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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

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Abstract

In order to further reduce the sulfur content in liquid hydrocarbon fuels (gasoline, diesel fuel and jet fuel) for producing ultra-clean transportation fuels and for fuel cell applications, we explored a new desulfurization process by selective adsorption for removing sulfur (SARS). An adsorbent was developed and used for adsorption desulfurization of diesel fuel, gasoline and jet fuel at room temperature. The results indicate that the transition metal-based adsorbent developed in this work is effective for selectively adsorbing the sulfur compounds, even the refractory sulfur compounds in diesel fuels. The SARS process can effectively remove sulfur compounds in the liquid hydrocarbon fuels at ambient temperature under atmospheric pressure with low investment and operating cost. On the basis of the present study, a novel integrated process is proposed for deep desulfurization of the liquid hydrocarbon fuels in a future refinery, which combines a selective adsorption (SARS) of the sulfur compounds and a hydrodesulfurization process of the concentrated sulfur fraction (HDSCS). The SARS concept may be used for on-site or on-board removal of sulfur from fuels for fuel cell systems.

Keywords: Adsorption; Desulfurization; Fuel cell; Gasoline; Diesel fuel; Jet fuel

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1. Introduction

Deep desulfurization of transportation 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. Recently, US Environmental Protection Agency has issued regulations that will require the refineries to reduce the sulfur content of gasoline from a current average of 300 to 30 parts per million by weight (ppmw) by 2006, and the sulfur content of highway diesel fuel from a current limit of 500 to 15 ppmw by 2006 [1].

In terms of technology availability, the sulfur content in gasoline can be reduced to less than 30 ppmw by current hydrotreating processes. The major problem for deep desulfurization of gasoline is that the conventional hydrotreating technology results in a significant reduction of octane number due to saturation of olefins in naphtha from fluid catalytic cracking, which also causes higher hydrogen consumption [1]. For diesel fuel, the current hydrotreating technology is difficult to reduce the sulfur content to less than 15 ppmw, because the remaining sulfur compounds in current diesel fuel with 500 ppmw S level are the refractory sulfur compounds [1–5]. These refractory

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sulfur compounds are the alkyl dibenzothiophenes (DBTs) with one or two alkyl groups at 4- and/or 6-positions, which strongly inhibit hydrodesulfurization of the compounds [6–8]. A kinetic study shows that in order to reduce the sulfur content of the diesel fuel from 500 to less than 15 ppmw using the current hydrotreating technology, the reactor volume or the catalyst activity must be at least three times larger than those currently used in refineries [2]. As is well known, the increase in volume of the high-temperature and high-pressure reactor is very expensive, although the further improvement of catalyst activity over existing hydrotreating catalysts is still possible through continued catalytic research and development.

The production of ultra-low-sulfur fuels is motivated in part by the need for using the new emission-control technologies that are sensitive to sulfur [1]. On the other hand, ultra-low-sulfur fuel is also needed for on-site or on-board use with a fuel cell system [9]. 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, liquid hydrocarbon fuels, including gasoline, jet fuel and diesel fuel, are ideal fuels due to their higher energy density, ready availability, and proven safety for transportation and storage. However, the liquid hydrocarbon fuels usually contain certain sulfur compounds that 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 (anode) catalysts in fuel cell stack. Thus, the sulfur compounds in the liquid hydrocarbons need to be reduced to less than 0.1 ppmw. 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.

The sulfur compounds in the current gasoline corresponding to the S level of 350 ppmw account for only about 0.12 wt.% of the whole gasoline, in the current diesel corresponding to the 500 ppmw S level account for only about 0.32 wt.% 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 wt.%) fuel in order to convert the fuel mass of less than 0.4 wt.%.

The idea behind our new approach is to selectively separate the less than 1 wt.% of fuel mass by selective adsorption for removing sulfur (SARS), and leave the 99 wt.% of non-sulfur-containing fuel mass untouched. In the present study, we explored a room-temperature adsorption process, which can effectively reduce the sulfur content in gasoline, jet fuel and diesel fuel at low investment and operating cost to meet the needs for ultra-clean transportation fuels and even for fuel cell applications. The 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.

