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Acylation Desulfurization of Oil Via Reactive Adsorption

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Excellent desulfurization is achieved via reactive adsorption using Friedel-Crafts acylation materials, that is, acylating reagents and Lewis acids, such as acetyl chloride (AC) and $AlCl_3$, being named as acylation desulfurization (ACDS). For model oil, thiophenic compounds, namely, dibenzothiophene, benzothiophene, and thiophene, are removed completely by AC–$AlCl_3$ within 30 min at room temperature. In this process, thiophenic compounds are acylated by AC under the catalysis of $AlCl_3$, and the acylated derivatives are stronger base than original ones due to incorporation of O-containing carbonyl group (C═O) and, thus, adsorbed more easily by $AlCl_3$ via Lewis acid–base complexation. Further, ACDS mechanism is identified by acylated product characterization and quantum chemistry calculation. Satisfactorily, ACDS is still effective for toluene-rich and real oils, and real oil quality is improved with desulfurization proceeding. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 2966–2976, 2013

Keywords: acylation desulfurization, reactive adsorption, thiophenic compounds, complexation, real oil

Introduction

Desulfurization of fuel oil is increasingly important due to the more and more strict limitation of sulfur content. Some thiophenic compounds, that is, dibenzothiophene (DBT), benzothiophene (BT), thiophene (T), and their alkyl substituted derivatives, are refractory sulfurs that are hard to be eliminated from real oils, because they have stable aromatic structures.[1,2] Traditional hydrodesulfurization shows harsh conditions, that is, high temperature and pressure,[1,3] which are inevitable due to the energy demand of C—S bond cleavage involved. Thus, some alternative methods, for example, adsorptive desulfurization,[4–8] extractive desulfurization,[9–13] and oxidative desulfurization (ODS),[14,15] are proposed and found to be feasible under mild condition. Some adsorbents or extractants, like activated carbon,[8] zeolite,[16] and 1-butyl-3-methyl imidazolium chloride (BmimCl),[17] show weak interaction with thiophenic compounds Lewis bases. To obtain a better interaction with thiophenic sulfurs, the above adsorbents or extractants need to be modified by some soft or hard Lewis acids. For example, activated carbon or zeolite modified by Cu^+ and Ag^+ can form good π-complexation with thiophenic sulfurs.[18,19] This complexation could be deemed as soft acid–soft base interaction, according to hard and soft acids and bases theory.[20] And, zeolite loaded with hard Lewis acid Ce^{4+} can remove selectively T by S-metal direct interaction even in the presence of benzene.[21] Moreover, the desulfurization efficiency of BmimCl can be increased significantly by adding $AlCl_3$,[9] $FeCl_3$,[17] or CuCl.[22] Obviously, for the weak Lewis acid systems, the increasing acidity will promote the acid–base interaction with a specific thiophenic sulfur regardless of their acidic hardness, because thiophenic sulfur is both hard and soft base.[23] However, for a strong enough Lewis acid system, its hardness will have a great influence on desulfurization efficiency for thiophenic sulfurs with different basic hardnesses. For example, sole $AlCl_3$, as a hard and strong acid, shows much weaker complexation with DBT than that with T and BT, because DBT is a softer base.[23] Thus, for a specific Lewis acid, its acidity and hardness are both crucial for the complexation with thiophenic sulfurs.

Besides modification of adsorbents or extractants, increasing Lewis basicity of thiophenic sulfur can also enhance the complexation with a specific acid. For example, the DBT sulfone or suloxide ($DBTO_2$ or DBTO) as the oxidative derivative of DBT shows stronger interaction with molecular seive, activated carbon, and ionic liquids by reactive adsorption or extraction,[7,24–27] due to the incorporation of suloxide (S═O) groups that increases the basicity and polarity of DBT molecule greatly. From the mechanism of reactive adsorption or extraction mentioned earlier, the better sulfur removal is ascribed to the contribution of O atom. Therefore, it is inferred that conventional Friedel-Crafts acylation materials, such as acetyl chloride (AC) and $AlCl_3$, may show excellent desulfurization performance as manifested by the following facts. First, thiophenic compounds are aromatic

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Additional Supporting Information may be found in the online version of this article.

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and can be acylated easily by AC under the catalysis of $AlCl_3$, that is, O-containing carbonyl group (C═O) is very easy to be incorporated to thiophenic molecules through the acylation reaction.[28,29] Besides, the C═O group on the acylated thiophenic compouds may interact more strongly with strong and hard acid $AlCl_3$ than S atom on thiophenic ring, because O atom on C═O group is a stronger and harder base.[20,30] In this process, AC is the C═O source, whereas $AlCl_3$ is both catalyst for acylation and adsorbent for acylated thiophenic compounds.

The aim of this work is to explore feasibility of acylation desulfurization (ACDS) for model oils at room temperature, interprete desulfurization mechanism through product characterization, and theoretical calculation, and investigate desulfurization performance for real oil.

Experimental

Chemical materials

The information of reagents, namely, model sulfur compounds, acylation materials, and oils, can be seen in Table 1. And the chemical structure of model thiophenic compounds and acylating reagents are shown in Figure S1, Supporting Information. All the reagents are used as received without further purification.

ACDS in model and real oils

The model oil used here is a binary solution of *n*-octane and a thiophenic sulfur, that is, DBT, BT, or T, and the sulfur content is 1000 ppm. And the ACDS materials used in this work include AC–$AlCl_3$, AC–$FeCl_3$, butyryl chloride (BC)–$AlCl_3$, propionyl chloride (PC)–$AlCl_3$, acetic anhydride (AA)–$AlCl_3$, butyric anhydride (BA)–$AlCl_3$, and propionic anhydride (PA)–$AlCl_3$. The model oil is mixed with a specific amount of acylating reagent like AC, and then a Lewis acid like $AlCl_3$ is added into the system with vigorous magnetic stirring at room temperature (30°C). For continuous sampling experiment, 30 g of model oil is used, and five samples (0.2 mL for each) at different time (5, 10, 15, 20, and 30 min) are taken out for S-content analysis. Meanwhile, 20 g of oil is used for the experiments, which just need one sample. For the investigation of sulfur selectivity, moreover, the desulfurization rate experiment is performed in toluene-rich oils (1000 ppm S, 25 wt % toluene), and the sulfur capacity of $AlCl_3$ with varied amount of AC is also investigated with 30-min reaction time in this oil. All the experiments are carried out at room temperature.

