



Deep Desulfurization of Diesel Fuels by a Novel Integrated Approach

Semi-annual Technical Progress Report
For the period
March 1 – August 31, 2002

Grant Number: DE-FG26-00NT40821

Xiaoliang Ma, Michael Sprague, Lu Sun and Chunshan Song*

**Clean Fuels and Catalysis Program, The Energy Institute, and
Department of Energy & Geo-Environmental Engineering
The Pennsylvania State University
University Park, 209 Academic Projects Building, PA 16802**

*E-Mail: cong@psu.edu/Tel: 814-863-4466/ Fax: 814-865-3248

**Submitted to
AAD Document Control Center, M/S 921-107
National Energy Technology Center
US Department of Energy Institute
P.O. Box 10940
Pittsburgh, PA 15236**

October 2002

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, mark manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

1. Abstract

In order to reduce the sulfur level in liquid hydrocarbon fuels for environmental protection and fuel cell applications, deep desulfurization of a model diesel fuel and a real diesel fuel was conducted by our SARS (selective adsorption for removing sulfur) process using the adsorbent A-2. Effect of temperature on the desulfurization process was examined. Adsorption desulfurization at ambient temperature, 24 h^{-1} of LHSV over A-2 is efficient to remove dibenzothiophene (DBT) in the model diesel fuel, but difficult to remove 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT). Adsorption desulfurization at $150\text{ }^{\circ}\text{C}$ over A-2 can efficiently remove DBT, 4-MDBT and 4,6-DMDBT in the model diesel fuel. The sulfur content in the model diesel fuel can be reduced to less than 1 ppmw at $150\text{ }^{\circ}\text{C}$ without using hydrogen gas. The adsorption capacity corresponding to the break-through point is 6.9 milligram of sulfur per gram of A-2 (mg-S/g-A-2), and the saturate capacity is 13.7 mg-S/g-A-2. Adsorption desulfurization of a commercial diesel fuel with a total sulfur level of 47 ppmw was also performed at ambient temperature and 24 h^{-1} of LHSV over the adsorbent A-2. The results show that only part of the sulfur compounds existing in the low sulfur diesel can be removed by adsorption over A-2 at such operating conditions, because 1) the all sulfur compounds in the low sulfur diesel are the refractory sulfur compounds that have one or two alkyl groups at the 4- and/or 6-positions of DBT, which inhibit the approach of the sulfur atom to the adsorption site; 2) some compounds coexisting in the commercial low sulfur diesel probably inhibit the interaction between the sulfur compounds and the adsorbent. Further work in determining the optimum operating conditions and screening better adsorbent is desired.

2. Table of Contents

1. Abstract.....	2
2. Table of Contents	3
3. List of Graphical	4
4. Introduction.....	5
5. Executive Summary	6
6. Experimental	8
6.1. Modifying the Flowing Adsorption Device	8
6.2. Feeds	8
6.3. Adsorbents.....	9
6.4. Adsorption Experiments.....	9
6.5. Sample Analysis	9
7. Results and Discussion	10
7.1. Identification of Sulfur Compounds in Commercial Diesel Fuels	10
7.2. Adsorption Desulfurization of Model Diesel over A-2	10
7.2.1. Adsorption Capacity	10
7.2.2. Adsorption Selectivity.....	11
7.2.3. Effect of Temperature	11
7.3. Molecular Configuration and Electron Density on the Sulfur Atom	12
7.4. Adsorption Desulfurization of Real Diesel over A-2	12
8. Conclusions.....	13
9. References.....	14

3. List of Graphical

Figure 1. GC-FPD/PFPD chromatograms of commercial diesel fuels

Figure 2. Sulfur concentration as a function of the treated MD-4 volume in adsorption desulfurization at 25 °C and 24 h⁻¹ of LHSV.

Figure 3. Molar concentration of each compound as a function of the treated MD-4 Volume at 25 °C and 24 h⁻¹ of LHSV.

Figure 4. Molar concentration of each compound as a function of the treated MD-4 Volume at 150°C, and 4.8 h⁻¹ of LHSV.

Figure 5. Electron density isosurface of DBT, 4-MDBT and 4,6-DMDBT

Figure 6. Sulfur concentration as a function of the treated low sulfur diesel at 25°C, and 24 h⁻¹ of LHSV.

