. S. Velu, Xiaoliang Ma and Chunshan Song, Selective Adsorption for Removing Sulfur from Jet Fuel over Zeolite-Based Adsorbents, *Ind. End. Chem. Res*. **2003**, 42, 5293-5304.
3. Xiaoliang Ma, Subramani Velu, Lu Sun, and Chunshan Song, Adsorptive Desulfurization of JP-8 Jet Fuel and Its Light Fraction over Nickel-based Adsorbents for Fuel Cell Applications, *Prepr., Div. Fuel Chem., Am. Chem. Soc*. **2003**, 48 (2), 688-689.
4. Xiaoliang Ma, Lu Sun, and Chunshan Song, Adsorptive Desulfurization of Diesel Fuel over a Metal Sulfide-Based Adsorbent, *Prepr., Div. Fuel Chem., Am. Chem. Soc*. **2003**, 48 (2), 522-523.
5. Uday T. Turaga, Xiaoliang Ma and Chunshan Song Influence of nitrogen compounds on deep hydrodesulfurization of 4,6-dimethyldibenzothiophene over Al2O3- and MCM-41-supported Co-Mo sulfide catalysts, *Catal. Today*, **2003**, 86, 265-275.
6. Jae-Hyung Kim, Xiaoliang Ma and Chunshan Song, Kinetic Study of Effects of Aromatic Compounds on Deep Hydrodesulfurization of 4,6-Dimethyldibenzothiophene, *Prepr., Div. Fuel. Chem., Am. Chem. Soc*. **2003**, 48(2), 553-554.
7. S. Velu, Xiaoliang Ma and Chunshan Song, Fuel Cell Grade Gasoline Production by Selective Adsorption for Removing Sulfur. *Am. Chem. Soc*. *Div*. *Petr*. *Chem. Prepr*., **2003**, 48 (2), 58-59
8. Chunshan Song and Xiaoliang Ma, New Design Approaches to Ultra-Clean Diesel Fuels by Deep Desulfurization and Deep Dearomatization, *Applied Catalysis B: Environ*, **2003**, 41 (1-2), 207-238.
9. Chunshan Song, Fuel Processing for Low-Temperature and High-Temperature Fuel Cells. Challenges, and Opportunities for Sustainable Development in the 21st Century. *Catalysis Today*, **2002**, 77 (1), 17-50.
10. Xiaoliang Ma, Lu Sun, and Chunshan Song, A New Approach to Deep Desulfurization of Gasoline, Diesel Fuel and Jet Fuel by Selective Adsorption for Ultra-Clean Fuels and for Fuel Cell Applications. *Catal. Today* **2002**, 77, 107-116.
11. S. Velu, S. Watanabe, Xiaoliang Ma and Chunshan Song, Development of Selective Adsorbents for Removing Sulfur from Gasoline for Fuel Cell Applications. *Am. Chem. Soc*. *Div. Petr. Chem. Prepr.,* **2003**, 48 (2), 56-57
12. Xiaoliang Ma, Jae-Hyung Kim and Chunshan Song, Effect of Methyl Groups at 4- and 6-Positions on Adsorption of Dibenzothiophenes over CoMo and NiMo Sulfide Catalysts. *Am. Chem. Soc*. *Div. Fuel Chem. Prepr*. , **2003**, 48, 135-137.
13. Xiaoliang Ma, Michael Sprague, Lu Sun, and Chunshan Song. Ultra-Deep Desulfurization of Gasoline and Diesel for Fuel Cell Applications by SARS Adsorbent and Process Materials Research Society Fall 2002 National Meeting**,** Boston, Dec. 2-6, 2002
14. Xiaoliang Ma, Michael Sprague, Lu Sun and Chunshan Song. Deep Desulfurization of Gasoline by SARS Process Using Adsorbent for Fuel Cells. *Am. Chem. Soc*. *Div*. *Fuel Chem. Prep.,* 2002, 47, 452
15. S. Velu, Xiaoliang Ma, and Chunshan Song. Zeolite-Based Adsorbents for Desulfurization of Jet Fuel by Selective Adsorption. *Am. Chem. Soc. Div. Fuel Chem. Prep.,* 2002, 47, 457
16. Uday T. Turaga and Chunshan Song, MCM-41-Supported Co-Mo Catalysts for Deep Hydrodesulfurization of Light Cycle Oil-Based

17. Uday T. Turaga, Gang Wang, Xiaoliang Ma, Chunshan Song, and Harold H. Schobert, Influence of Nitrogen on Deep Hydrodesulfurization of 4,6-Dimethyldibenzothiophene. *Am. Chem. Soc. Div. Petr. Chem. Prep.,* 2002, 47, 89.

18. Uday T. Turaga and Chunshan Song, MCM-41-Supported Co-Mo catalysts for deep hydrodesulfurization of light cycle oil, *Am. Chem. Soc. Div. Petr. Chem. Prep.,* 2002, 47, 97.

19. Xiaoliang Ma, Lu Sun, Zequn Yin and Chunshan Song, A New Approach to Deep Desulfurization by Adsorption of Sulfur Compounds from Diesel Fuel, Jet Fuel, and Gasoline. *Am. Chem. Soc. Div. Fuel Chem. Prep.,* 2001, 46 (2), 648-649.

20. Uday T. Turaga and Chunshan Song, Deep hydrodesulfurization of diesel and jet fuels using mesoporous molecular sieve-supported Co-Mo/MCM-41 catalysts, *Am. Chem. Soc. Div. Petr. Chem. Prep,* 2001, 46, 275.

21. Uday Turaga and Chunshan Song, Novel Co-Mo/MCM-41 catalysts for deep hydrodesulfurization of jet fuels, Proceedings of the 17th North American Catalysis Society Meeting, Oral Presentations Volume (2001) 465.

22. Uday Turaga and Chunshan Song, Novel mesoporous Co-Mo/MCM-41 catalyst for deep hydrodesulfurization of jet fuels, Student Poster Contest of the Catalysis Club of Philadelphia (2001).
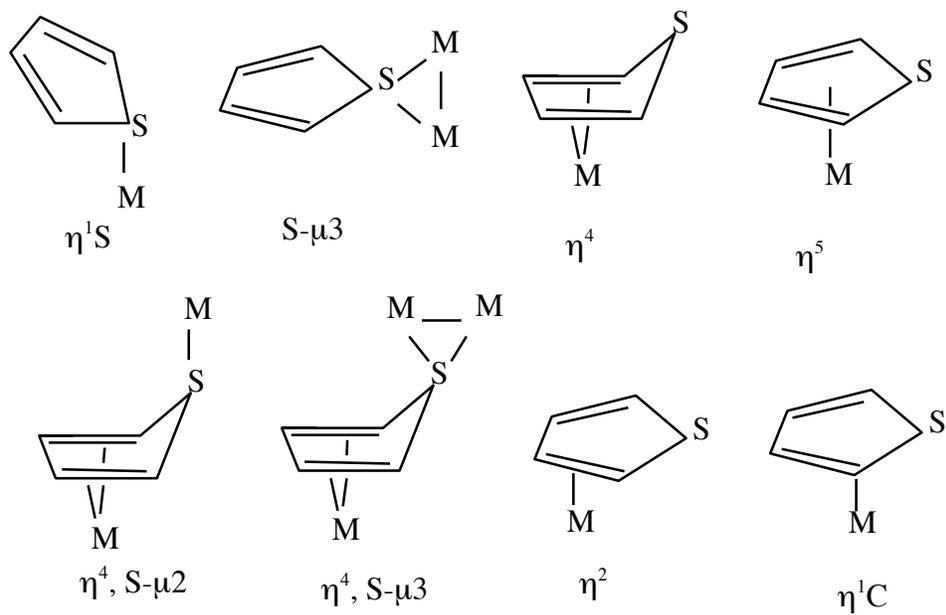
Figure 1. Known Coordination Geometries of Thiophene with Metal Species in Organometallic Complexes