Table 1. Chemical Reagent Information in This Work

Chemicals	Manufacturer	Purity (%)
DBT	ACROS	99
BT	ACROS	99
T	J&K	99
n-Octane	Tianjin Guangfu Fine Chemicals	AR
AC	Sinopharm, Beijing	99
PC	Aladdin	98
BC	Aladdin	98
AA	Zhengzhou Chemicals	98
PA	Aladdin	98
BA	Aladdin	98
Toluene	Beijing Chemical Works	AR
$AlCl_3$	Xilong Chemicals	99
$FeCl_3$	Xilong Chemicals	99
Heavy pyrolysis oil	Puyang Petrochemical	–

To investigate ACDS performance for real oil, a heavy pyrolysis oil containing large amount of thiophenic sulfurs (6234 ppm S, 0.892 g cm^{-3}) is used. Similarly, the desulfurization experiments are conducted using AC–$AlCl_3$ or AC–$FeCl_3$ at room temperature.

Characterization for the acylated products and real oil

To obtain the sulfur components adsorbed by $AlCl_3$, the oil layer is removed after desulfurization experiments, and HCl aqueous solution and CH_2Cl_2 are added to the flask with vigorous stirring for 10 min. As such, the sulfur compounds can be released and transferred to CH_2Cl_2 phase, and then they can be recovered by evaporating CH_2Cl_2 under vacuum condition at 50°C. The as-obtained products are analyzed qualitatively by high performance liquid chromatography (HPLC, Shimadzu 10A-VP, equipped with UV–vis detector and a C-18 column; wavelength = 240 nm for T, 251 nm for BT, 310 nm for DBT; methanol:water = 8:2 for T and BT, 9:1 for DBT; flow rate = 0.9 mL/min for T, 1 mL/min for BT and DBT). Besides they are also characterized by UV–vis (Beijing Labtech) and NMR (AV400, Bruker) using, respectively, CH_2Cl_2 and DMSO-d_6 as solvent.

For the real oil, the sulfur compound distribution in crude oil is analyzed directly by gas chromatography-flame photometric detector (GC-FPD, Agilent 7890A, with a HP-5 column, 30 m × 320 μm × 0.25 μm; high-purity N_2 as carrier gas; temperature program: 70°C for 0.5 min-temperature rising 20°C/min to 300°C for 3 min), and contrasted with standard sample containing known thiophenic compounds. And the hydrocarbon ratio (H/C) of real oil is obtained by elemental analysis using EuroEA Elemental Analyser, the N-content is determined by sulfur and nitrogen analyzer. Moreover, the substances adsorbed by $AlCl_3$ are obtained by the method described earlier and analyzed by gas chromatography-mass spectrometry (GC–MS, Agilent 7890-5795, with a HP-5MS column, 30 m × 250 μm × 0.25 μm; high-purity He as carrier gas; temperature program: 49°C for 1 min-temperature rising 9°C/min to 310°C for 9 min).

Sulfur content determination

The S-contents with respect to model and real oils are measured by sulfur and nitrogen analyzer (KY-3000SN, China, Analysis details: high-purity Ar and O_2 as carrier gas; furnace temperature = 1303 K; flow rate (Ar) = 170 mL/min, flow rate (O_2) = 290 mL/min for high S-content (>100 ppm), 330 mL/min for low S-content (<100 ppm); injection volume = 5 μL for high S-content, 20 μL for low S-content) with its minimum detectable S-content being about 0.3 ppm. For each sample, the S-content analysis is repeated three times to obtain average value. The maximum relative errors between known S-content and detected one are within 3% (>10 ppm S) and 15% (<10 ppm S), respectively. External standard method is used, and the standard curve needs to be calibrated beforehand by samples with known S-content.

Theoretical calculation details

The electronic properties of different compounds are theoretically investigated using Gaussian 09 program.[31] The density functional theory of B3LYP is used to optimize the geometry with 6–31+G* basis set for the thiophenic compounds.[25] To obtain the most stable geometries, frequency calculation is performed to verify the global minimum. The dipole moment, heteroatom electron density, and bond order of thiophenic compounds involved are calculated at the

B3LYP/6–311++G** level.[32] For $AlCl_3$ and $FeCl_3$, atom charge distribution is calculated. The Al and Fe atoms are optimized at B3LYP/LanL2DZ, and their charges are obtained at the same level.[17] Meanwhile, the Cl atom is optimized at B3LYP/6–31+G*, and its charge is obtained at B3LYP/6–311++G**. The calculated results obtained in this work are used to explore qualitatively ACDS mechanism.

Results and Discussion

Exploration of ACDS feasibility in model oil

To explore the ACDS feasibility for thiophenic sulfur removal of fuel oil, the parallel experiments are conducted in model oil (*n*-octane, 1000 ppm S) at room temperature using fivefold $AlCl_3$ (mol/mol S) with or without twofold AC for three sulfurs. With stirring proceeding in six experimental systems, different kinds of oil-insoluble complexes may be formed gradually between different sulfur species and $AlCl_3$, as indicated by their color difference of bottom phase. Specifically, the complexes in AC-containing system show white for T and orange for BT and DBT, while the counterparts in AC-free system show yellow for T, dark red for BT, and brown for DBT. Figure 1 compares the desulfurization rate of model oil in the presence and absence of AC. Surprisingly, the system with AC shows much stronger desulfurization activity than that without AC for three thiophenic compounds, especially for DBT that is removed hardly by sole $AlCl_3$.[23] For example, the desulfurization yields of $AlCl_3$ without AC at 15 min are 5.3% for DBT, 42.1% for BT, and 64.8% for T, whereas the counterpart data of AC–$AlCl_3$ are 91.3% for DBT, 98.1% for BT, and 98.9% for T. And the three sulfurs can be removed completely by AC–$AlCl_3$ after 20 min. The results indicate that adding AC promotes significantly desulfurization rate of adsorbent $AlCl_3$, implying a stronger complexation between sulfurs and $AlCl_3$ in AC-containing system than that in AC-free system. The better desulfurization rate of AC–$AlCl_3$ is ascribed to the contribution of acylation reaction, as manifested by the characterization results, that is, HPLC, NMR, and UV–vis spectrums. Thus, the ACDS method is a viable process for thiophenic sulfur removal of oils.