The liquid hydrocarbon fuels contain usually not only sulfur compounds, but also aromatic hydrocarbons at concentrations in the range of 5–35 wt.%, which have the framework and electronic properties similar to those of co-existing aromatic sulfur heterocycles. Gasoline, especially the FCC naphtha, which is a major blend component for gasoline and the dominant source of sulfur compounds in gasoline, also contains high concentration of olefins [1]. Thus, a major challenge for separating the sulfur compounds from the fuels is to find an adsorbent that selectively adsorbs the sulfur compounds, but does not adsorb (or only weakly adsorb) the co-existing aromatic hydrocarbons and olefins. This is because the thiophenic sulfur compounds and pure aromatic and olefinic compounds have some common features due to the presence of one or more double bonds to which metal species can interact [10–12].

2. Experimental

The diesel fuel and gasoline samples used in this study were purchased from a local Sheetz gasoline station and an Exxon gasoline station, respectively, in State College, Pennsylvania. The jet fuel is a JP-8 sample obtained from US Air Force Wright Research Laboratory, WPAFB, in Dayton, Ohio. A model diesel fuel was made for quantitative adsorption analysis.

Table 1
Composition of model diesel fuel density

Name	Content (wt.%)	S content (ppmw)
Sulfur compounds		
DBT (98%)	0.167	286
4,6-DMDBT (97%)	0.195	290
Total	0.362	576
Unsaturated HC		
Naphthalene	0.120	
2-Methylnaphthalene	0.127	
n-Butylbenzene	11.6	
1-Octene	4.7	
Paraffin		
n-Dodecane	19.6	
Tetradecane	62.5	
Others	1.0	
Total	100.0	

The model diesel fuel contains 0.167 wt.% of DBT and 0.196 wt.% of 4,6-DMDBT, corresponding the sulfur contents of 286 and 290 ppmw, respectively. Naphthalene (NA) and 2-methylnaphthalene (2-MNA) with the same molar concentration as that of DBT were added into the fuel for selectivity analysis. The fuel also contains 12 wt.% of aromatic hydrocarbons and 4.7 wt.% olefin for mimic real diesel fuel. The detailed composition of the fuel is listed in Table 1.

The adsorbent (A-1) used in this study was prepared in our laboratory. It is a transition metal compound supported on silica gel with 5.0 wt.% loading of the metal compound. The adsorption experiments were performed at ambient temperature and pressure in a fixed bed using a glass adsorption column with an internal diameter of 11 mm and length of 300 mm. About 5 g of the prepared adsorbent was placed in the column. The fuels were poured into the glass column and flowed down through the adsorption bed. The quantitative analysis of sulfur compounds and aromatic hydrocarbons in the model diesel fuel and treated model diesel fuel was conducted by using the HP5890 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 untreated and treated real fuels were analyzed using a HP5890 gas chromatograph with a capillary column, XTI-5 (Restek, 30 m long, 0.25 mm i.d.) and a sulfur-specific flame photometric detector (FPD). Identification of the sulfur components in the gasoline, jet fuel and diesel is based on a combination of various techniques including GC, HPLC, sulfur-selective ligand exchange chromatography [13], retention time comparison with literature data [14–16], GC–MS [2,16], HDS reactivities of various sulfur compounds [2,5,7] and understanding of the elution order of the isomers [16]. The thiophene (T), 3-methylthiophene (3-MT), benzothiophene (BT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in the samples were identified by GC–MS and further confirmed by direct comparison of retention time with the standards from Aldrich.

3. Results and discussion

3.1. Theoretical considerations

We have considered a theoretical basis for possible adsorption patterns that could distinguish between sulfur-containing and non-sulfur-containing species. Fig. 1 shows the known coordination geometries of thiophene in organometallic complexes. There are eight coordination configurations of thiophene in organometallic complexes [10–12]. There are various interactions between thiophene and metal species through one or more C=C double bonds. However, for exploring selective adsorption, we are interested in the two specific configurations where thiophene coordinates directly with the metal through sulfur–metal interaction, η^1S or S–μ^3-bonding. These configurations suggest that there are likely adsorbents that are able to adsorb the thiophenic compounds selectively through η^1S or S–μ^3-bonding. We have also performed a computational analysis for the electronic properties by using molecular orbital package from CAChe software system (MOPAC). The calculated results show that the highest occupied molecular orbital (HOMO) of thiophene, benzothiophene and dibenzothiophene is located more on the sulfur atom, whereas the HOMO of alkyl benzenes and naphthalene on the conjugated six-member ring. These results suggest that it may be possible to achieve preferential adsorption by interaction of sulfur atom with certain metal species through the interaction of HOMO on sulfur with lowest unoccupied molecular orbital (LUMO) on metal species.