N₂

H₂

Gas regulator

Mass flow controller

Convection oven

Temp. Controller

HPLC Pump

Digital Thermometer

Solvent   **Feed**   **Column**

Samplin
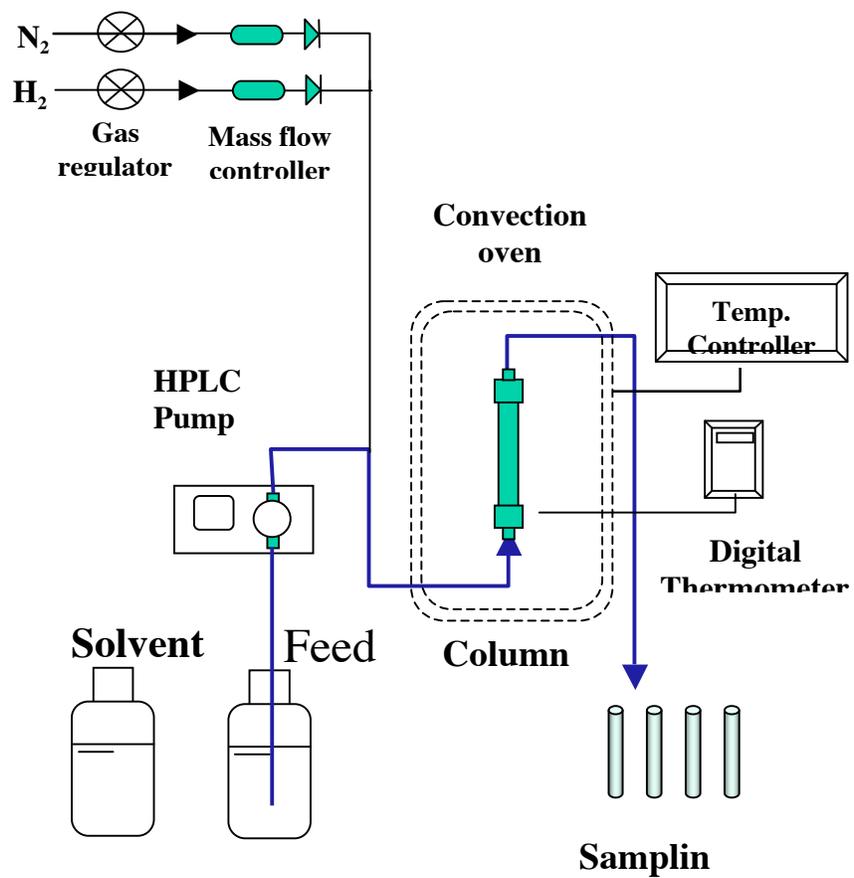
Figure 2. Experimental Device for Adsorptive Desulfurization
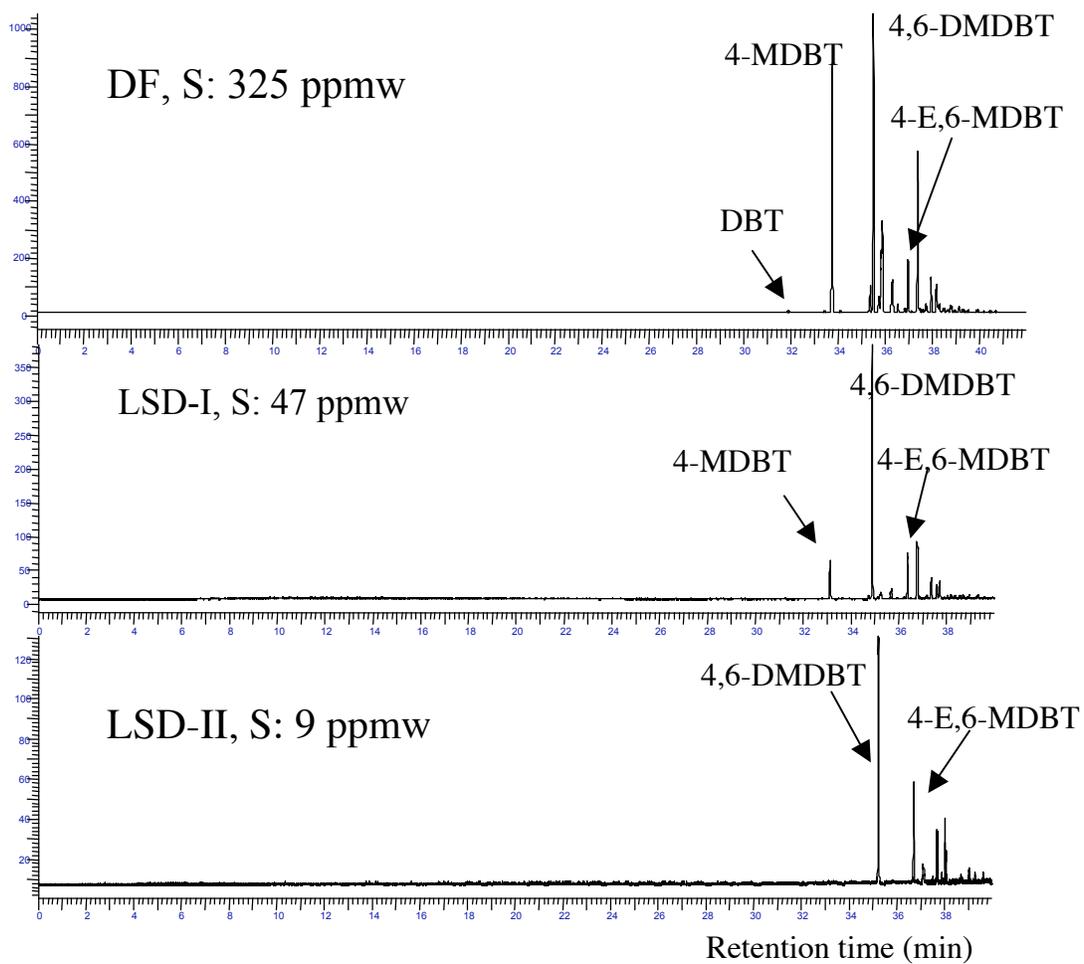
Figure 3. GC-PFPD chromatograms of a commercial regular diesel fuel (DF)
and a low sulfur diesel fuels (LSD-I, LSD-II)
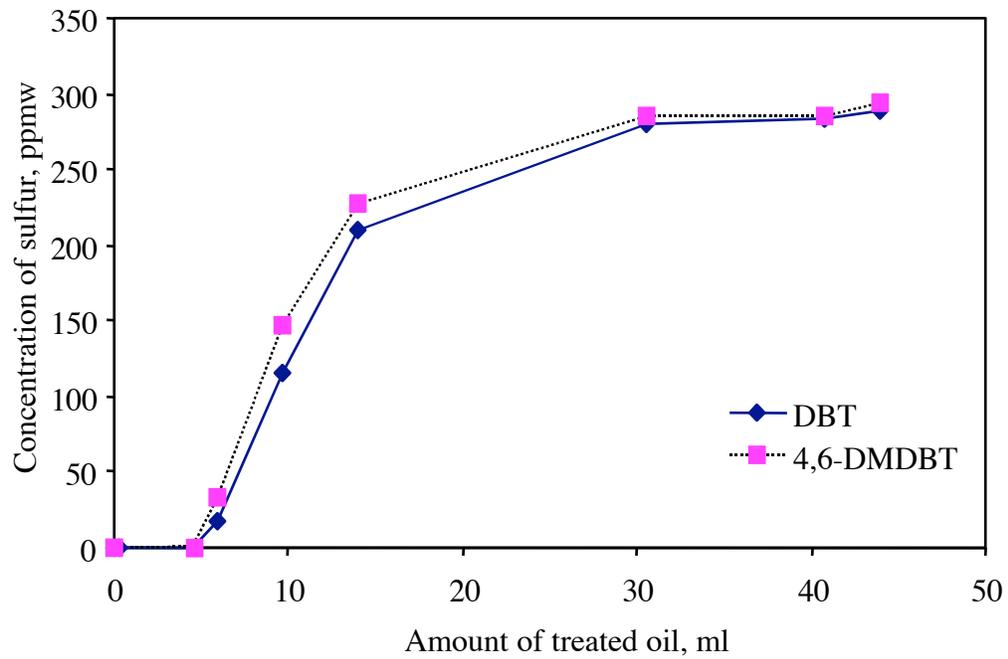
Figure 4. Break-through curves of MDF-I over A-1, at room temperature