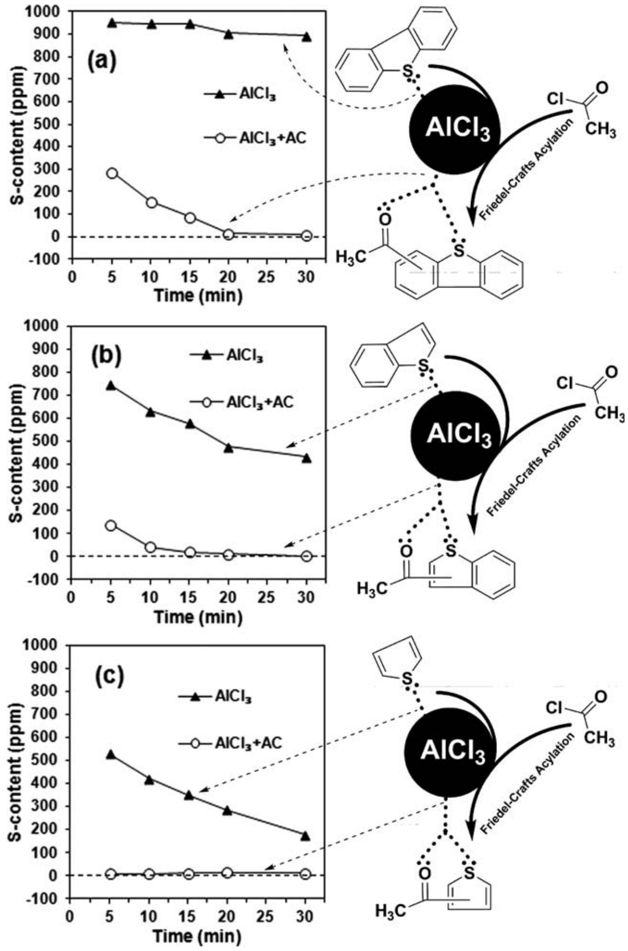


Figure 1. Desulfurization rate with or without AC in the presence of $AlCl_3$.

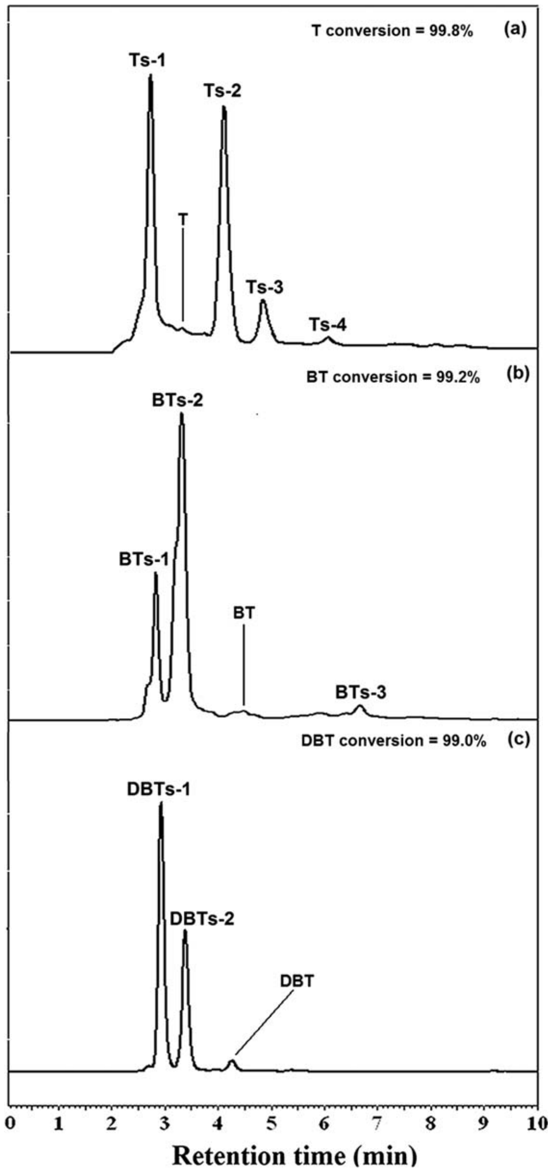
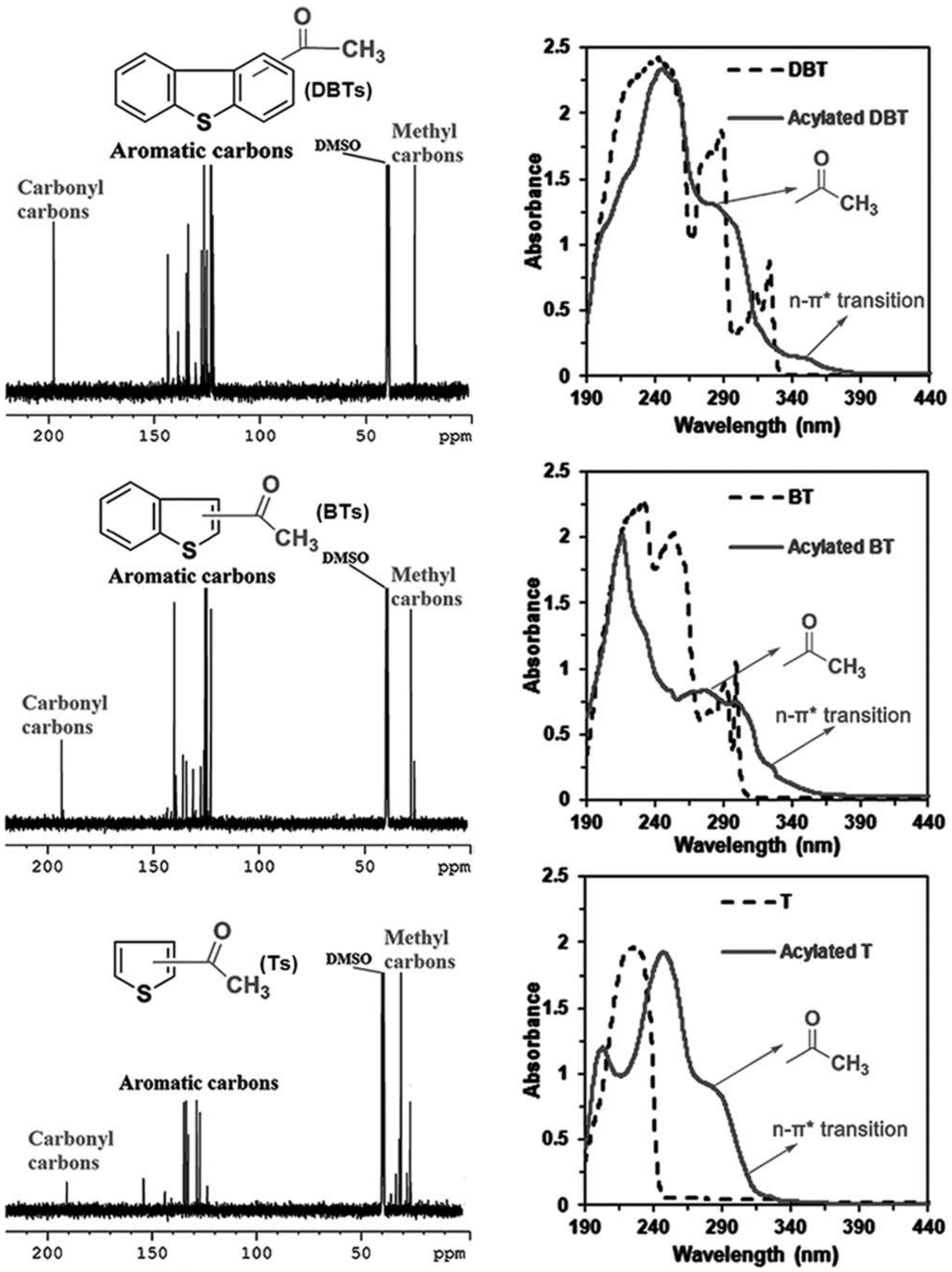