4. Introduction

The overall objective of this project is 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 in diesel fuels.

The major challenge to our proposed approach is to attract and 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.

Recently, ultra-deep removal of sulfur from transportation fuels is becoming very important and is a very hot topic in R&D worldwide not only because the heightened interest for cleaner air and thus increasingly stringent environmental regulations for fuel sulfur content such as US EPA's tier II sulfur regulations for Yr. 2006, but also because the great need for making ultra-low-sulfur fuels for use in fuel cells as well as new vehicles that are much more efficient and environmentally friendly than existing cars and trucks today (Song and Ma, 2002).

For the automotive fuel cells and micro-fuel cells, liquid hydrocarbons are promising candidate fuels due to their higher energy density and safety for transportation and storage. For the automotive fuel cells, especially for the current developing SOFC and PEFC auxiliary power unit for automobile, gasoline and diesel are preferred fuels as their ready availability and the existing infrastructure in production, delivery and storage. However, the current commercial gasoline and diesel usually contain significant amounts of sulfur up to 350 and 500 ppmw, respectively. The sulfur compounds in the fuels and H_2S produced from these sulfur compounds in the hydrocarbon reforming process are poisonous to both the catalysts in hydrocarbon fuel processor and the electrode catalysts

in fuel cell stack. Thus, for fuel cell applications, the sulfur content in the fuels needs to be reduced to a very low level (< 0.1 ppmw for PMCF and < 5 ppmw for SOFC).

In terms of technology availability, the current hydrotreating technology is difficult to reduce the sulfur content in diesel to less than 50 ppmw, because the remaining sulfur compounds in current commercial diesel are 4-methyldibenzothiophene (4-MDBT), 4,6-dimethyldibenzothiophene, and other alkyl dibenzothiophenes with one and/or two alkyl groups at the 4- and/or 6-position (Ma et al., 2001), which are difficult to remove. Consequently, development of new deep desulfurization processes of diesel becomes one of the major challenges in hydrocarbon processing for the diesel-based fuel cell applications. We are proposing and exploring a new process called SARS (selective adsorption for removing sulfur) (Ma et al., 2001; Song, 2002; Song and Ma, 2002; Ma et al., 2002a, 2002b). Our recent studies involved SARS-I (Ma et al., 2001; Ma et al., 2002b; Song, 2002a; Song and Ma, 2002) and SARS-II processes (Ma et al., 2002a, 2002c, Song, 2002b) by using adsorbent A-1 and adsorbent A-2, respectively, for ultra-deep desulfurization of liquid hydrocarbon fuels. The SARS-I and SARS-II differ from each other with respect to the type and nature of the adsorbent materials (A-1 for SARS-I and A-2 for SARS-II) and the optimum conditions of adsorption and desorption or regeneration. In our previous reports (Ma et al., 2002d) and papers (Ma et al., 2002a, 2002c), we have reported our approaches in adsorbent screen and adsorption desulfurization of gasoline and jet fuel (JP-8) by SARS-I and SARS-II processes using adsorbent A-1 and A-2, respectively. We found that the A-2 is one of the most promising adsorbent for removing sulfur from liquid hydrocarbons in terms of the adsorption capacity and selectivity. In the present report, we will report our new approaches in deep desulfurization of model diesel and real diesel over adsorbent A-2 for environmental protection and fuel cell applications.

5. Executive Summary

In the present period of performance, our approaches focused on 1) modifying the flowing adsorption device; 2) conducting the adsorption desulfurization of diesel by

SARS-2 process; 3) measuring capacity and selectivity of the adsorbent A-2; 4) examining the effects of operating conditions on adsorption process.

- The flowing adsorption device in our laboratory has been modified to become a four-channel flowing adsorption device, which allows testing four adsorbents simultaneously. Pretreatment of adsorbents and regeneration of the spent adsorbents can also be run by using the same device at different temperature and pressure with different carrier gases or liquids.
- Identification of sulfur compounds in a commercial diesel and low sulfur diesel was performed.
- Adsorption desulfurization of a model diesel fuels have been conducted at different conditions by our developed SARS-II process using A-2 adsorbent to examine the A-2 performance and capacity.
- Adsorption desulfurization of a model diesel fuels have been conducted at different temperatures over A-2 to examine the A-2 performance and capacity for diesel desulfurization.
- The adsorption selectivity of A-2 in desulfurization of the model diesel fuel have been examined and measured.
- Molecular configuration of the some refractory sulfur compounds existing in the commercial diesel has been simulated and the electron density on sulfur atom in the sulfur compounds has been calculated for discussing their different selectivity.