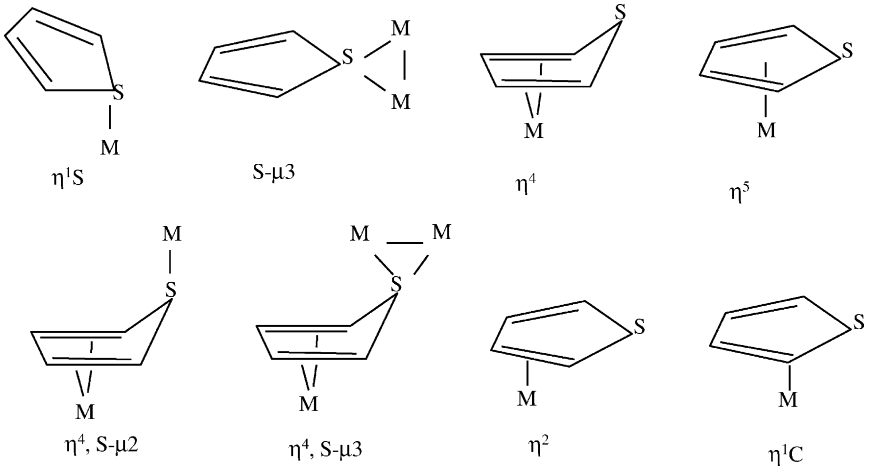

Fig. 1. Known coordination geometries of thiophene with metal species in organometallic complexes.

On the basis of these considerations, we are exploring various transition metal-based adsorbents. The adsorbent that was found to be effective in our initial work is a transition metal compound supported on a porous silica gel which we call A-1 whose performance for SARS is discussed below.

3.2. Identification of sulfur compounds

Fig. 2 presents the FPD gas chromatograms for the gasoline, jet fuel and diesel fuel along with the results of sulfur identifications from our laboratory. The major sulfur compounds that exist in the commercial gasoline are thiophene, 2-methylthiophene (2-MT), 3-methylthiophene, 2,4-dimethylthiophene (2,4-DMT) and benzothiophene. No mercaptans, dialkyl sulfides and dialkyl disulfides were detected, indicating these sulfur compounds have higher reactivity and have been removed from gasoline fraction in the current refining processes. The major sulfur compounds existing in JP-8 jet fuel are 2,3-dimethylbenzothiophene (2,3-DMBT), 2,3,7-trimethylbenzothiophene (2,3,7-TMBT), 2,3,5-trimethylbenzothiophene (2,3,5-TMBT) and/or 2,3,6-trimethylbenzothiophene (2,3,6-TMBT). All these methylbenzothiophenes have two methyl groups at 2- and 3-positions, respectively, implying that the benzothiophenes with two methyl groups at 2- and 3-positions are more difficult to be removed than other sulfur compounds in hydrotreating of the jet fuel. No dibenzothiophenes were detected in the JP-8 sample as the boiling point of dibenzothiophenes is beyond the boiling range of the jet fuel (160–300 °C). The sulfur compounds in the commercial diesel fuel include both alkyl benzothiophenes and alkyl dibenzothiophenes, but the major sulfur compounds are dibenzothiophene derivatives with alkyl groups at 4- and/or 6-positions, including 4-MDBT, 4,6-DMDBT, 3,6-DMDBT and 2,4,6-TMDBT. It implies that the major sulfur compounds remaining in the diesel fuel are the refractory sulfur compounds as they are difficult to be removed by the conventional HDS process [2,3,17]. Thus, we need to pay more attention to these sulfur compounds in deep desulfurization by adsorption.