 in the absence of hydrogen gas
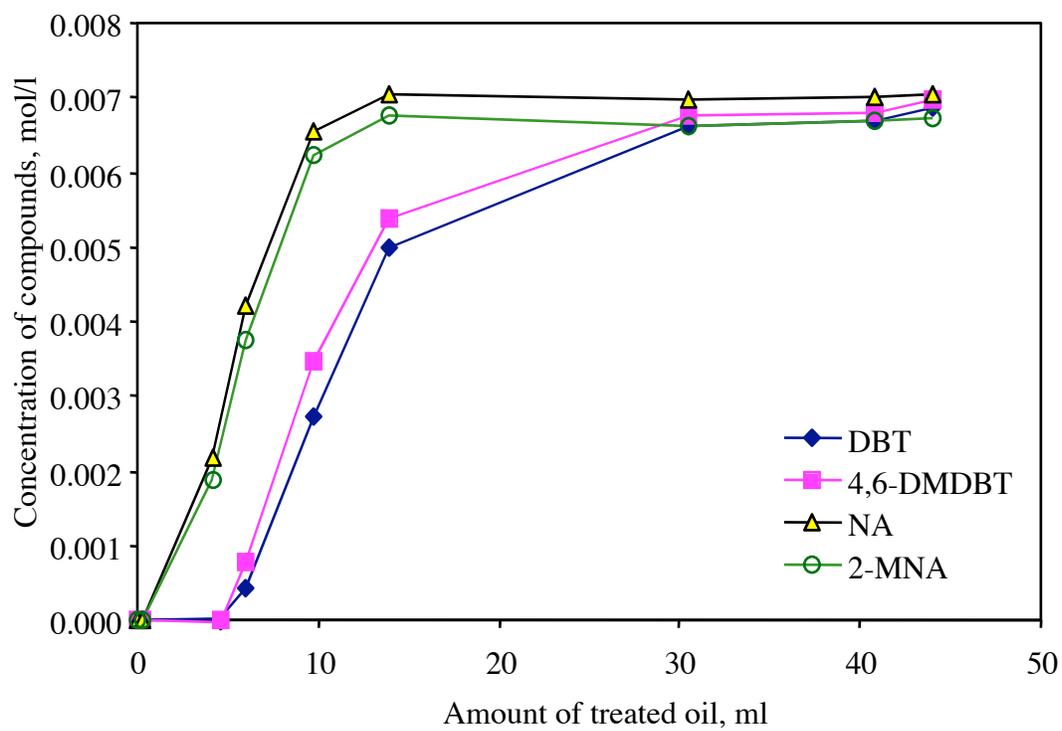
Figure 5. Adsorptive Selectivity of A-1 for Sulfur Compounds and Aromatics
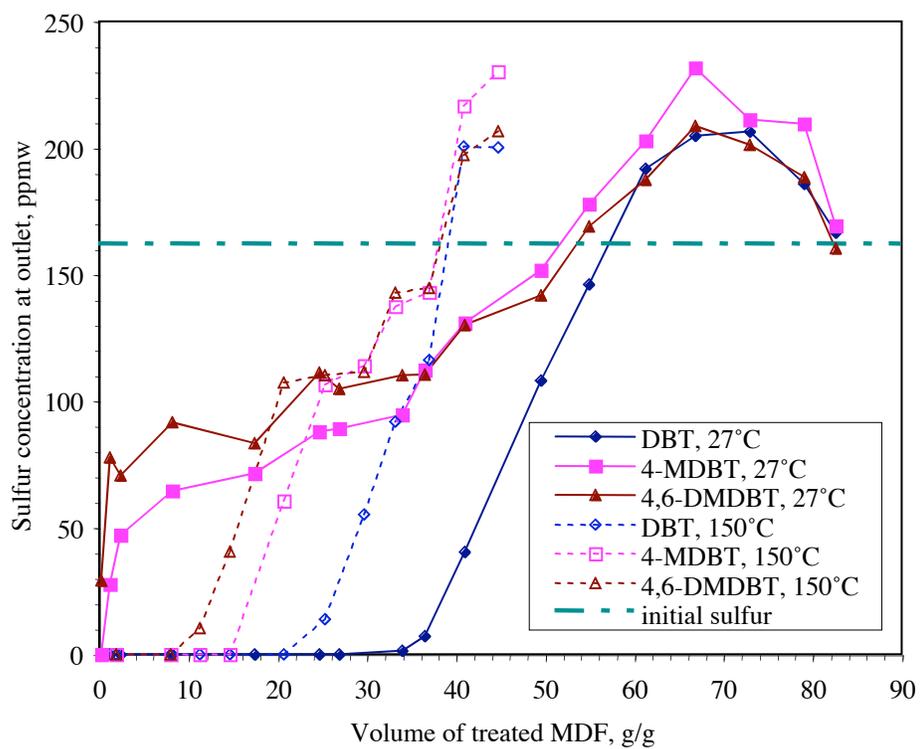
Figure 6. Break-through Curves of Various Sulfur Compounds over A-2 at 27 ˚C and 150 ˚C, LHSV: 24 h⁻¹
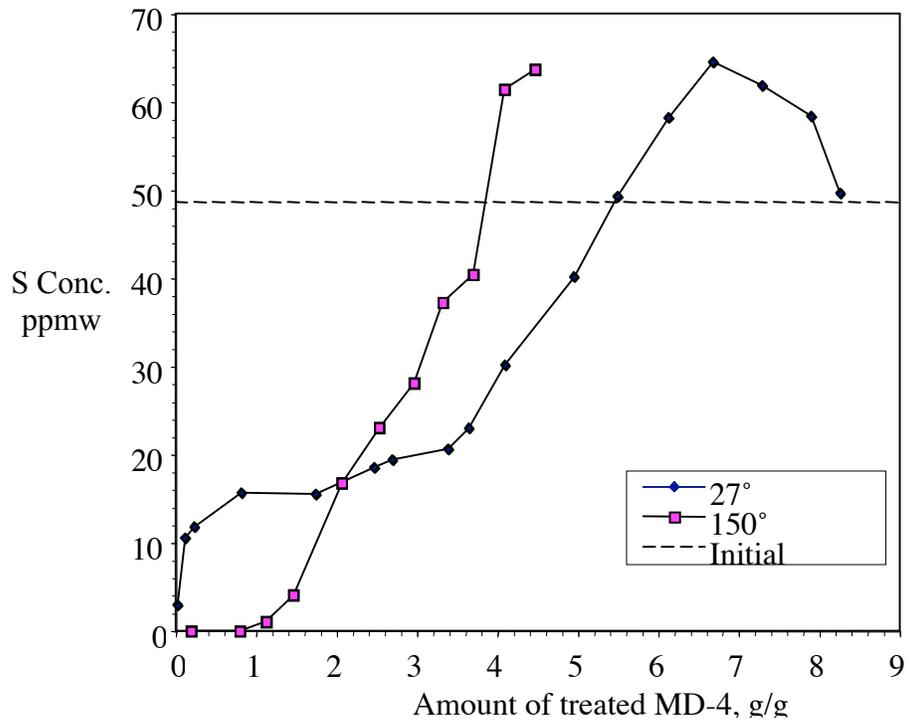
Figure 7. Break-through Curves of Total Sulfur over A-2 at 27 ˚C and 150 ˚C, LHSV: 24 h^{-1}
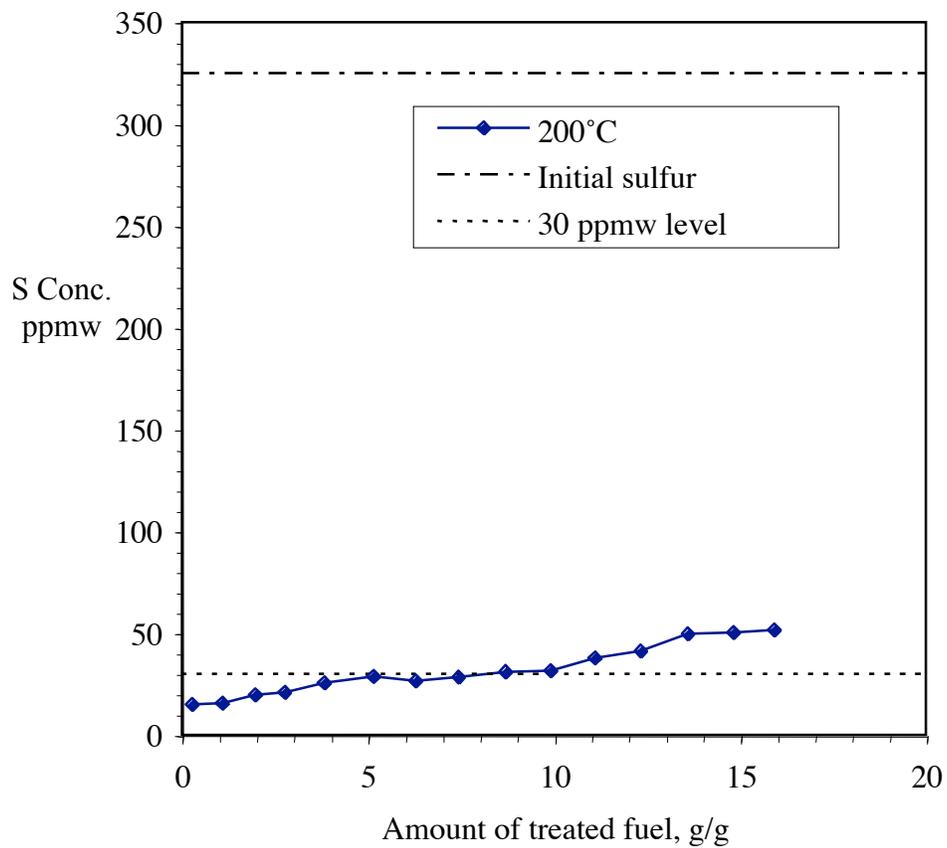
Figure 8. Break-through curves of real diesel fuel over A-2 at 200 ˚C and 4.8 h⁻¹ of LHSV