Figure 2. HPLC for the sulfur compounds adsorbed by $AlCl_3$.

Characterization of acylated thiophenic compounds

To identify the acylation reaction in this system, the sulfur components adsorbed by $AlCl_3$ are obtained after experiments and then analyzed by HPLC as shown in Figure 2. It is obvious that, for the three sulfur systems, each of them should be a mixture containing a variety of sulfur



(a) ^{13}C NMR (b) UV-vis

Figure 3. ^{13}C NMR and UV spectrums for the sulfur compounds adsorbed by $AlCl_3$.

compounds due to the presence of many peaks in HPLC spectrum. The original sulfur compounds (DBT, BT, and T) are determined in HPLC spectrum by referring to their standard compounds and found to be almost disappeared and converted to the other derivatives (DBTs, BTs, and Ts). The results suggest that acylation reaction occurs, considering the limited possible reaction for the reagents used in this system. Meanwhile, some derivatives (DBTs-1, DBTs-2, BTs-1, BTs-2, and Ts-1) show shorter retention time than their corresponding original sulfurs. The phenomena indicate that these derivatives are more polar than the original ones according to the HPLC theory, and, thus, imply the formation of acylated products, because the C═O group shows very high polarity. Further, some derivatives (BTs-3, Ts-2, Ts-3, and Ts-4) show longer retention time than original ones (BT and T), indicating that these compounds have the much larger molecular weight than original ones, which may be explained by the formation of multiacetyl substituted BT and T.

To confirm the formation of acylated thiophenic compounds further, the ^{13}C NMR and UV–vis spectrums are recorded for the adsorbed S-components, as presented in Figure 3. As shown in Figure 3a, taking BTs as an example, two peaks at 192.5 and 193.4 ppm are detected by ^{13}C NMR, and the other two peaks at 26.6 and 28.2 ppm are also found out. It is evident that these carbons may not be the aromatic ones, because the chemical shifts of aromatic carbons are generally from 100 to 160 ppm.[33] The results indicate that the BTs show the different chemical structure from the original BT, because sole BT only has the aromatic carbons. After referring to the standard spectrum of 2-acetyl BT shown in Figure S2, Supporting Information, it can be concluded that the carbons at 192.5 and 193.4 ppm belong to the carbonyl carbons (C═O), and the carbons at 26.6 and 28.2 ppm are methyl carbons. Thus, the sulfur acylation in the ACDS process is identified undoubtedly. Meanwhile, for DBTs system, two overlapped peaks at 197.5 ppm for C═O carbons are detected, and other two peaks at 26.8 and 26.9 ppm for methyl carbons are also appeared. Obviously, the acylation of DBT is also confirmed. For Ts system, some peaks overlapped at 190.7 ppm are carbonyl carbons, and about seven peaks from 26.2 to 33.3 ppm are methyl carbons, which implies the formation of multiacetyl substituted T. Moreover, Figures S3–S5, Supporting Information, compare the NMR spectrum between the orginal sulfurs and corresponding acylated ones in terms of ^{1}H and ^{13}C. Through the comparison between corresponding compounds, the occurrence of acylation reaction is more reliable and compelling. In Figure 3b, UV–vis spectrum shows that adsorbed sulfur compounds have different UV spectrum from corresponding original components. The medium intensity peaks at 280–290 nm should be due to characteristic absorption of C═O group, and the broader absorbance bands are attributed to the increasing number of conjugation units and $n–\pi^*$ transition formed by lone pair electrons on O atom and thiophenic rings.[33] According to the above results, it can be concluded that the sulfur species adsorbed by $AlCl_3$ are dominantly acylated thiophenic compounds.

ACDS mechanism

In this process, AC is the C═O source, while $AlCl_3$ is the catalyst for acylation and adsorbent for sulfur removal. The thiophenic compounds are acylated, accompanying with being removed by $AlCl_3$. The excellent desulfurization performance is ascribed dominantly to the formation of acetyl substituted thiophenic compounds that have more electron-rich sites, that is, stronger Lewis basicity, and higher polarity than the original ones, as listed in Table 2. The more electron-rich sites may bring in the dual complexation between acylated sulfurs and $AlCl_3$, that is, O–$AlCl_3$ and S–$AlCl_3$ interactions as shown in Figure 1.[23,34,35] And, addition of C═O group increases the polarity of thiophenic molecules, lowering their solubility in oil phase, and accordingly making them removed more readily from the oils. Further, the ACDS activity for three thiophenic compounds shows the order of DBT < BT < T, which may originate from their difference of acylation and adsorption activity.