3.3. Adsorption desulfurization of the model diesel fuel

Desulfurization of the model diesel fuel by adsorption over adsorbent A-1 was performed at ambient (room) temperature and pressure. The sulfur concentration of the outlet fuel as a function of treated fuel volume is shown in Fig. 3. No sulfur was detected in the treated model diesel fuel ($S < 1$ ppmw) when the elution volume was less than 4.5 ml, indicating the sulfur compounds, even 4,6-DMDBT, were removed by adsorption. After elution volume of 4.5 ml, the sulfur concentration increases with the elution volume

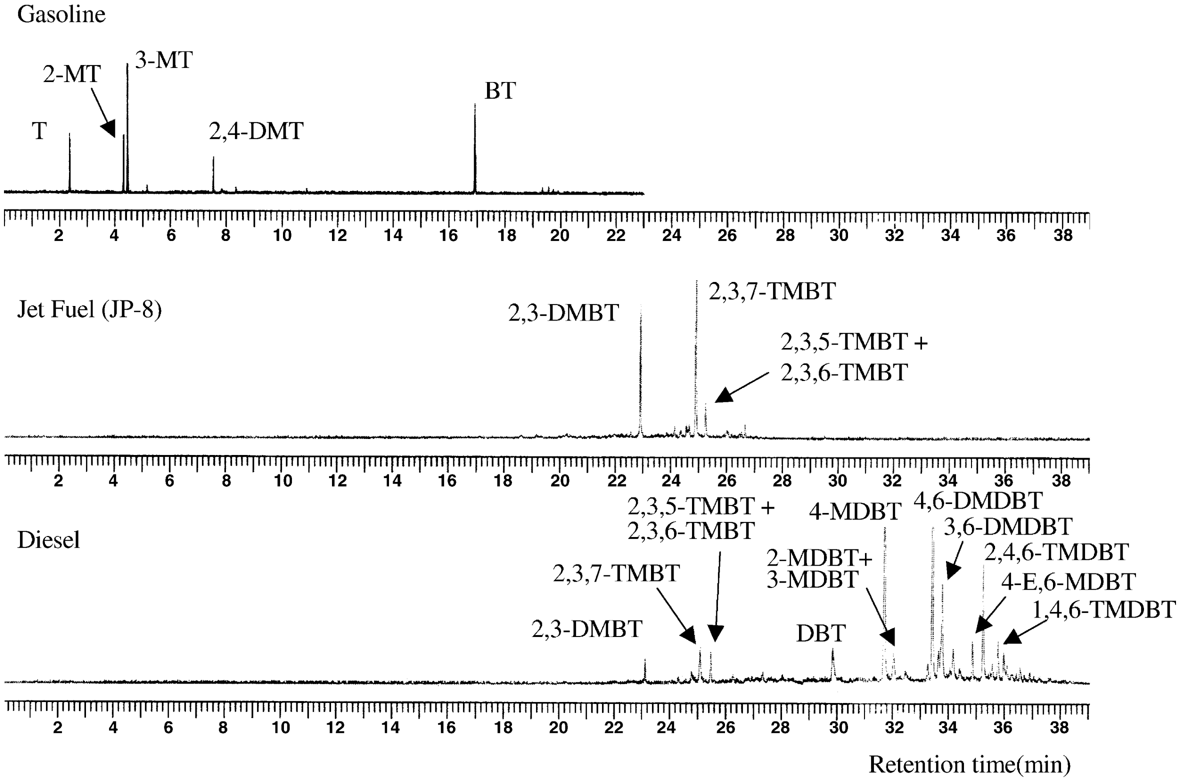

Fig. 2. GC–FPD chromatograms of gasoline, jet fuel and diesel fuel for identification of sulfur compounds.

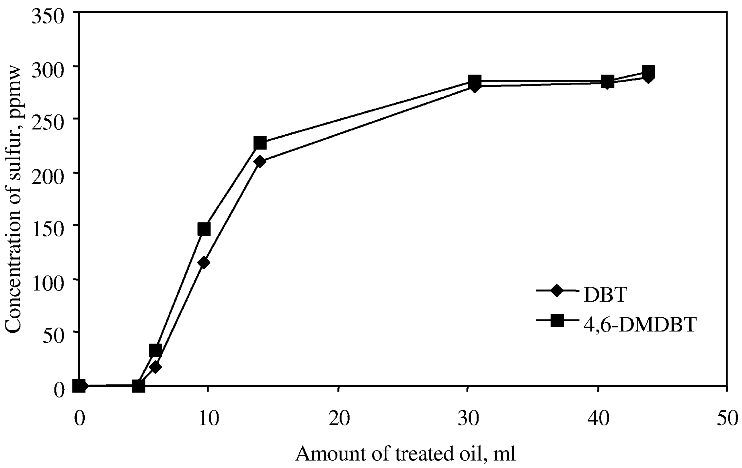

Fig. 3. The sulfur concentration of the outlet fuel as a function of treated fuel volume for model diesel fuel over adsorbent A-1.

