DEEP DESULFURIZATION OF TRANSPORTATION FUELS WITH NANOREACTIONS

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Introduction

Burning sulphur-laden transportation fuels results in misty and fuggy air of large cities. The combustion products of sulphur-laden fuels poison the exhaust conversion catalyst and invalidate the catalyst box. As results, the vehicle emission gets worse and worse no matter how advanced the auto technology is. Some sulphur compounds converted to sulphates after combustion and emitted into the atmosphere in the form of superfine particles. Suspension of these superfine particles and the inefficiently converted hydrocarbons yield misty and foggy atmosphere. Stringent regulations on the sulphur content of transportation fuels have been issued in developed countries, but not yet in developing countries. Nonetheless, deep desulfurization of transportation fuels has drawn the global research attention. Thiophene and its derivatives are the sulphur species most difficult to remove, and research on deep desulfurization is targeting at the removal of this kind of sulphur compounds.

The present state of deep desulfurization technology was extensively reviewed in literature.[1-4] Hydrodesulfurization is the technology practically applied. Most sulphur compounds such as thiols, sulfides, disulfides and a considerable portion of thiophenes were removed in hydrodesulfurization. However, some benzothiophenic compounds such as dibenzothiophenes and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are still remained after the treatment. Hydrodesulfurization technology is not dependable for the target of deep desulfurization. Due to saturation of double bonds in olefin and/or aromatic components, excessive hydrodesulfurization of gasoline leads to decrease of octane number. The effectiveness of hydrodesulfurization decreases either for diesel following the increase of aromatic compounds and nitrides. In addition, deep hydrodesulfurization of diesels subject to constraints on fuel density, cetane number, and operation cost. Meanwhile, the catalytic activity decreases as a result of catalyst coking in deep hydrodesulfurization.[5,6]

The other desulfurization technologies reported in literature need further developments before commercialisation. These methods include oxidation, extraction, adsorption, alkylation and biodesulfurization. Adsorption and oxidation (oxidation-adsorption or oxidation-extraction) are considered promising among them for industry. The oxidation method changes sulphur compounds to sulfones or sulfoxides , and then the polarity difference with other components is utilized in a subsequent treatment. Different techniques were proposed for the oxidation method.[7-9] Catalysts are usually used in oxidation, and organic acids,[10,11] heteropoly acids and their salts,[12,13] and Ti-silica molecular sieve[14] were

reported. The oxidant used includes 30% aqueous hydrogen peroxide[10,11,13,14], nitrogen dioxide,[15] oxygen[16] and air.[17] Polar organic solvents or ionic liquids were used as extractant.[18] The oxidation desulfurization method bears merits in mild operation condition and without expense of hydrogen. However, this method becomes disabled in fuels containing too much aromatic components and/or dissolved water. Adsorption method can be applied with or without hydrogenation, and the latter is classified into physical or chemical adsorption. The S-Zorb SRT (Sulfur Removal Technology)[19] is a representative of the hydrogenation-based adsorptive desulfurization techniques. Although the method bears merits in less loss of octane number and relatively high desulfurization efficiency, it is not a cost efficient technology since the fuel has to be vaporized and reacted at 380-420 ^{o}C. The desulfurization method basing on physical adsorption seems not applicable due to the low selectivity for thiophenic compounds. Prominent success was reported in chemical adsorption, and the IRVAD (Irvine Robert Varraveto Adsorption Desulfurization) method,[20] the π-complexion method,[21,22] and the SARS (selective adsorption for removing sulphur) method[23] are well known representatives. The IRVAD method is suitable for many liquid hydrocarbons and more than 90% sulphur can be removed. However, the sulphur capacity of adsorbents is low, and the adsorbents need to be frequently regenerated. The sulphur capacity of adsorbent was considerably increased relying on the principle of π-complexion. However, the adsorption performance declines greatly where aromatic compounds, oxidants and moisture are present in fuels.[24] The SARS method[4,23] preloads transition metals on an adsorbent, for example, Ni/SiO2-Al2O3, and reached the same or little higher sulphur capacity in comparison with the π-complexion method. The alkylation method is to increase the boiling point of sulphur compounds through alkylation reaction and separate sulphur via a subsequent operation. This kind of methods is limited by competitive reaction of aromatic components and the polymerisation of olefins.[25] Biodesulfurization might have industrial potential, but a lot of fundamental developments are required for a better industrial performance.[2,26,27]

The proposed method uses adsorbents, but the desulfurization function is not due to adsorption of sulphur compounds, but to conversion of them via a characteristic reaction occurring in the pore spaces of adsorbents. For the removal of thiophenic and benzothiophenic compounds, the condensation reaction with formaldehyde is characteristic. This reaction needs strong acid as catalyst, and different acids are suitable. The adsorbent may also have different choices in accordance with the catalyst. Since real fuels contain more sulphur compounds than thiophenic/benzothioiphenic, the total sulphur content of real fuels cannot reach the goal of deep desulfurization relying only on the condensation reaction. Therefore, oxidation was used as a succeeding characteristic reaction after removing thiophens.