6. Experimental

6.1. Modifying the Flowing Adsorption Device

In order to increase the experimental efficiency, a single-channel flowing adsorption device in our laboratory has been modified to become a four-channel flowing adsorption device 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 different temperatures and different LHSV. Pretreatment and regeneration of adsorbent can be also conducted by using the same device at a temperature range from ambient temperature to 700 °C. The flowing rate of liquid phase and gas phase can be controlled. The loading of adsorbent sample can be changed from 1.25 to 20 ml.

6.2. Feeds

A model diesel feed was made for examining the adsorption capacity and selectivity. The model diesel (MD-4) contains 0.096 wt % of dibenzothiophene (DBT), 0.102 wt % of 4-MDBT, and 0.109 wt% of 4,6-DMDBT, corresponding the sulfur contents of 164, 159.9 and 161.6 ppmw, respectively. MD-4 also contains 10 wt% of butylbenzene for mimicking the aromatics in the real diesel. The saturates in the model diesel are n-hexadecane, n-dodecane and decalin. The model diesel also contains naphthalene and 2-methylnaphthalene with a molar concentration as the same as each sulfur compound in MD-4 for analysis of selectivity. All chemicals contained in the model diesel were purchased from Aldrich, and were utilized without further purification. The detailed composition of MD-4 is listed in Table 1.

A real low sulfur diesel fuel was also used in the adsorption experiment. The composition and property of the fuel are listed in Table 2.

6.3. Adsorbents

The adsorbent used in the present study is A-2, which is a metal-based adsorbent prepared from a transition metal with a surface area of 80-100 m²/g. A-2 is one of the most promising adsorbents that we screened from many candidates.

6.4. Adsorption Experiments

All adsorption experiments of MD-4 and the real diesel over A-2 were performed at designed temperatures by using the flowing adsorption device under ambient pressure. A stainless column with an internal diameter of 4.6 mm and length of 150 mm was used. The adsorbent bed volume is 2.49 ml. The feed was pumped into the column and flowed up through the adsorption bed at a flowing rate of 1.0 ml/min or 0.20 ml/min. The treated fuel flowed out from the top of the column and was collected for analysis.

6.5. Sample Analysis

The quantitative analysis of sulfur compounds and aromatic hydrocarbons in the model diesel and the treated model diesel was conducted by using the 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 sulfur compounds in the real diesel fuels were analyzed using the same GC and capillary column with a pulsed flame photometric detector (PFPD).

Identification of the sulfur components in the fuels is based on a combination of various techniques, including HPLC, sulfur-selective ligand exchange chromatography (Ma et al., 1997), GC-MS (Ma et al., 1994, 1997), retention time comparison with literature data (Depauw and Froment, 1997; Chawla and Sanzo, 1992) HDS reactivities of various sulfur compounds (Ma et al., 1994; 1997)] and understanding of the elution order of the isomers (Lai and Song, 1995).

The total sulfur concentration of the real diesel and the treated diesels 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 a commercial diesel and a commercial low sulfur diesel used in the present study are shown in Figure 1. The sulfur compounds in the currently commercial diesel with sulfur content around 500 ppmw are alkyl benzothiophenes, DBT and alkyl DBTs. The major sulfur compounds are alkyl DBTs with one or two alkyl group(s) at the 4- and/or 6-position. In the low sulfur diesel (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. These sulfur compounds are the refractory sulfur compounds, including 4-MDBT, 4,6-DMDBT, 4-ethyl-4-methyldibenzothiophene (4-E,6-MDBT) and 2,4,6-trimethyldibenzothiophene.