Sample	Amount g/g	Sulfur ppmw
101-10	9.9	32ppm
101-15	15.9	52ppm
DF Feed		320ppm
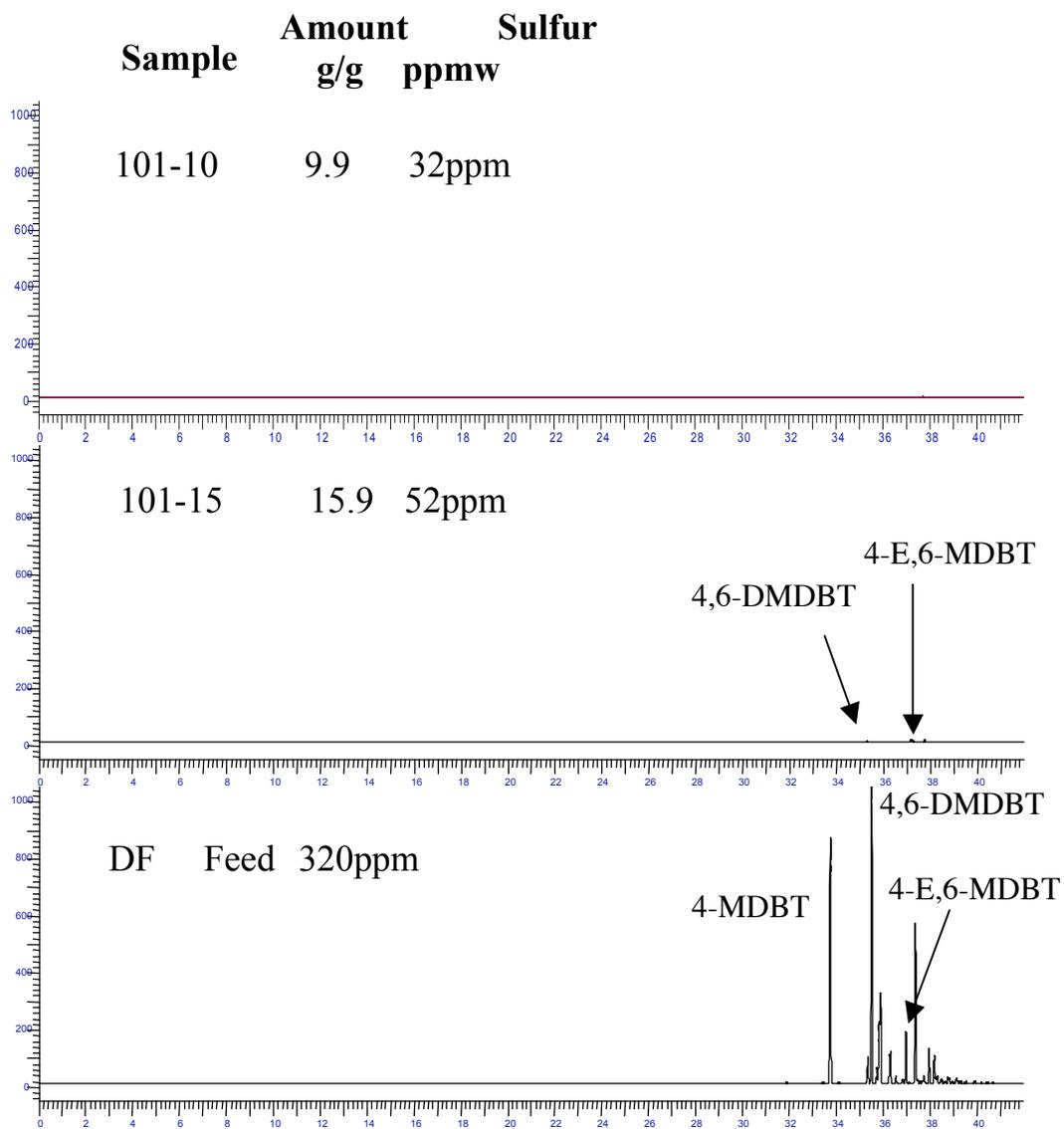
Figure 9. GC-PFPD chromatograms of the diesel fuel (DF) and
the treated diesel fuels over A-2
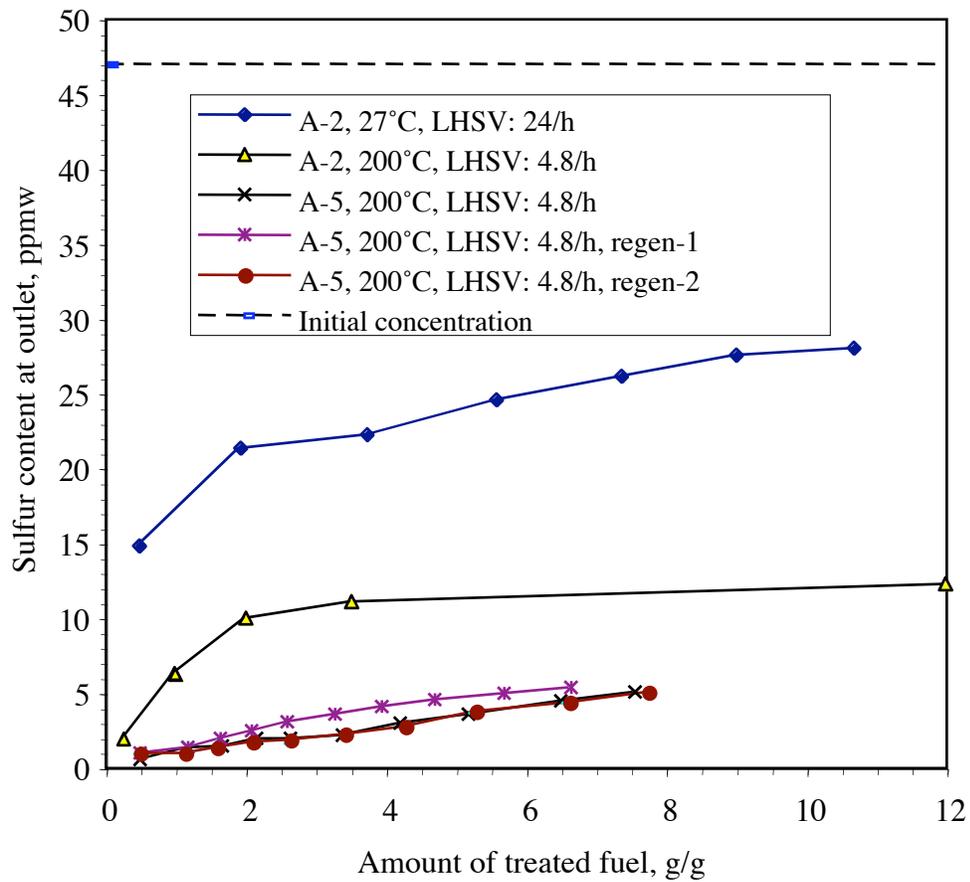
**Figure 10.** Break-through curves of LSD-I over A-2 and A-5 at different conditions