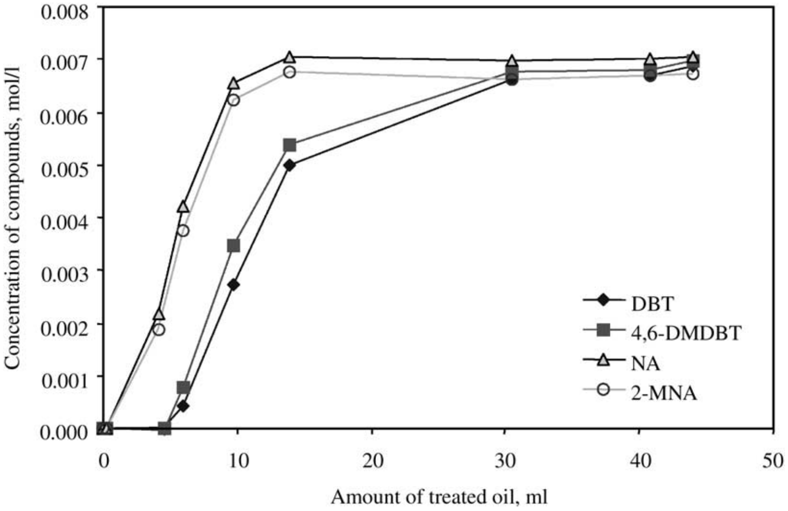

Fig. 4. Adsorption selectivity of adsorbent A-1 for thiophenic aromatic sulfur compounds and non-sulfur aromatic compounds in the model diesel fuel.

increasing. When the elution 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 currently developed adsorbent A-1 was calculated, being 0.123 mol of sulfur per mol of the metal compound. More work is necessary for increasing capacity of the adsorbent.

Fig. 4 shows the selectivity of the adsorbent for sulfur compounds and aromatic hydrocarbons, in which the molar concentration of DBT, 4,6-DMDBT, NA and 2-MNA are shown as a function of the elution 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 concentrations of the four compounds are almost the same in the model diesel fuel. 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. This result is in agreement with the coordination adsorption through η^1S or S–μ^3-bonding.

3.4. Adsorption desulfurization of real gasoline and diesel fuel

Desulfurization of the gasoline and diesel fuel by adsorption over adsorbent A-1 was performed at the ambient temperature. Fig. 5 shows a comparison of the GC–FPD chromatograms of the gasoline feed and the treated gasoline. Almost no sulfur signal was detected in the treated gasoline, indicating that most of the sulfur compounds in the gasoline were removed by the adsorption. Fig. 6 shows a comparison of the diesel feed and the treated diesel. The substantial sulfur compounds, including the refractory sulfur compounds, in the diesel were removed. The desulfurization experiment of the jet fuel by adsorption also gives similar results. These experimental results show further that the adsorbent A-1 is efficient for selective adsorption of the sulfur compounds in the liquid hydrocarbon fuels, even for adsorbing the refractory sulfur compounds in the fuels since the adsorption mechanism is based on the selective chemical coordination of the thiophenic compounds with the metal compounds.

The recovery of the adsorbed sulfur compounds from the spent adsorbent was conduced by elution using a polar organic solvent. A concentrated sulfur fraction was obtained by evaporating the polar organic solvent from the eluate. Analysis of the concentrated