Table 2. Dipole Moments and Heteroatom Electron Density for the Thiophenic Compounds

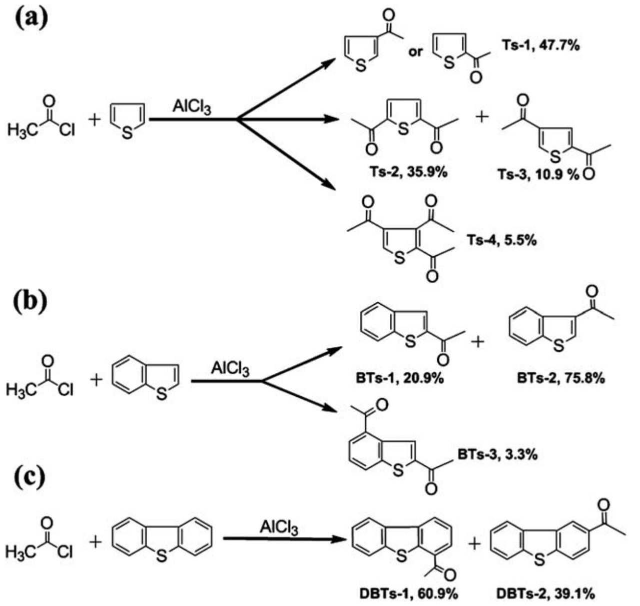
		Electron Density	
Sulfur Compound	Dipole Moment	S Atom	O Atom
DBT	0.774	5.613	–
2-Acetyl DBT	2.520	5.599	6.565
4-Acetyl DBT	3.371	5.625	6.575
BT	0.637	5.610	–
3-Acetyl BT	3.280	5.560	6.569
2-Acetyl BT	4.081	5.545	6.551
T	0.513	5.586	–
3-Acetyl T	3.305	5.547	6.561
2-Acetyl T	3.188	5.561	6.556
2,5-Diacetyl T	3.395	5.540	6.543
2,4-Diacetyl T	5.749	5.540	6.543

The conclusion that acylated thiophenic compounds are removed more easily can also be demonstrated by quantum chemistry calculation in terms of electron density of heteroatom and dipole moment of thiophenic molecules,[8] as listed in Table 2. From the table, O atom shows larger electron density than S atom, which suggests that O atom shows much stronger Lewis basicity, and accordingly, stronger complexation with Lewis acid $AlCl_3$. Thereby, the acylation reaction in the process appears important all the more for the sulfur removal. Further, dipole moments of acylated derivatives are all much larger than those of original sulfur compounds, indicating that acylation reaction increases significantly the polarity of thiophenic molecules and accordingly reduces sulfur solubility in the oil phase. Obviously, the chemical properties of thiophenic compounds are changed through incorporation of O-containing group (C═O), and both theoretical results and experimental ones confirm the contribution of acylation reaction for sulfur removal. Therefore, thiophenic compounds can be removed successfully by Friedel-Crafts acylation material.

Acylation reaction for model thiophenic compounds

As described previously, the thiophenic compounds are converted to their acylated derivatives during ACDS process. As presented in Figure 2, the distribution of acylated sulfurs may be determined through the analysis of their retention time recorded by HPLC. For the Ts system in Figure 2a, the derivative Ts-1 shows shorter retention time than original T. The results suggest that Ts-1 is likely to be monoacetyl T because of its much higher polarity and slightly larger molecular weight than those of T. Meanwhile, Ts-2, Ts-3, and Ts-4 could be the multiacetyl T due to their much larger molecular weight, based on their longer retention time than that of T. Further, for the multiacetyl T, Ts-2 and Ts-3 show close retention time, that is, 4.1 and 4.8 min, respectively, and, thus, they may be the isomers of diacetyl T. As such, Ts-4 at 6 min may belong to triacetyl T. Similarly, for BTs system in Figure 2b, BT-1 and BT-2 are the isomers of monoacetyl BT, whereas BTs-3 is diacetyl BT. For DBTs system in Figure 2c, DBTs-1 and DBTs-2 are the isomers of monoacetyl DBT. Moreover, for the isomers stated earlier, the dipole moments listed in Table 2 may distinguish them further. As such, the possible acylated products are presented in Scheme 1,[28,29,36,37] and the percent of each product can also be seen.

As shown in Figure 2, with the reaction ending, the conversions of orginal sulfurs are 99.0% for DBT, 99.2% for BT, and 99.8% for T. And the derivative numbers for three original sulfurs show the order of DBT (2) < BT (3) < T (4). Thereby, it is assumed that the acylation reactivity of three orginal sulfurs shows the order of DBT < BT < T. To explain the phenomenon theoretically, the bond order concerning sulfur compounds involved are calculated, considering that bond order represents the electron density on unsaturated bonds, and the acylation reaction is an electrophilic substitution process. As shown in Figure 4, the maximum bond order of DBT (1.478) is much lower than that of BT (1.695) or T (1.635), thereby DBT shows the lowest reactivity. However, the phenomenon that T shows higher activity than BT is ascribed to the more the number of active double bond with maximum bond order. As shown from Figure 4a, the maximum bond order of the acylated derivative DBTs is almost consistent



Scheme 1. Potential acylated products for three model thiophenic compounds.

with DBT, but the reducing number of active double bond may prohibit further acylation besides the steric hindrance. For the BT group in Figure 4b, the decreasing maximum bond order of thiophenic ring, the number of active double bond, and steric hindrance concerning the monoacetyl BTs implies a decreasing reactivity in thiophenic ring, on the contrary, the maximum bond order of benzene ring in the monoacetyl BTs is increased slightly, which is helpful for the successive acylation, forming small amount of diacetyl BTs. For the T group in Figure 4c, the maximum bond order of 3-acetyl T is even higher than that of T, which favors significantly the formation of diacetyl T, however, maximum bond order of diacetyl Ts are much lower than neat T and monoacetyl T, and their steric hindrances are quite large, thereby, the formation of triacetyl T is very limited. Therefore, acylated DBTs contain only monoacetyl DBT, acylated BTs are composed of monoacetyl BT and small amount of diacetyl BT, and acylated Ts contain monoacetyl and diacetyl T and small amount of triacetyl T.

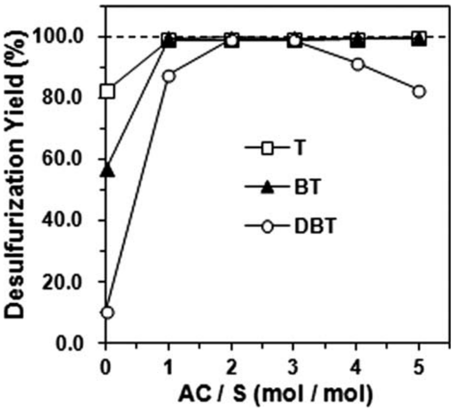


Figure 5. Influence of amount of AC on desulfurization performance.