Why does the characteristic reaction reside in adsorbents? First of all, it is to increase the probability of sulphur compounds contacting a pore/reactor; second, it is because the concentration of sulphur compounds is too low to have the reaction occurred in bulk phase, though the content of hundreds or thousands ppm is too high to be tolerant. When excessive quantity of catalyst/reagent was preloaded in the pore space of adsorbent, sulphur

compound will change to another species of larger molecular weight and different property as soon as it touches the pore. Then the reaction product is adsorbed inside the pore. The large specific surface area/pore volume of the adsorbent greatly increases the probability of the touch. Finally, it is because the increase of catalytic activity in a reactor of nanometers dimension.[28]

Experimental

Adsorbent is the carrier of the reaction characteristic for sulphur compounds; therefore, it must load reagent and catalyst before desulfurization. The adsorbent must match with catalyst. For example, loading H_2SO_4 on carbonaceous material[29] and HCL[30] or phosphomolebdic acid (PMA) [31] on silica materials. Reagent of the condensation reaction is formaldehyde (FA), which is pre-loaded in adsorbent via vapor adsorption. H_2SO_4 or HCL may be then dropped in the adsorbent, while PMA may be loaded by soaking method before loading FA. Silica gel is used to load peracetic acid for the oxidation reaction, which is used for commercial fuels following the condensation reaction. The weight ratio of peracetic acid to silica gel was 0.4/1.0.

The desulfurization performance was firstly studied with model fuels and then tested in commercial fuels bought from a Sinopec gas station in Tianjin, China. Considering the difference in reactivity of different type of hydrocarbons, three types of model fuels were prepared. Octane was used to represent the aliphatic fuel (ALF) and benzene to represent the aromatic fuel (ALF). A mixture of 80 wt % octane and 20 wt % benzene to represent mixed type fuels (MXF). Since thiophenes and benzothiophenes constituted the obstacle of deep desulfurization, thiophene of 2000 ppm (equivalent to 760 ppm of sulfur element) and 4,6-DMDBT of 1000 ppm (equivalent to 151 ppm of sulfur element) were used to represent sulfur compounds. The sulfur content of thiophene in model fuels was detected by GC4000 gas chromatograph. The sample size was 2 μl and the minimum detectable sulfur content was about 1 ppm. The total sulfur content in commercial fuels varies time to time and is detected by a coulometric detector Model WK-2D.

The desulfurization condition was firstly searched in batch tests carried out in a flask with temperature control and agitation facilities. Then the testing fuel flows continuously passing through a packing bed at appropriate condition aiming to collect breakthrough curves, from which the sulfur capacity was determined. Dosage in a batch test is 20-30 g model fuel and 1-2 g adsorbent.[29-31] The sulfur content of fuel was analyzed intermittently. Breakthrough experiments were carried out in a vertical glass column (length 250 mm, diameter 10 mm) filled with the adsorbent at a constant temperature. The fuel was pumped up by a mini creep pump model BT01-YZ1515 and flowed down through the column at a constant rate. Breakthrough curves were drawn on plotting the transient sulfur content of fuel versus the cumulative fuel volume. The transient sulfur content was normalized with the initial sulfur content in feed while the cumulative fuel volume was reduced to unit mass of adsorbent. The reduced capacity of the adsorbent was calculated with following equations:

$$Q_b = (\frac{v\rho x_i}{m}) \times t_b \times 100\% \tag{1}$$

$$Q_s = (\frac{v\rho x_i}{m})\int_0^{t_s}[1-\frac{c_t}{c_i}]dt \times 100\% \tag{2}$$

Where Q_b is the breakthrough capacity per unit mass of adsorbent, wt%; Q_s is the saturation capacity per unit mass of adsorbent, wt%; v is the flow rate of fuel, cm^3/min; ρ is the measured fuel density, g/cm^3; c_i is the initial sulfur content, ppm; c_t is the sulfur content in the effluent fuel at time t, ppm; m is the mass of support packed in the column, g; x_i is the content of sulfur in fuel, wt%; t_b is the breakthrough time, min, and t_s is the saturation time when $c_t/c_i=1$, min.