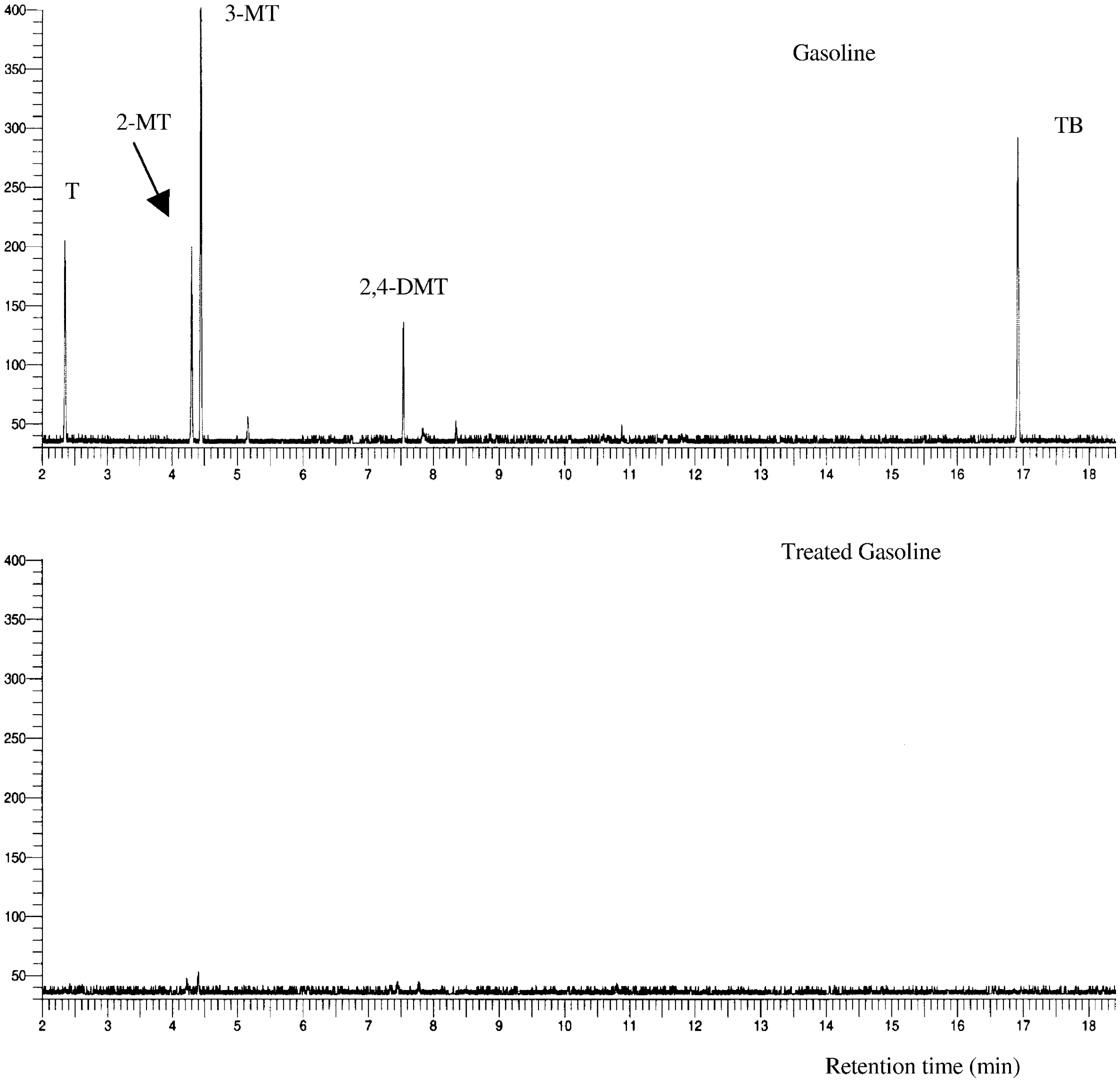

Fig. 5. GC–FPD chromatograms of real gasoline and treated gasoline over adsorbent A-1 at room temperature.

sulfur fraction shows that more than 90 wt.% of compounds in the fraction are sulfur compounds, demonstrating further that the adsorbent A-1 has excellent selectivity for adsorbing the sulfur compounds. The regeneration of the spent adsorbent was also conduced. The preliminary results show that the spent adsorbent could be regenerated by solvent elution followed by removal of the solvent from the adsorbent. Further experiments are necessary to determine the best regeneration method and the best conditions.