No.	treated volume ml	S ppmw
2	1	0.0
8	32	10
15	90	17
22	157	21
34	308	26
51	596	39
feed		

4-E,6-MDBT

4,6-DMDBT

4-E,6-MDBT

4-MDBT
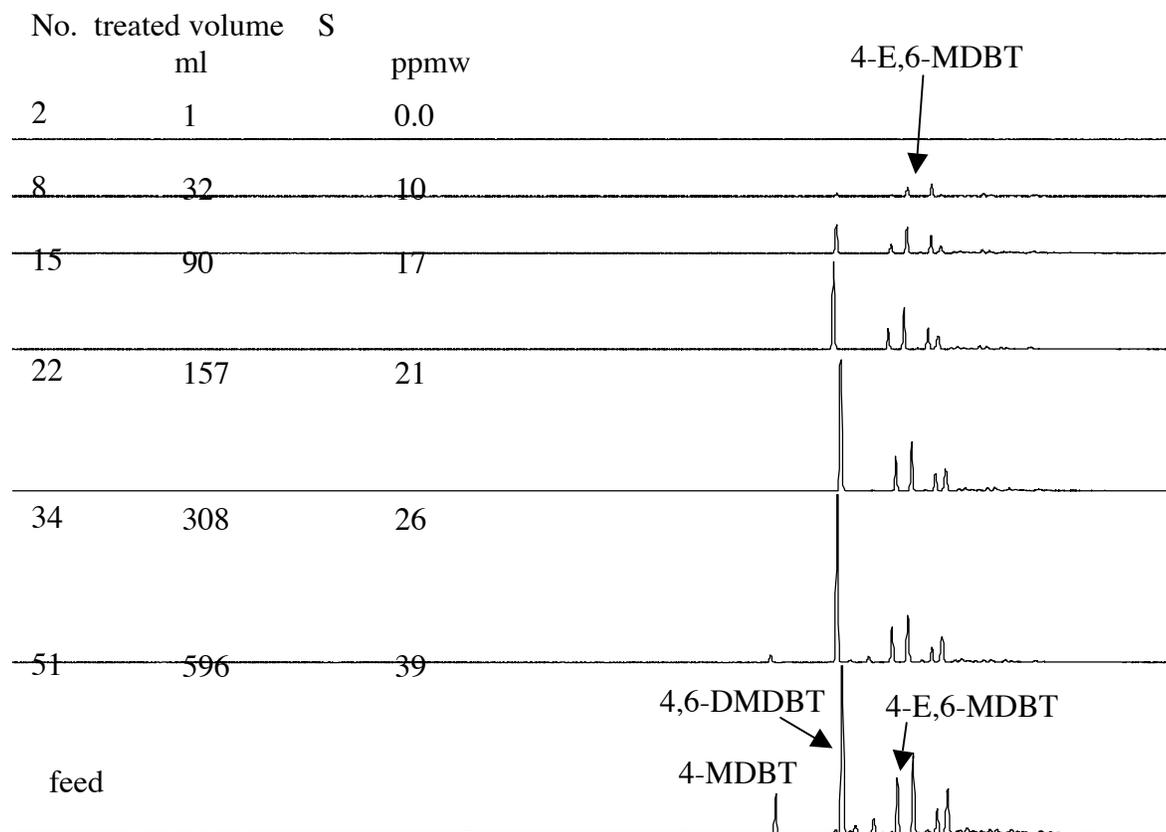
Figure 11. GC-PFPD chromatograms of the low sulfur diesel fuel (LSD-I) and the treated fuels over A-2 at 200 ˚C, LHSV: 4.8 h^{-1}
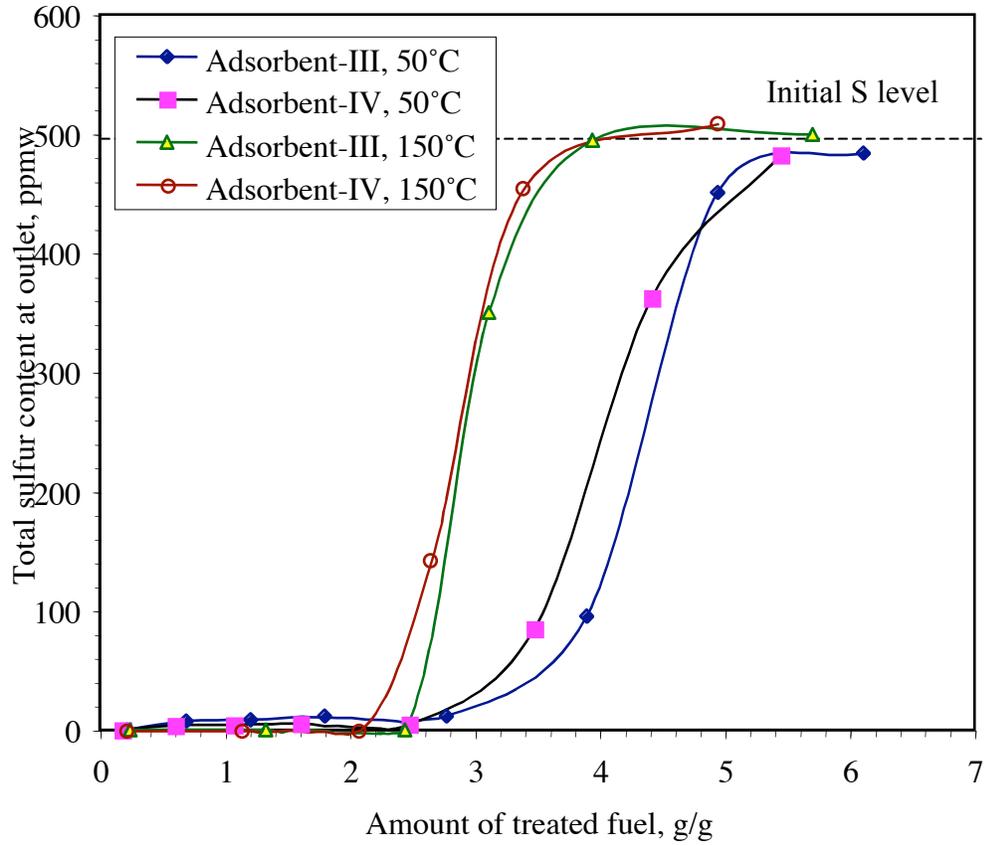
Figure 12. Break-through curves of MDF over A-6-1 and A-6-2 at ambient pressure and 4.8 h^{-1} of LHSV
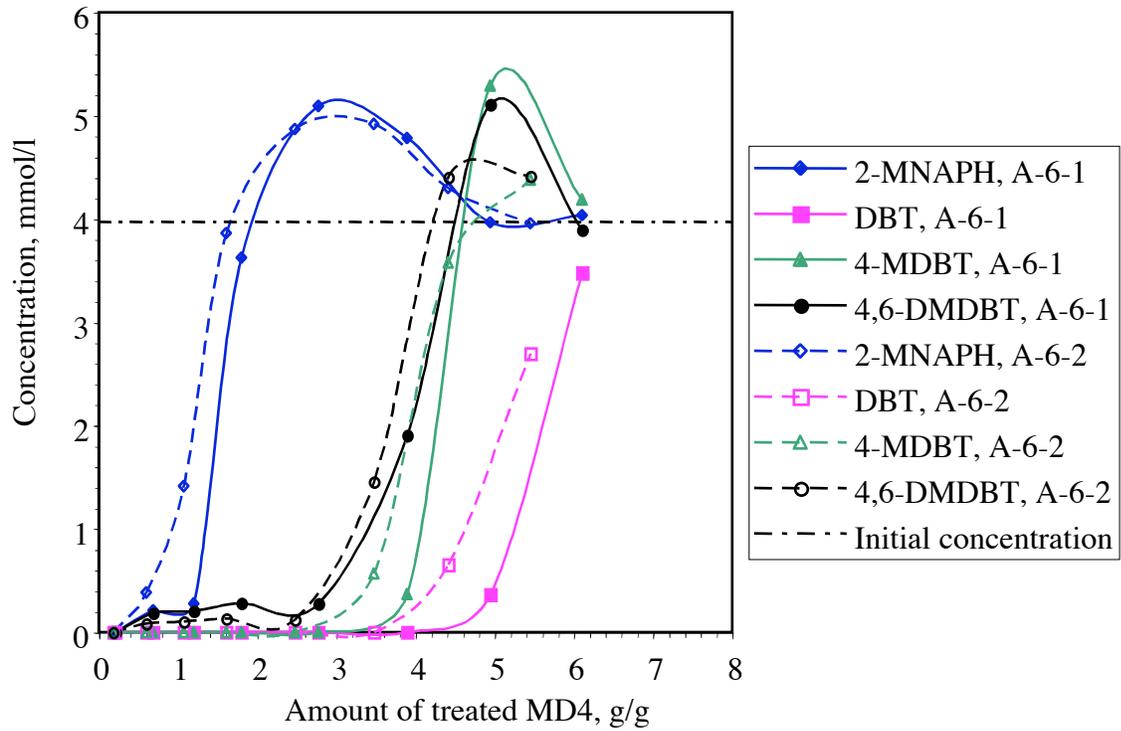
Figure 13. Adsorption Selectivity: The Break-through Curves of Coexisting Sulfur Compounds and 2-Methylnaphthalene at 50°C over A-6-1 and A-6-2.