Result and Discussion

Tests in model fuels

Desulfurization was operated at ambient pressure. The appropriate temperature is 70 ^{o}C for the removal of thiophen and 80 ^{o}C for benzothiophene as shown in Figures 1 and 2.
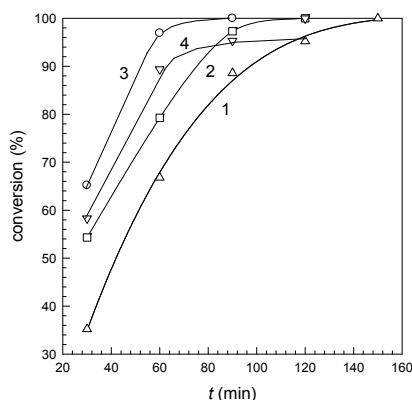

Fig. 1. Effect of temperature on thiophene conversion. 1: 50 ^{o}C; 2: 60 ^{o}C; 3: 70 ^{o}C; 4: 80 ^{o}C (Activated carbon as the carrier of H$_2$SO$_4$ and formaldehyde in ARF model fuel).
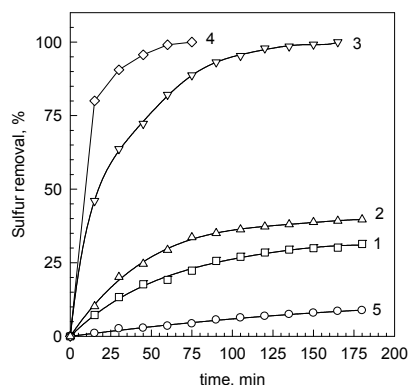
Fig. 2. Effect of temperature on the rate of removing 4,6-DMDBT contained in MXF fuel (catalyzed by PMA). 1: 50 ^{o}C; 2: 60 ^{o}C; 3: 70 ^{o}C; 4: 80 ^{o}C; 5: at 80 ^{o}C without loading formaldehyde.

The reaction rate increases following the increase of reagent (formaldehyde) loading amount from 20 to 40 wt % as shown in Fig. 3. However, too much quantity of catalyst (PMA) is not necessary as shown in Fig. 4. Larger quantity of reagent, longer period of operation for a given content of sulfur; therefore, larger specific surface area and/or pore volume is preferred in selecting adsorbent. Complete removal of 4,6-DMDBT from fuel may take longer time following the increase of sulfur content, but the content of 4,6-DMDBT does not much affect the desulfurization function as shown in Fig. 5. The function of desulfurization is valid for all types of fuels, though the aromatic fuel may retard the conversion rate to some extent, as shown in Fig. 6.

Tests in commercial fuels

The reaction/adsorption method of deep desulfurization was tested in commercial fuels bought from a gas station of Sinopec in Tianjin, China. The sulfur content in #93 gasoline is 480 ppm and that in #0 diesel is 1300 ppm and 1697 ppm respectively in two samples bought at different time. The sulfur content dropped to 202, 360 and 970 ppm, respectively in three samples. The remained sulfur compounds are not thiophenic, and most of them were removed through oxidation. The final sulfur content is below 15 ppm in all samples. The desulfured fuel was then treated with silica gel. The fuel quality of the clean fuel meets the National Standards of China, as shown in Table 1 for example.
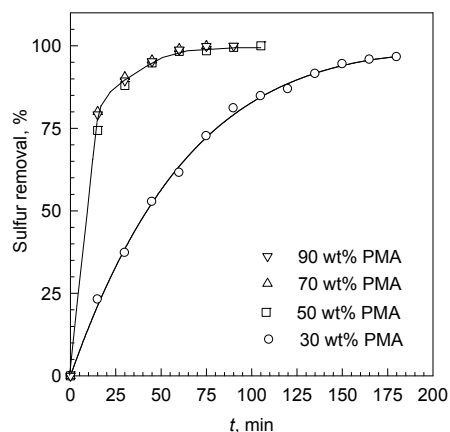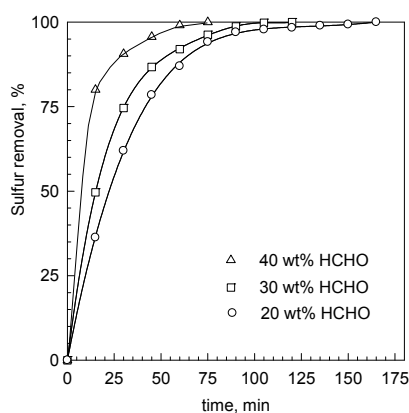

Fig. 3. Effect of loading quantity of formaldehyde on reaction rate (loading 70 wt % PMA at 80 °C).