7.2. Adsorption Desulfurization of MD-4 over A-2

7.2.1. Adsorption Capacity

Adsorption desulfurization of MD-4 was conducted at ambient temperature and ambient pressure by using adsorbent A-2. The flowing rate of MD-4 was 1.0 ml/min and the LHSV was 24 h⁻¹. The sulfur concentration of each sulfur compound at the outlet as a function of volume of the treated MD-4 is shown in Figure 2. The total sulfur concentration in the first collected fraction, corresponding to 1.2 ml of the effluent volume, is 15 ppmw, and then, it increases with increasing volume of the treated MD-4. The adsorbent A-2 is saturated when the effluent volume reaches about 250 ml. After the saturate point, the sulfur concentration increases continuously with increasing of effluent volume, and then, decreases to the concentration close to that in the initial feed. It indicates that some adsorbed sulfur compounds are carried out by the effluent. The adsorption capacity of A-2 corresponding the saturation point is 13.9 milligram of sulfur per gram of the adsorbent (mg-S/g-A-2).

7.2.2. Adsorption Selectivity

Figure 3 presents the molar concentration of sulfur compounds, naphthalene and 2-methylnaphthalene as a function of volume of the treated MD-4. By comparing various sulfur compounds, no DBT is detected in the treated MD-4 when the effluent volume is less than 167 ml. However, 4-MDBT and 4,6-DMDBT break through at the beginning and then, their concentration increases with increasing volume of the treated MD-4. The concentration of 4-MDBT and 4,6-DMDBT at outlet before the saturation point (250 ml) is much higher than that of DBT, while the concentration of 4,6-DMDBT is slightly higher than that of 4-MDBT, as shown in Figure 3. This result indicates that the alkyl groups at 4- and 6-positions inhibit the interaction between the sulfur atom in the sulfur compounds and adsorption site, thus, reduce the adsorption capacity of A-2. Naphthalene and 2-methylnaphthalene have the same molar concentration as 4-MDBT and 4,6-DMDBT in the initial fuel. Their molar concentration at the outlet, as shown in figure 3, is similar to those of 4-MDBT and 4,6-DMDBT, indicating that at such operating conditions the adsorbent A-2 does not exhibit the selective adsorption toward 4-MDBT and 4,6-DMDBT.

7.2.3. Effect of Temperature

Adsorption desulfurization of MD-4 at 150 °C, 24 h⁻¹of LHSV was also conducted to examine the temperature effect. The total sulfur concentration at the outlet as a function of volume of the treated MD-4 is shown in Figure 2. No detectable sulfur compounds were found in the treated MD-4 when the effluent volume is less than 55 ml, indicating that all sulfur, including the sulfur in 4-MDBT and 4,6-DMDBT in MD-4, was removed by the selective adsorption. The corresponding break-through adsorption capacity is 6.9 mg-S/g-A-2. After the break-through point, the concentration of the total sulfur increases with increasing volume of the treated MD-4. The adsorbent was saturated when the effluent volume increases to about 180 ml. The saturate capacity is about 13.6 mg-S/g-A-2. The results imply that increase in the operating temperature can enhance the break-through capacity, but fails to enhance the saturate capacity.

By comparing the concentration of various sulfur compounds at the outlet, it is clear that the break-through volume decreases in the order of DBT > 4-MDBT > 4,6-DMDBT, being 112, 83 and 49 ml, respectively, as shown in Figure 4. The results show that the adsorption selectivity of sulfur compounds decreases in the order of DBT > 4-MDBT > 4,6-DMDBT, although the increase in the operating temperature can increase the adsorption selectivity toward 4-MDBT and 4,6-DMDBT.

7.3. Molecular Configuration and Electron Density on the Sulfur Atom

In order to explaining the different adsorption selectivity, molecular simulation of DBT, 4-MDBT, 4,6-DMDBT was performed by using a semi-empirical quantum chemical calculation, MOPAC-PM3, to get the information in the molecular configuration and the electron density on sulfur atom. The simulation results are shown in Figure 5. There are usually two factors that affect the selectivity: electron factor and geometrical factor. According to the calculated results, there is no significant difference in the electron density on the sulfur atom in the three sulfur compounds. However, the methyl groups at the 4- and/or 6-position show a strongly steric hindrance, which block the way for the sulfur atom to approach the adsorption site. The calculations suggest that the steric hindrance of methyl group be a major factor that results in the low adsorption selectivity of 4-MDBT and 4,6-DMDBT.