ACDS performance with varied amount and species of acylating reagent

To investigate the influence of AC amount on desulfurization performance under fixed fivefold $AlCl_3$, experiments are conducted using varying amount of AC (mol/mol S) at room temperature with 30-min reaction time. As shown in Figure 5, for BT and T, onefold AC is sufficient for high ACDS performance, however, complete DBT removal requires twofold AC. Further, DBT removal efficiency encounters a steady reduction as the amount of AC is above threefold, suggesting that the excessive amount of AC is not always helpful for desulfurization. The phenomenon may be

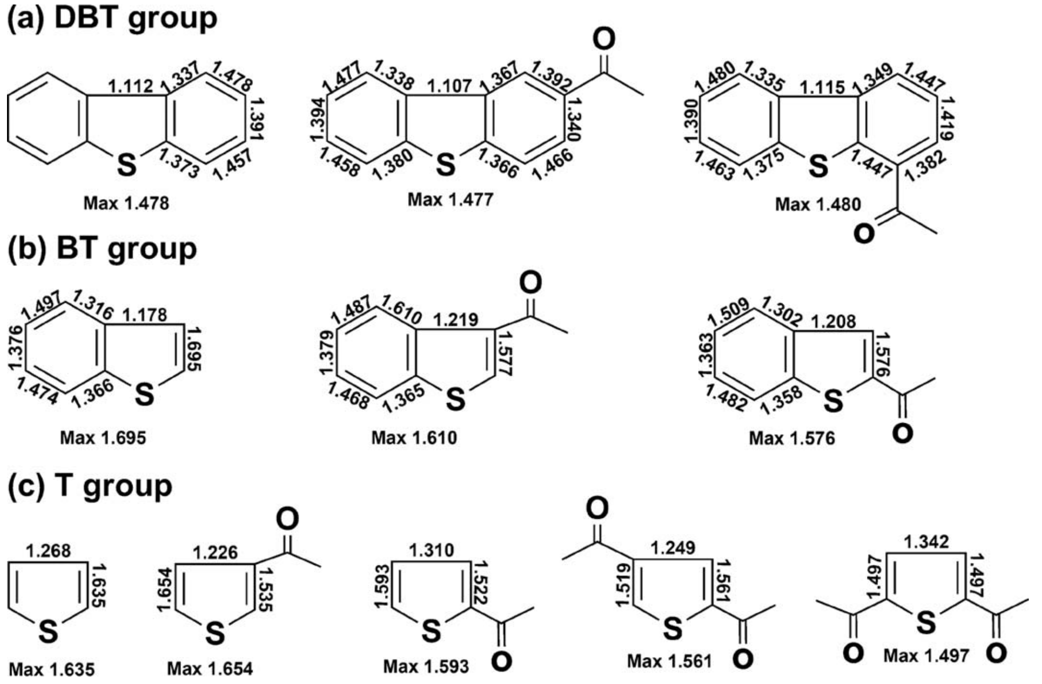


Figure 4. Bond order of original and acylated sulfur compounds.

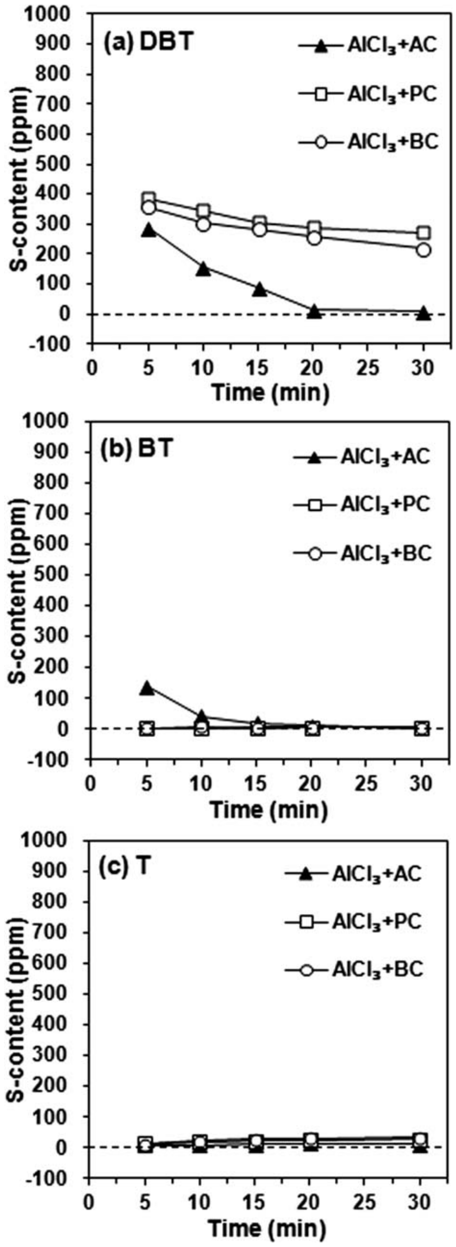


Figure 6. Desulfurization activity comparison between other acyl chlorides and AC in the presence of $AlCl_3$.

attributed to the fact that AC is a Lewis base containing O and Cl atoms, and its excessive presence may lower the catalytic and adsorptive activity of $AlCl_3$ caused by undesirable stable interaction between AC and $AlCl_3$. Thus, adding amount of AC needs to be controlled within threefold. In contrast, desulfurization efficiency of BT and T do not decrease with increasing amount of AC, which may be due to the fact that their stronger acylation and adsorption ability than DBT covers the undesirable effect of excessive AC.

Besides AC, the other acylating reagents are also studied for their ACDS performance in the presence of $AlCl_3$. For example, the acyl chlorides (PC and BC) are investigated for sulfur removal, and the experiments are conducted using twofold acyl chloride and fivefold $AlCl_3$. As shown in Figure 6, PC–$AlCl_3$ and BC–$AlCl_3$ can remove T and BT completely, but they also show lower removal ability for DBT than AC–$AlCl_3$ due to their larger steric hindrance. Moreover, acid anhydrides, that is, AA, BA, and PA, are also used to investigate DBT and BT removal, and the experiments are conducted using twofold acid anhydride and fivefold $AlCl_3$ with a fixed reaction time 30 min. AA–, BA–, and PA–$AlCl_3$ all show weak ACDS activity for DBT, as listed in Table 3, since the resulting O-containing carboxylic acids generated from acid anhydrides will result in a competitive complexation with $AlCl_3$, and, thus, reduce the catalytic and adsorptive activity of $AlCl_3$. Therefore, the combination AC–$AlCl_3$ seems to be the most effective ACDS material.