3.5. 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 [18–21]. The selective adsorption process (SARS) explored in this work can also be applied for

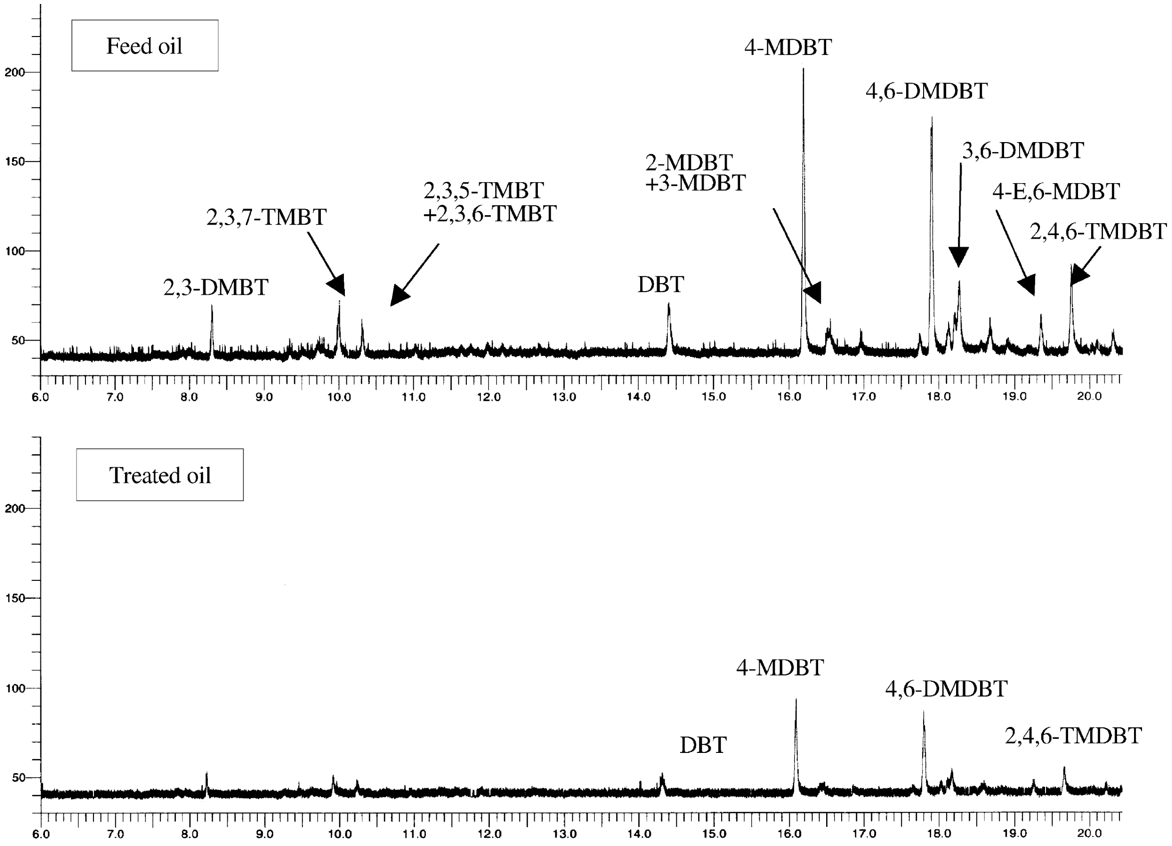

Fig. 6. GC–FPD chromatograms of real diesel and treated diesel fuel over adsorbent A-1 at room temperature.

on-site or on-board removal of sulfur from hydrocarbon fuels for fuel cell systems. It is advantageous to use the selective adsorption for sulfur removal from fuels for fuel cells, since this approach can be used at ambient (room) temperatures without using hydrogen. As indicated recently by Bellows of International Fuel Cells [22], sulfur is a severe poison for catalysts in fuel processors for fuel cells, especially downstream of reformer; some developers are using sulfur traps before or after the reformer, but “other developers ignore sulfur removal and simply assume that when fuel cells are commercialized the refineries will produce sulfur-free or ultra-low-sulfur fuels” [22]. 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.