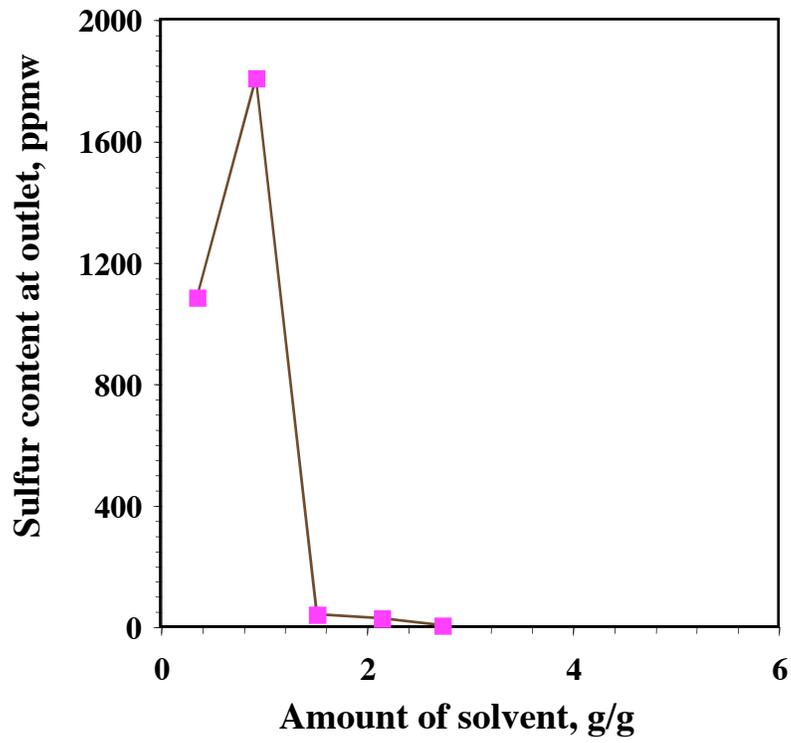
Figure 14. Sulfur concentration at outlet as a function of the eluate amount in solvent washing at 60 ˚C and ambient pressure.
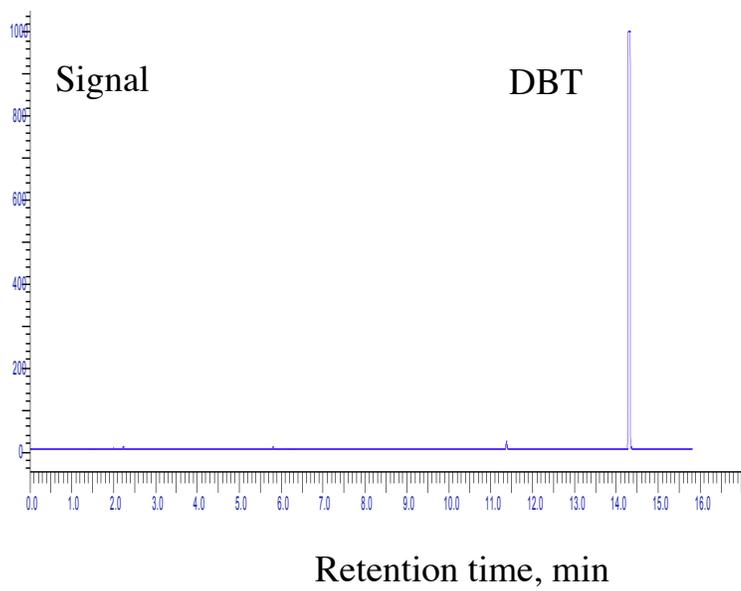
Figure 15. GC-PFPD of the eluate
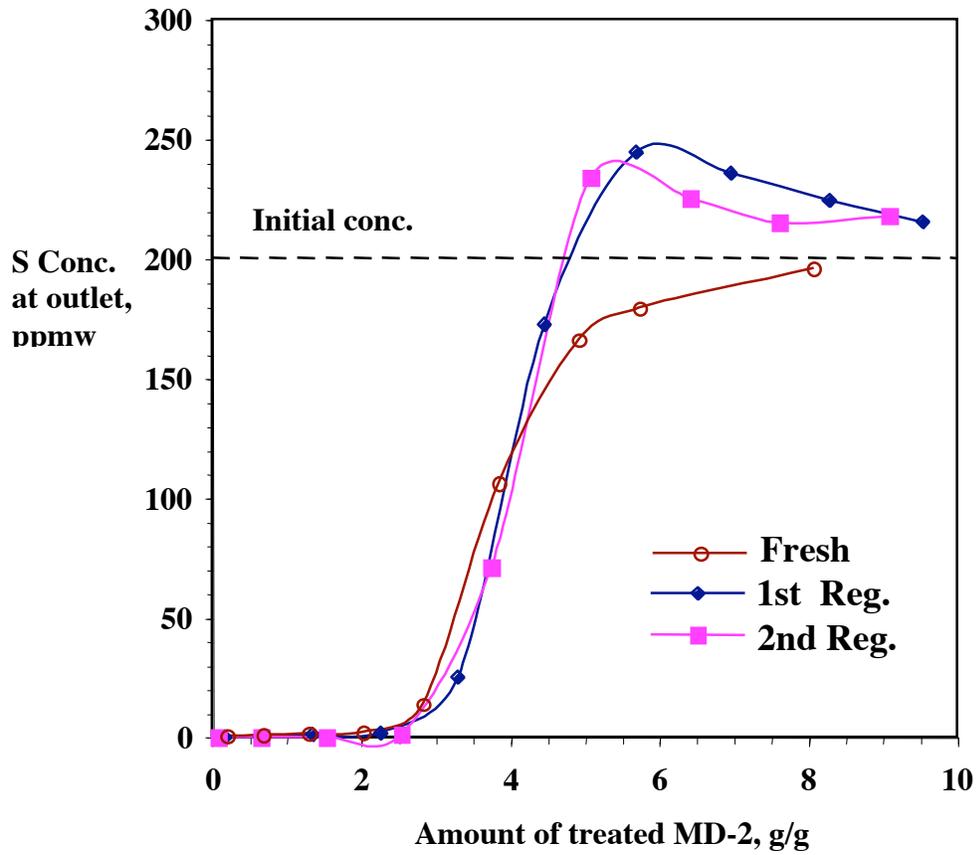
**Figure 16.** Break-through Curves of MDF-II over A-6-1 at 50°C, 4.8 h^{-1} of LHSV
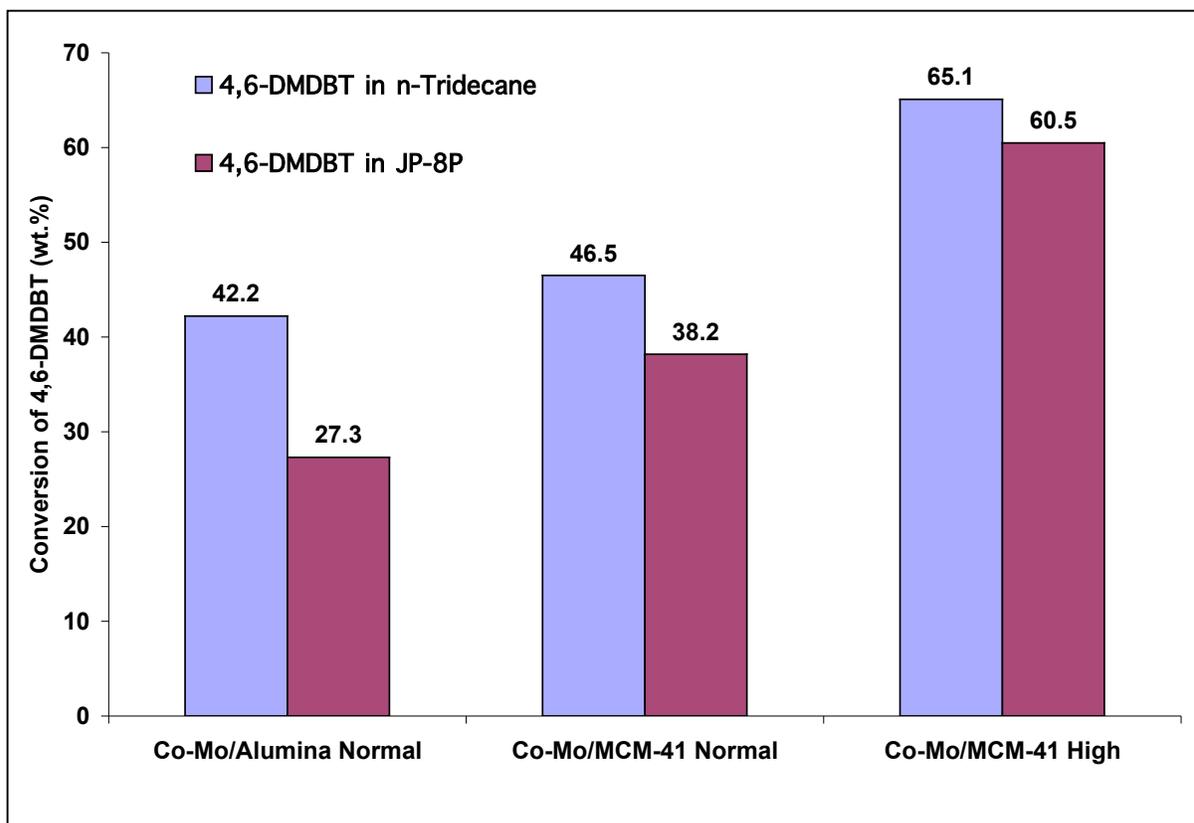
Figure 17. Conversion of 4,6-DMDBT in n-tridecane and petroleum-derived jet fuel (JP-8P) over different catalysts.
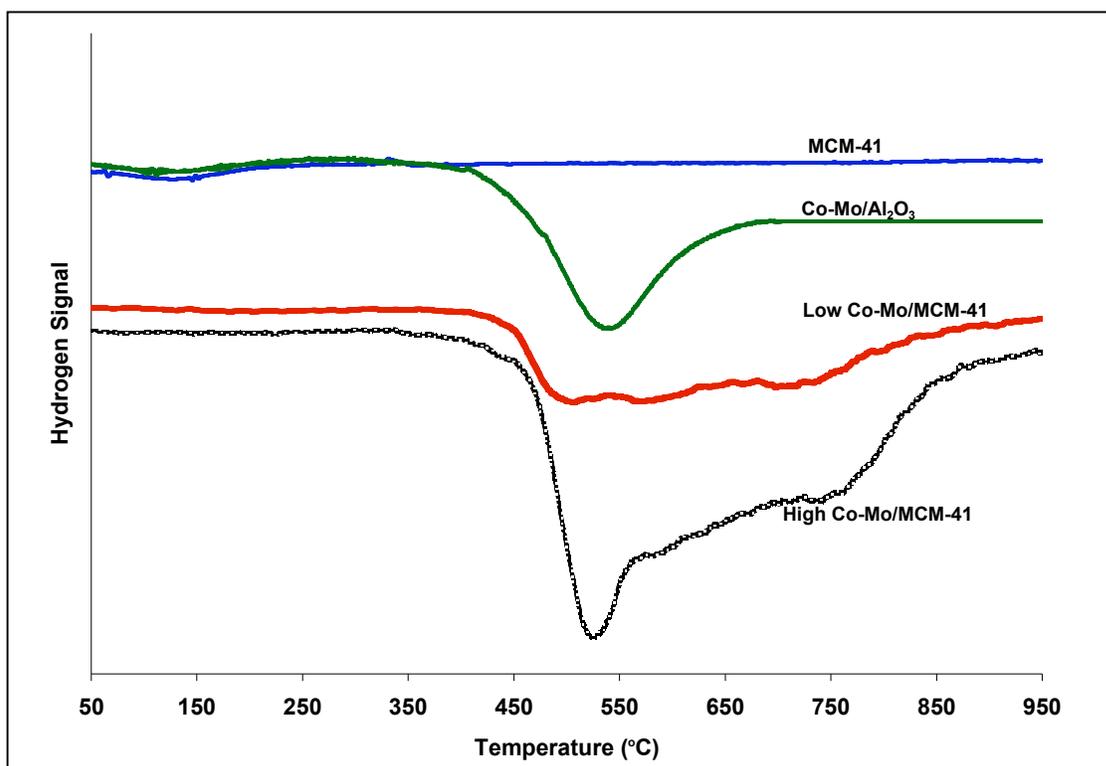
**Figure 18**. Temperature-programmed reduction traces of different catalysts.
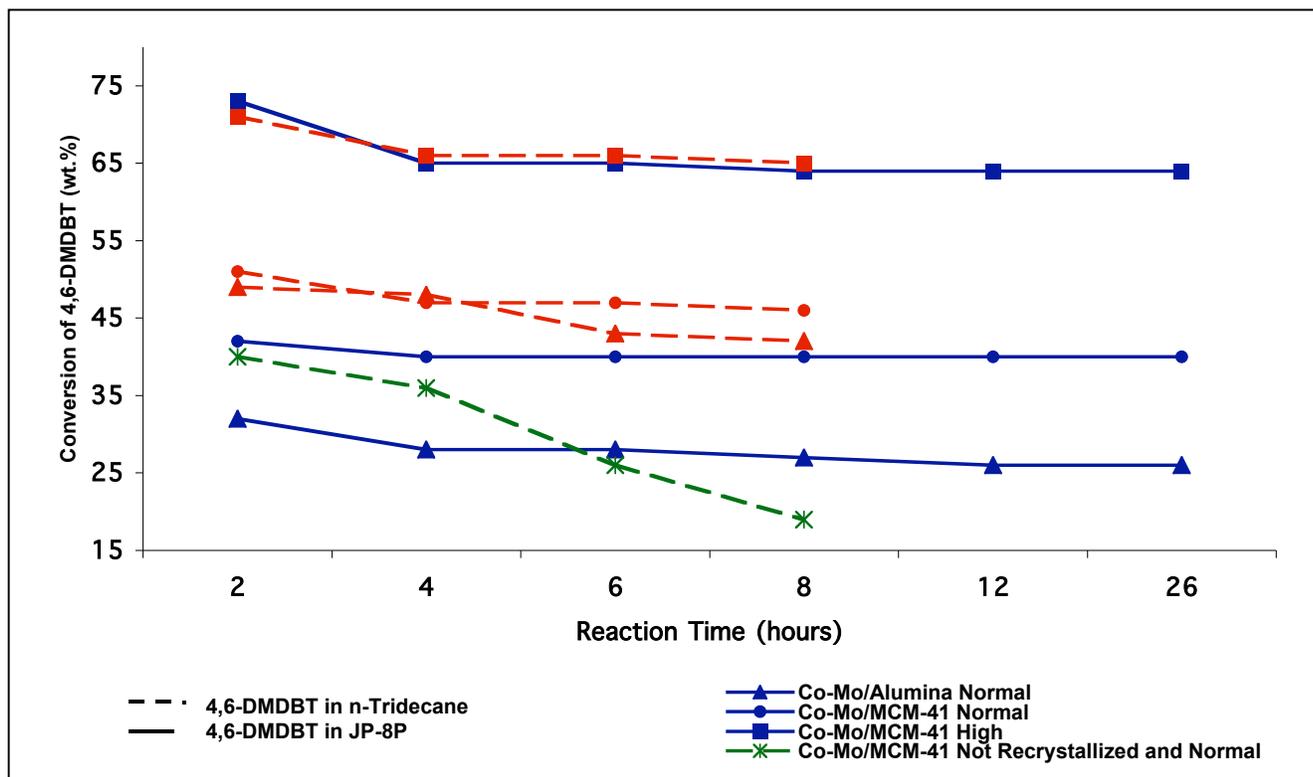