ACDS performance with different Lewis acids

In contrast to $AlCl_3$, $FeCl_3$ also is one of the Lewis acids and may show the ACDS activity. Thereby, the experiments concerning $FeCl_3$ are carried out, and fivefold $FeCl_3$ is used

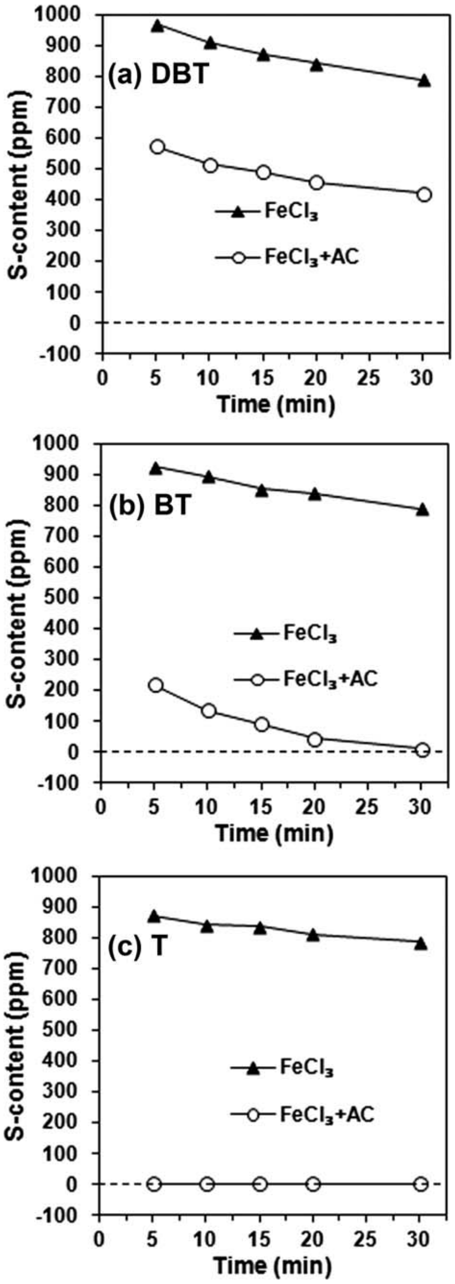


Figure 7. Desulfurization rate with or without AC in the presence of $FeCl_3$.

Table 3. Desulfurization Yield Comparison between Acid Anhydrides and AC in the Presence of $AlCl_3$

Acylation Material	Thiophenic Compounds	Desulfurization Yield (%)
AA–$AlCl_3$	DBT	30.5
	BT	62.9
PA–$AlCl_3$	DBT	31.9
	BT	97.5
BA–$AlCl_3$	DBT	44.5
	BT	99.1
AC–$AlCl_3$	DBT	99.2
	BT	99.6

with or without twofold AC at room temperature. As shown in Figure 7, the combination of AC–$FeCl_3$ always shows the better sulfur removal than sole $FeCl_3$, which indicates the presence of acylation reaction. And the desulfurization efficiency of AC–$FeCl_3$ is effective for the removal of BT and T, but unsatisfactory for DBT removal.

Table 4 lists the comparison between AC–$FeCl_3$ and AC–$AlCl_3$ in terms of rate constant (k) for catalysis and desulfurization yield (%) for adsorption. For these two catalysts for the acylation, it is seen that k of $FeCl_3$ and $AlCl_3$ are 0.383 and 6.175 L mol^{-1} min^{-1} for DBT, respectively, whereas the counterpart data are 5.055 and 6.294 L mol^{-1} min^{-1} for BT. Further, for these two adsorbents with AC, the desulfurization yields of $FeCl_3$ and $AlCl_3$ are 58.0 and 99.2% for DBT respectively, whereas the corresponding data are 98.8 and 99.6% for BT. Obviously, the results indicate that the catalytic and adsorptive activity of $FeCl_3$ are both poorer than those of $AlCl_3$. The phenomenon might be explained by the difference of their Lewis acidity. For $FeCl_3$ and $AlCl_3$, their Lewis acidity is ascribed to the electron deficiency of metal atom, being represented by the positive charge of metal atoms. As presented in Figure S6, Supporting Information, the positive charge of two metal atoms show the order of Fe $(+0.472) <$ Al $(+1.565)$, identifying the weaker acidity of $FeCl_3$, and accordingly, resulting in its lower ACDS performance.

ACDS in toluene-containing system

For the desulfurization of real oil, the sulfur selectivity is crucial, because other aromatic compounds have similar aromaticity and much higher concentration (15–40 wt %). For ACDS system, the competition of other aromatics like toluene, may show the following types: (1) toluene are acylated competitively, consuming the amount of AC and (2) the acylated toluene are adsorbed competitively.[21,34] Apparently, these competitions might deteriorate the ACDS process and decrease the desulfurization yield. Thus, the sulfur selectivity of the ACDS method needs to be tested in aromatic-rich system first. Figure 8 shows ACDS performance in toluene-rich (25 wt %) and toluene-free oils using fivefold $AlCl_3$ (mol/mol S) and twofold AC. The desulfurization yields at 30 min are 72.0% for DBT, 97.9% for BT, and 98.2% for T. Compared with toluene-free system, the sulfur removal in toluene-rich system is reduced to some degree, suggesting the presence of competition of toluene. It is worth noting that ACDS has done a good job for the sulfur removal in such a high aromatic-content system, that is, the mole ratio of toluene to sulfur being about 87.