7.4. Adsorption Desulfurization of Real Diesel over A-2

Adsorption desulfurization of a real diesel over A-2 was performed at ambient temperature and ambient pressure. The flow rate of the diesel was 1.0 ml/min with LHSV of 24 h⁻¹. The total sulfur concentration at the outlet as a function of volume of the treated diesel is shown in Figure 6. There is 15 ppmw of sulfur in the first collected fraction, corresponding to the effluent volume of 3.7ml, although the low sulfur diesel fuel contains only 48 ppmw of sulfur. After that, the sulfur concentration increases gradually with increasing effluent volume. When the effluent volume reaches 488 ml, the sulfur concentration increase to 41 ppmw, lower than the sulfur concentration in the

Feed. The corresponding adsorption capacity is 0.65 mg-S/g-A-2, much lower than that for the model diesel MD-4. This capacity is also much lower than those for desulfurization of real gasoline and real Jet fuel on A-2 (Ma et al., 202a, 2002c). It might imply that 1) some sulfur compounds in the low sulfur diesel are more difficult to be removed due to the steric hindrance of alkyl groups; 2) some compounds coexisting in the diesel probably inhibit the adsorption of the sulfur compounds on the adsorbent.

8. Conclusions

During this period, we explored the deep desulfurization of diesel by selective adsorption over the adsorbent A-2.

- Our experimental results show that DBT in diesel fuel can be removed efficiently by selective adsorption over A-2 at ambient temperature without using hydrogen gas.
- 4-MDBT and 4,6-DMDBT in the model diesel fuel can be removed partially at ambient temperature and 24 h⁻¹ of LHSV without using hydrogen gas.
- Adsorption desulfurization at 150°C, 24 h⁻¹ of LHSV over A-2 can efficiently remove 4-MDBT and 4,6-DMDBT as well as DBT. The break-through adsorption capacity is 6.9 mg-S/g-A-2 and the saturation capacity is about 13.6 mg-S/g-A-2. Increase in the operating temperature can enhance the break-through capacity, but fails to enhance the saturate capacity.
- Molecular simulation suggests that the steric hindrance of methyl group be a major factor that results in the low adsorption selectivity of 4-MDBT and 4,6-DMDBT.
- Adsorption desulfurization of a real diesel over A-2 shows that about a half of sulfur in the low sulfur diesel can be removed at ambient temperature and 24 h⁻¹

of LHSV. In order to reduce the sulfur level in the diesel to less than 1 ppmw, higher operating temperature and/or lower LHSV are required.

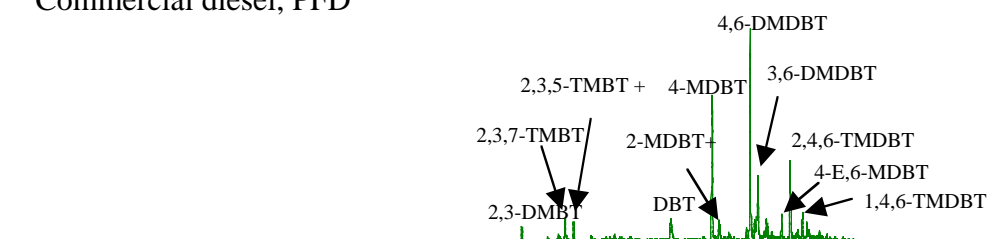
9. References

- Chawla, B., Sanzo, F. D. 1992, J. Chromatogr. 589, 271-279
- Depauw, G. A., Froment, G. F., 1997, J. Chromatogr. A 761, 231-247.
- Lai, W. C., Song, C., 1995, Fuel, 74, 1436.
- Ma, X., Sakanishi, K., Mochida, I., 1994, Ind. Eng. Chem. Res. 33, 218-222.
- Ma, X., Sakanishi, K., Isoda T., Mochida, I. 1997, Fuel, 76, 329-339.
- Ma, X., Sun, L., Yin, Z. and Song, C. 2001, Am. Chem. Soc. Div. Fuel Chem. Prepr., 46 (2), 648-649.
- Ma, X., Sprague, M., Sun, Lu., and Song, C., 2002a, Am. Chem. Soc. Div. Petrol. Chem. Prepr., 47 (1), 28.
- Ma, X.; Sun, L.; Song, C. 2002b, Catal. Today, in press.
- Ma, X., Sprague, M., Sun, Lu., and Song, C., 2002c, Am. Chem. Soc. Div. Fuel Chem. Prepr., 47 (2), 452.
- Ma, X., Sprague, M., Sun, Lu., and Song, C., 2002d, DOE semi-annual report, March 1, 2002 – August 31, 2002, Grant Number: DE-FG26-00NT40821
- Song, C., 2002a, Keynote paper, Proceedings of the 5th International Conference on Refinery Processing, AIChE Spring 2002 National Meeting, New Orleans, LA, March 10-14, 2002.
- Song, C., 2002b, Am. Chem. Soc. Div. Fuel Chem. Prepr., 47 (2), 438.
- Song, C., Ma, X., 2002, Appl. Catal. B, in press.