Figure 19. Time on stream studies of different catalysts for 4,6-DMDBT in n-tridecane and petroleum-derived jet fuel (JP-8P).
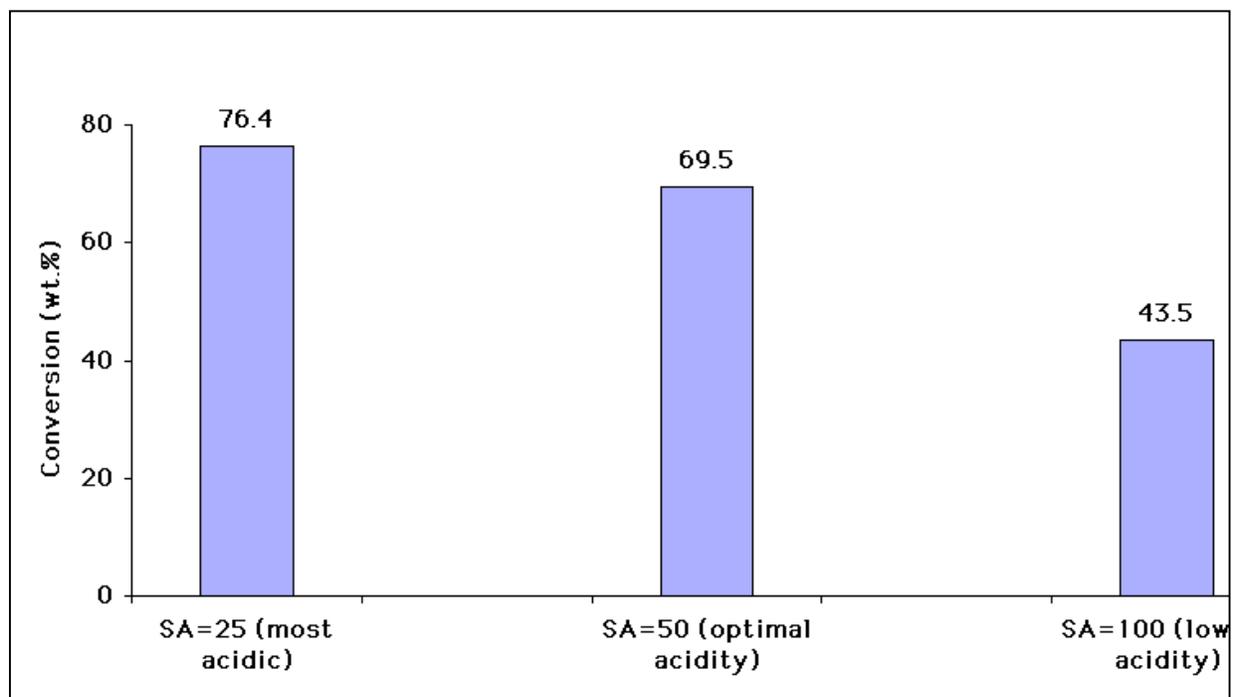
Figure 20. Influence of SiO_2/Al_2O_3 ratio on conversion of 4,6-DMDBT in n-tridecane.
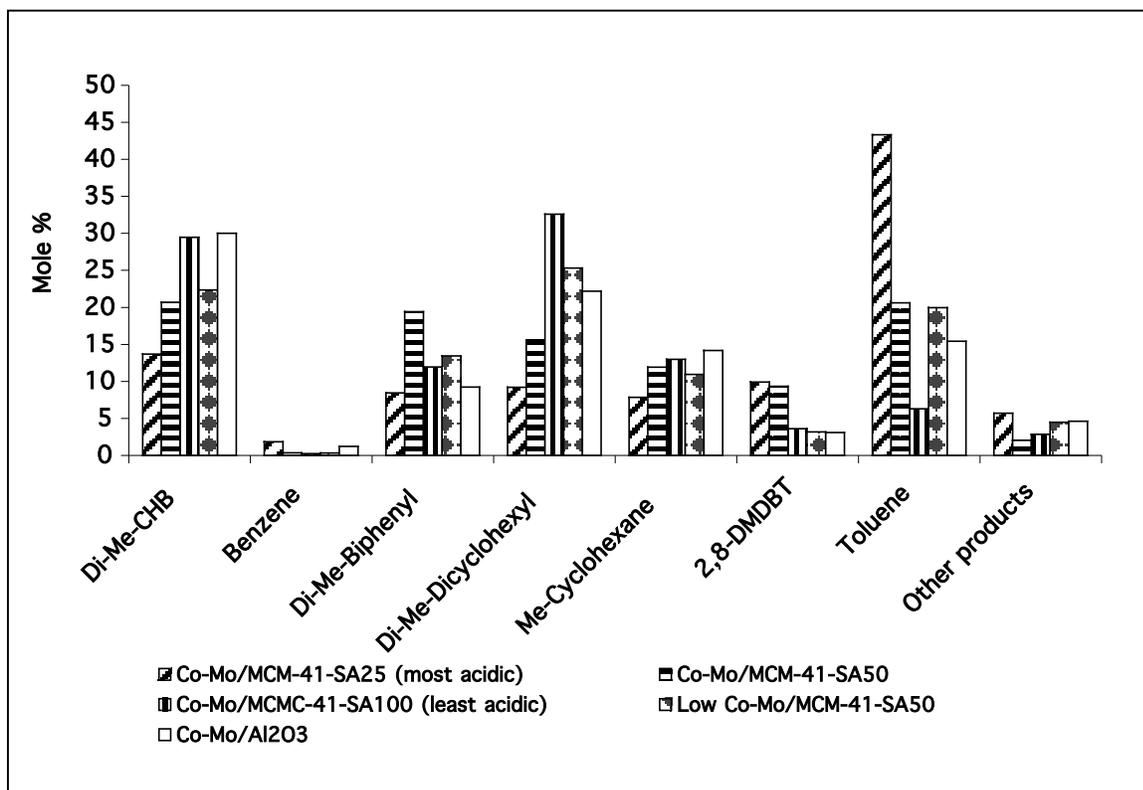
**Figure 21.** Product distribution of HDS of 4,6-DMDBT in n-tridecane over different catalysts.
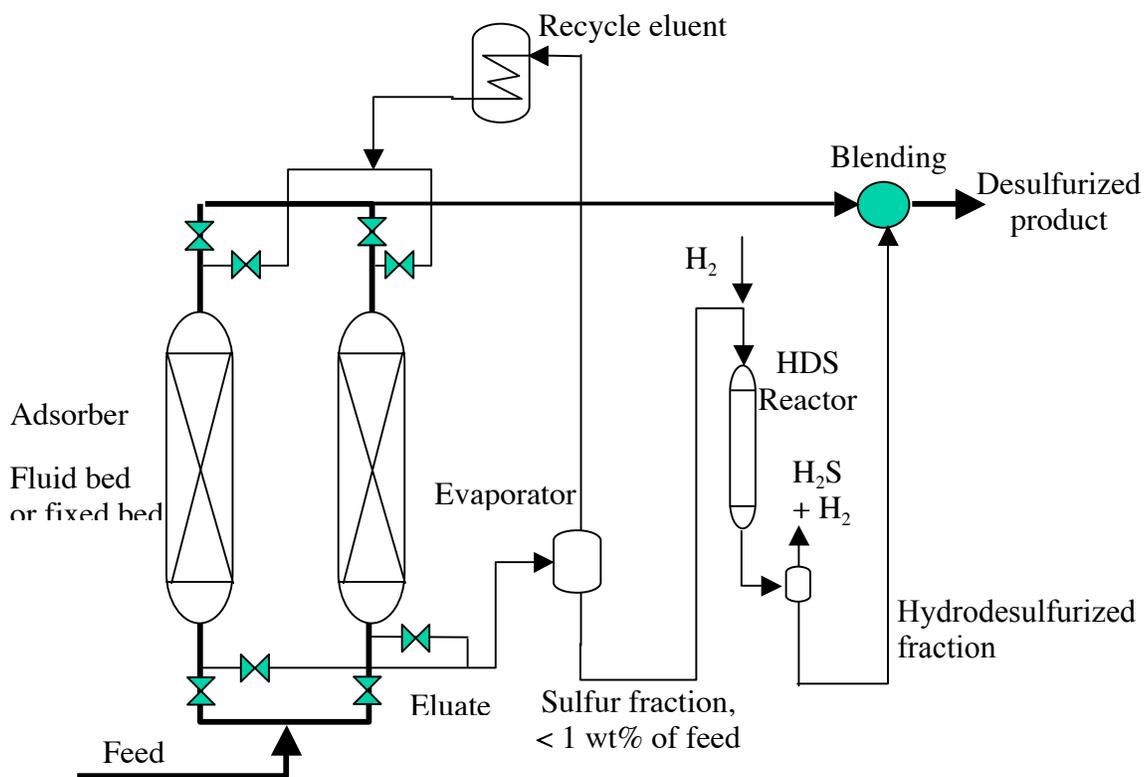
Figure 22. The proposed integrated process (PSU-SARS)for ultra-deep desulfurization based on selective adsorption and hydrodesulfurization of concentrated sulfur fraction