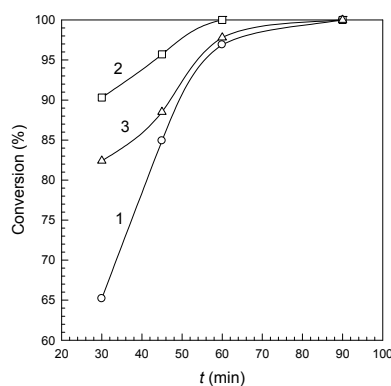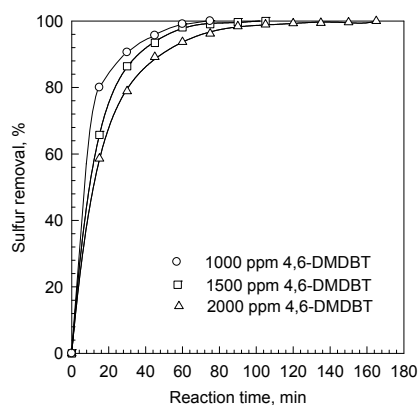**Fig. 4.** Effect of loading quantity of PMA on reaction rate.

Fig. 5. Effect of 4,6-DMDBT content on reaction rate at 80 °C.

Fig. 6. Compatibility of the desulfurization method for different types of fuels. 1: ARF; 2: ALF; 3: MXF.

Regeneration

Two regeneration methods were tested. The first method is washing with alcohol, and most reaction products dissolved in it. However, little by-product was produced due to

another reaction mechanism[32] and could not dissolve in alcohol. Therefore, the second method was used in the case that remarkable decrease in sulfur capacity was observed. The saturated carrier was heated at 400 °C in the air for 3 h and the by-product was decomposed and removed with a stream of inert gas. The PMA catalyst remained in regeneration, but formaldehyde needs to reload at room temperature. The sulfur capacity is basically recovered as shown in Fig. 7.

Table 1. Result of corrosion tests.

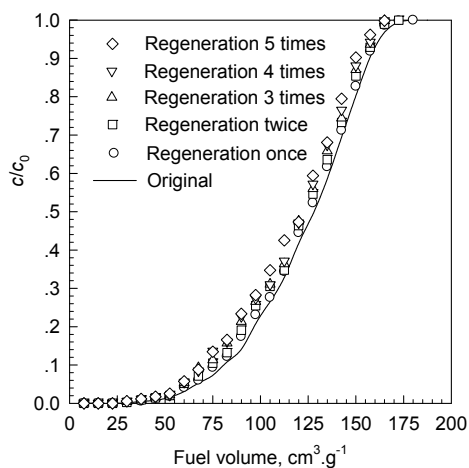| Test	Test standard	93# Gasoline	0# Diesel	Standard for gasoline (GB/T 17930-1999)	Standard for light diesel (GB 252-2000)
Copper corrosion	GB/T5096-85(91)	1a	1a	Less than Grade 1 at $50^{o}C$ for 3 h	Less than Grade 1 at $50^{o}C$ for 3 h
Acidity	GB/T258-77(88)	1.9	2.1	< 3	< 7
Soluble acid	GB/T259-88	None	None	None	None

Fig. 7. Breakthrough curves of MXF fuel containing thiophene at 70 ^{o}C on regeneration.
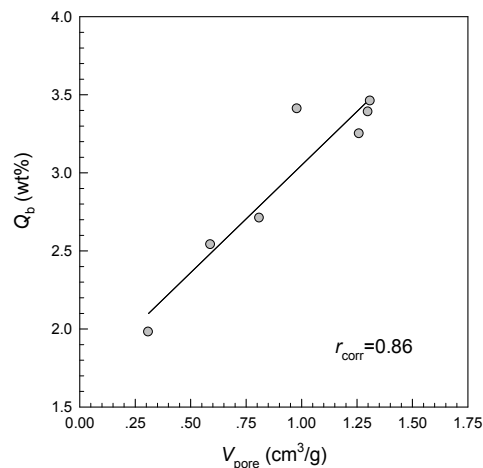
Fig. 8. Correlation of sulfur capacity with pore volume of carbon materials.

Preferred property of adsorbent

As the carrier of desulfurization reactions, the number, size and volume of adsorbent pores must affect the desulfurization performance. To test the dependence of sulfur capacity on porous structure, the breakthrough capacity was in turn correlated with the specific surface area, pore volume, and nominal pore size. Linear correlation coefficients obtained are 0.61, 0.89 and 0.50, respectively. It seems that pore volume exerts the largest effect and the correlation is shown in Fig. 8.

CONCLUSION

1. Reactions characteristic for sulfur species are effective for the deep desulfurization of transportation fuels provided the reaction is resided is an adsorbent.
2. The condensation reaction with formaldehyde and catalyzed by a strong acid completely removed thiophenes and benzothiophenes from transportation fuels. The remained sulfur species are removed by oxidation reaction.
3. Adsorbent can be regenerated with alcohol washing and heating in air at 400 ^{o}C. The washed out products are sulfur resin that may have other applications.
4. The proposed method is suitable for low sulfur content; therefore, is better to couple with the available HDS (hydrodesulfurization) technology.

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