Table 1. Composition of Model Diesel Fuel (MD-4)

	name	Weight percent wt %	S content ppmw	Molar concentration mmol/l
Sulfur compounds				
1	DBT	0.0948	165	3.93
2	4-MDBT	0.1020	160	3.81
3	4,6-DMDBT	0.1092	162	3.85
	total		486	
Hydrocarbon				
4	naphthalene	0.0659		3.93
5	2-methylnaphthalene	0.0717		3.93
6	n-Hexadecane	39.97		
7	n-Dodecane	39.50		
8	n-Tetradecane	0.109		
9	Decalin	9.988		
10	t-butylbenzene	9.988		

Commercial diesel, PFD



Commercial low sulfur diesel (47 ppmw), PFPD

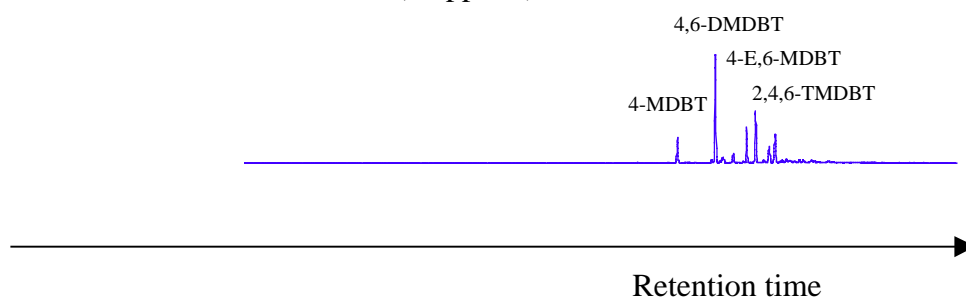


Figure 1. GC-FPD/PFPD Chromatograms of Commercial Diesel Fuels

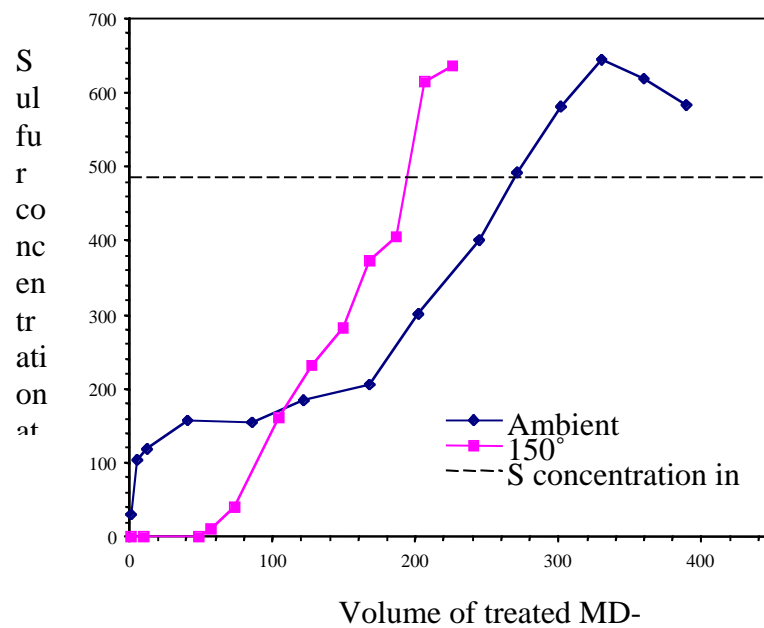


Figure 2. Sulfur concentration as a function of the treated MD-4 volume in adsorption desulfurization at 25 °C and 24 h⁻¹ of LHSV.