List of Tables

Table 1. Composition of model diesel fuel I (MDF-I)

No	nam	Conte wt	S wt
Sulfur			
	DBT(98	0.16	29
	4,6-	0.19	29
	tot	0.36	58
Unsaturated			
	naphthale	0.12	
	2-	0.12	
	n-	11.	
	1-	4.	
Paraff			
	n-	19.	
	Tetradeca	62.	
Othe		1.	
Tot		100.	

Table 2. Composition of MDF-II

No.	name	Concentration		
		wt %	mmol/l	ppmw
	Sulfur compounds			
1	**DBT**	0.095	3.93	165
2	**4-MDBT**	0.099	3.81	160
3	**4,6-DMDBT**	0.107	3.85	162
	Total		11.59	486
4	Naphthalene (99%)	0.067		
5	2-methylnaphthalene (98%)	0.074		
6	n-Hexadecane(99+%)	39.97		
7	n-Dodecane(99+%)	39.50		
8	n-Tetradecane (99+%)	0.109		
9	Decalin(99+%)	9.988		
10	t-Butylbenzene(99%)	9.988		

Table 3. Composition of MDF-III

No.	name	Concentration		
		wt %	mmol/l	ppmw
1	**DBT(99+%)**	0.115	4.84	200
2	1-methylnaphthalene(97%)	0.090	4.89	
3	n-Hexadecane(99+%)	88.67		
4	n-Tetradecane (99+%)	0.122		
5	n-butylbenzene(99%)	10.01		
	others	1.00		
	total	100.0		

Table 4. Composition and Property of DF

Density, 60	0.8324
Cetane No.	46.8
Cetane	47.3
Sulfur,	325
Carbon	0.07
Polycyclic aromatic hydrocarbon content	
(GC-SFC,	8.29
Viscisity at 40 ˚C	2.482
Pour point	-
Cloud point	-
Distillation temperature,	
IB	344
T50	496
FBP	627

Table 5. Composition and Property of LSD-I

Density, 60	0.8331
Cetane No.	55.4
Cetane	51.8
Sulfur,	47
C, wt %	86.22
H, wt%	13.78
N, wt%	0.00
Aromatics,	21
Oledins,	1.8
Parafins,	77.2
Distillation temperature,	
IBP	343
10	409
30	459
50	503
70	554
90	617
FBP	664

Table 6. Summary of flow reactor experimental conditions.

CATALYST SULFIDATION	
Temperature	350°C
10% H_2S in H_2 (vol.%) flow rate	200 ml/min
Time	4 hours
DEEP HDS REACTION	
Temperature	350°C
Pressure	660 psi
WHSV	2 h^{-1}
Hydrocarbon/hydrogen (ml/ml)	300
Pellet size	0.5-1.0 mm (18-35 mesh)
Catalyst + diluent volume	5 ml