3.6. A new integrated deep desulfurization process

On the basis of the present study, we propose a novel integrated process in a future refinery for deep desulfurization of liquid hydrocarbons, which combines the selective adsorption of the sulfur compounds (SARS unit) and the hydrodesulfurization of the concentrated sulfur fraction (hydrodesulfurization process of the concentrated sulfur fraction (HDSCS) unit), as shown in Fig. 7. The sulfur compounds in fuels are first adsorbed on the adsorbent in an adsorber and the hydrocarbon fuel with ultra-low-sulfur content is obtained. The sulfur compounds adsorbed on the surface of the adsorbent are recovered by solvent elution. The

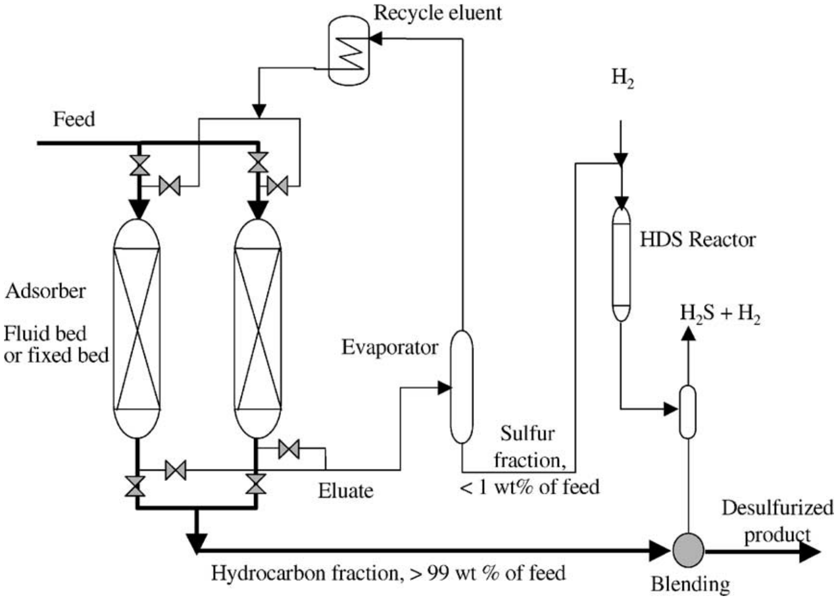

Fig. 7. The proposed integrated process for ultra-deep desulfurization based on selective adsorption at ambient temperature (SARS) and hydrodesulfurization of concentrated sulfur fraction (HDSCS).

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 blended with the hydrocarbon fraction from the adsorber. The sulfur contents of the ultra-clean fuels produced from such an integrated SARS–HDSCS process may be as low as in the range of <1 to <5 ppmw, depending on whether the fuel is needed for fuel cells (<1 ppmw) or for automotive IC engines (<5 ppmw).

The proposed SARS process and the new integrated process based on SARS–HDSCS illustrated in Fig. 7 is different from IRVAD process [18,19], S Zorb process by Phillips Petroleum [20] and TReND process by RTI [21] with respect to adsorption mechanism, adsorbent, and regeneration method. There are several potential advantages of the proposed SARS process: (1) The SARS process is effective for ultra-deep desulfurization of liquid hydrocarbon fuels including gasoline, diesel fuel and jet fuel at room temperature. (2) The SARS adsorption process is operated at ambient temperature and ambient pressure, without using any H_2, which leads to low energy consumption, low investment and low operating cost. (3) For a refinery operation, the hydrodesulfurization following the SARS only deals with the sulfur fraction (HDSCS), which leads to low hydrogen consumption and low energy consumption, as well as 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 co-existing polycyclic aromatics are strong inhibitors for HDS of the refractory sulfur compounds. (5) Little or no octane penalty is expected for gasoline, because in the adsorption desulfurization process olefins with high octane number are kept in the gasoline without suffering hydrogenation.

4. Conclusions

In this study we explored a new approach for deep desulfurization by selective adsorption for removing sulfur using a solid adsorbent at ambient temperatures under atmospheric pressure without using hydrogen.

Our experimental results, though still preliminary, demonstrate that organic sulfur compounds in gasoline, diesel fuel and jet fuel can be removed by selective adsorption using a transition metal compound loaded on a porous support.

The selective adsorption (SARS) could be used for on-site or on-board removal of sulfur from fuels for fuel cell systems. Further improvement in adsorption capacity is desired.

On the basis of the present study, a novel integrated process is proposed for deep desulfurization of the liquid hydrocarbon fuels in a future refinery, which combines a selective adsorption of the sulfur compounds (SARS) and a hydrodesulfurization process of the concentrated sulfur fraction.

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