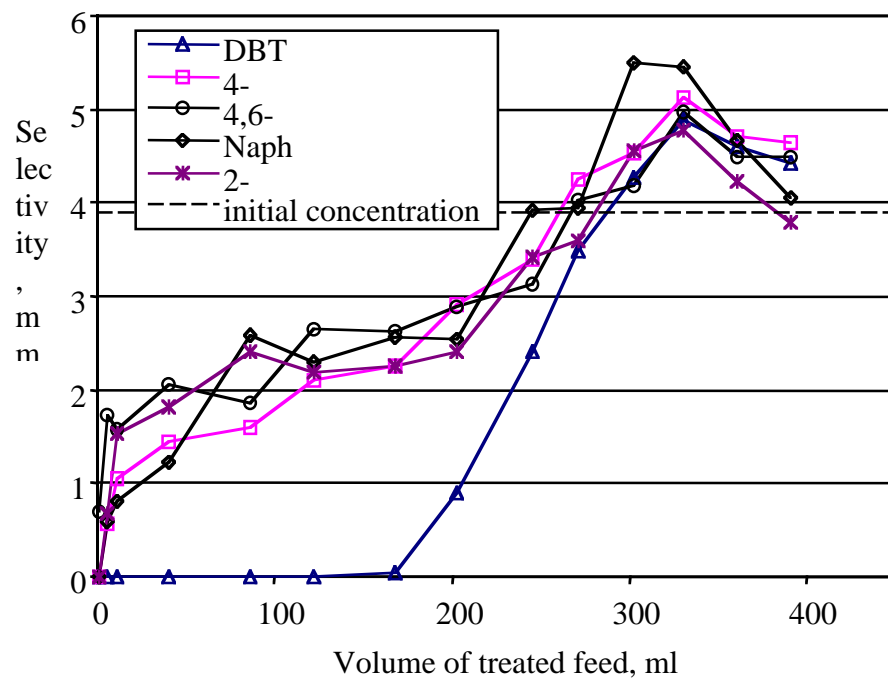


Figure 3. Molar concentration of each compound as a function of the treated MD-4 volume at 25 °C and 24 h⁻¹ of LHSV.

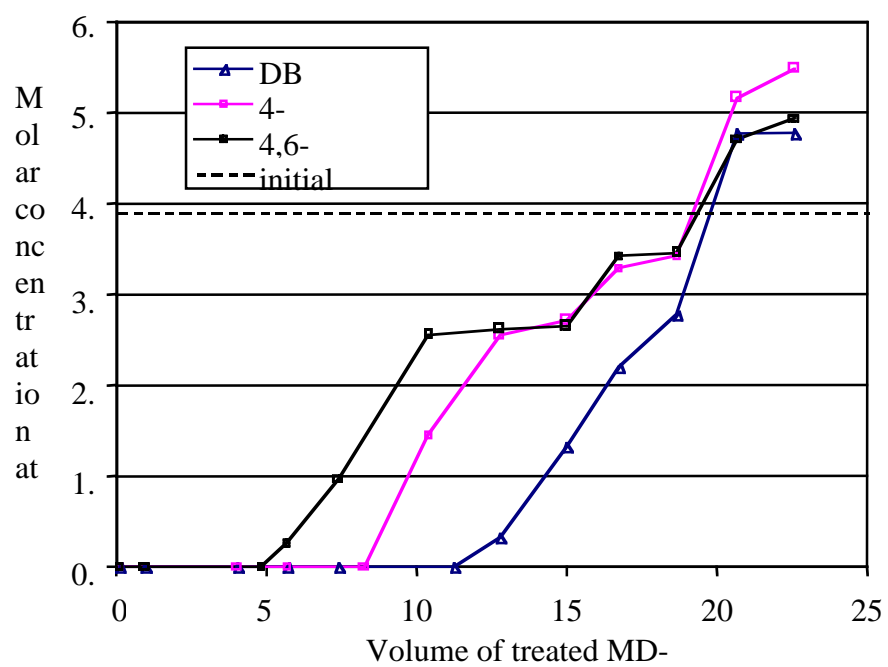


Figure 4. Molar concentration of each compound as a function of the treated MD-4 volume at 150°C , and 4.8 h^{-1} of LHSV.

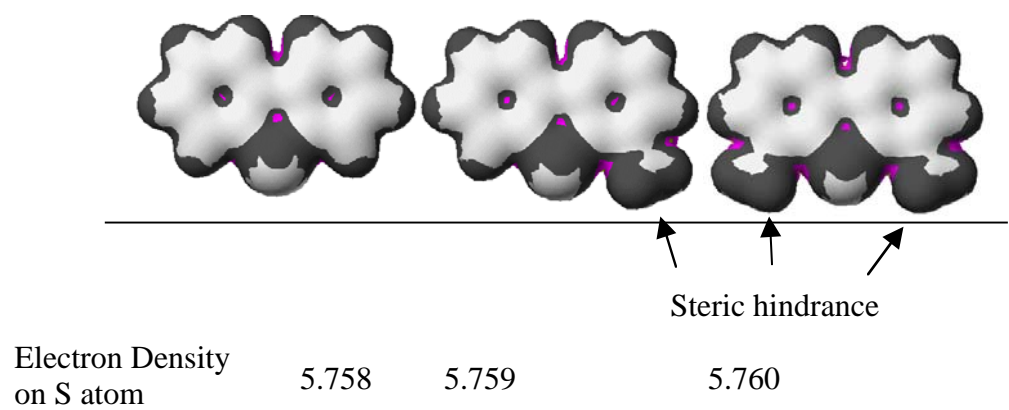


Figure 5. Electron density isosurface of DBT, 4-MDBT and 4,6-DMDBT

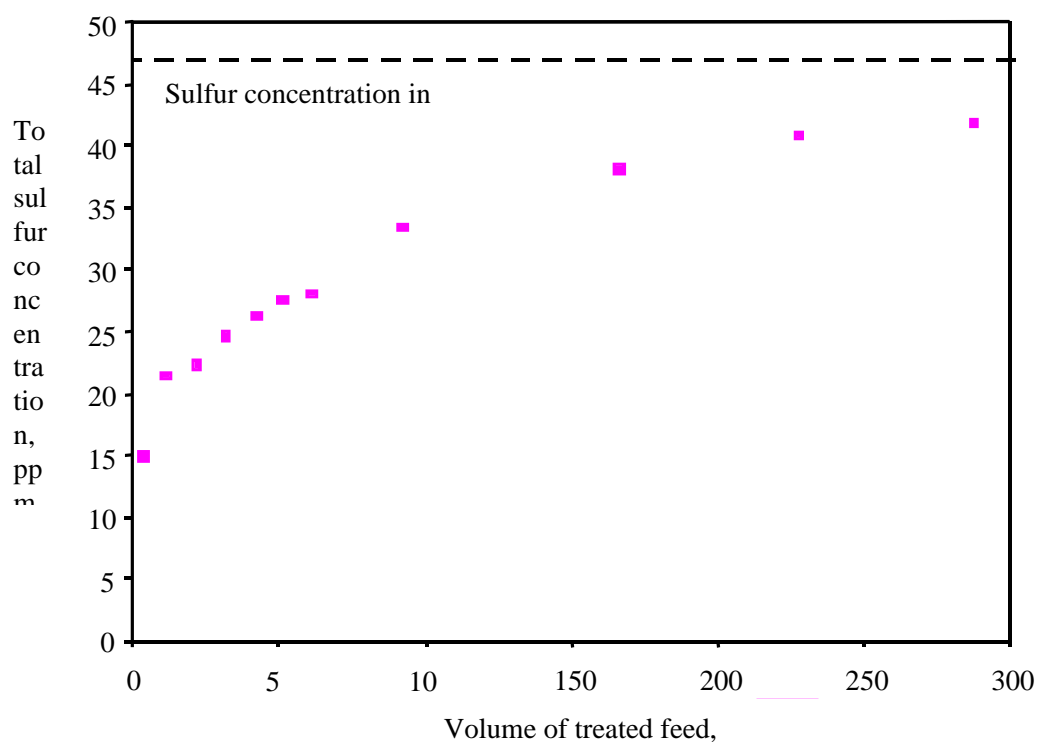


Figure 6. Sulfur concentration as a function of the treated low sulfur diesel at 25°C, 24 h⁻¹ of LHSV