As stated previously, $AlCl_3$ can remove sulfurs with the help of AC. However, for the adsorbent $AlCl_3$, the sulfur adsorbance (mg S/g) may not reach maximum value due to its excess presence. To obtain the maximum sulfur capacity of $AlCl_3$ with AC, onefold $AlCl_3$ is used with AC ranging from 0- to 0.8-fold in the toluene-rich oil. As shown in Figure 9, the sulfur capacity of $AlCl_3$ for DBT is increased from 0 to 27.3 mg S/g with AC increasing from 0- to 0.8-

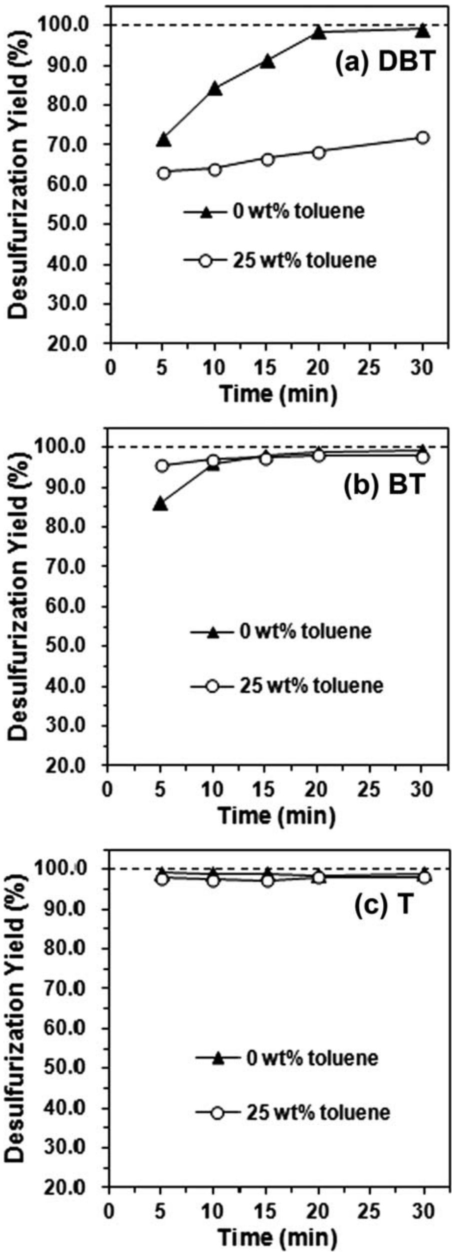


Figure 8. ACDS performance in toluene-rich model oil.

Table 4. Comparison of Desulfurization Activity Between AC–$AlCl_3$ and AC–$FeCl_3$

	k (L mol^{-1} min^{-1})		Desulfurization Yield (%)	
Acylation Material	DBT	BT	DBT	BT
AC–$AlCl_3$	6.175	6.294	99.2	99.6
AC–$FeCl_3$	0.383	5.055	58.0	98.8

Note: (1) k represents rate constant obtained from Supporting Information; (2) desulfurization yield is the data at 30 min reaction time; and (3) Conditions: fivefold $AlCl_3$, twofold AC, 303 K.

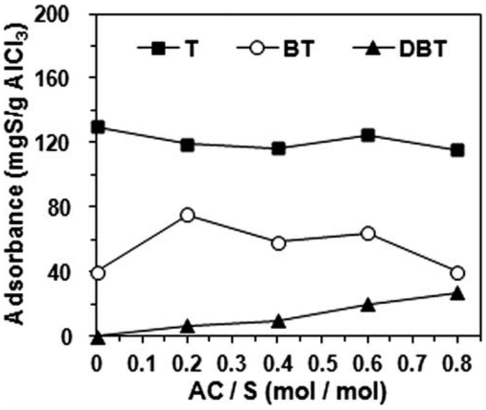


Figure 9. Sulfur capacity of $AlCl_3$ for three thiophenic compounds with varying amount of AC.

fold, which indicates that acylation reaction promotes the adsorbed quantity of sorbent for DBT. Further, the adsorption tendency of BT is not consistent with that of DBT, showing increased first and then reduced sulfur capacity with increasing amount of AC, and the maximum value (75.4 mg S/g) occurs when 0.2-fold AC is used. This phenomenon might be ascribed to the competitive adsorption of acylated toluene against unreacted BT in the presence of more than 0.2-fold AC. However, the sulfur adsorbance of $AlCl_3$ with AC is always higher than that without AC (40.3 mg S/g). For T, unexpectedly, the adsorbed sulfur quantity of $AlCl_3$ with AC is not increased but decreased slightly compared with that without AC. The result indicates that sole $AlCl_3$ has been effective enough for T, and the acylated toluene produced by adding AC show the competitive adsorption against original T. Thereby, the addition of AC is not beneficial for T in terms of the sulfur capacity, though it can improve the adsorptive rate of T.

ACDS in real oil

Table 5. ACDS Investigation for Real Oil

	Desulfurization Yield (%)	
AC (mol/mol S)	$AlCl_3$	$FeCl_3$
0	56.6	16.5
1	72.7	16.9
2	84.5	18.8

Note: The amount of Lewis acids are both fivefold (mol/mol S).

As mentioned earlier, AC–$AlCl_3$ shows good sulfur removal in toluene-rich system. For the real oil, however, more complex aromatics are present, and most of them are polycyclic aromatics. Thereby, ACDS performance for real oil may encounter greater challenge, because polycyclic aromatics show higher activity for electrophilic substitution. Before the ACDS experiments, the sulfur compound distribution in heavy pyrolysis oil used is analyzed by GC-FPD method[19,38] and compared with sulfur compounds in standard sample, as shown in Figure 10. With the analysis of peak retention time, the sulfur compounds in this oil are composed mainly of BT, DBT, and their alkylated derivatives, indicating that the sulfurs in this oil are all the refractory ones.[1]

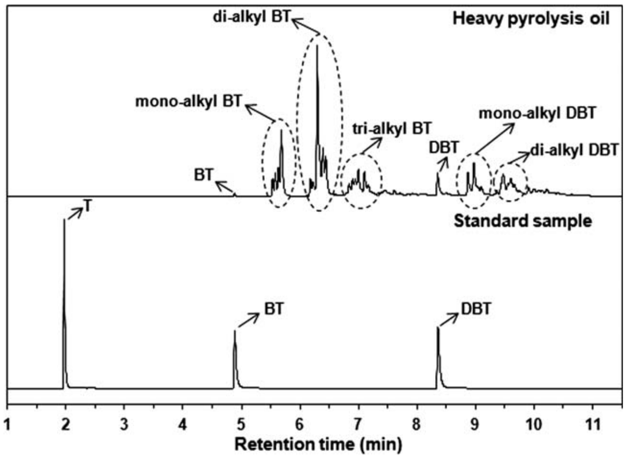


Figure 10. GC-FPD for the sulfur distribution in heavy pyrolysis oil.

The ACDS experiments in heavy pyrolysis oil are carried out at room temperature with a fixed reaction time 30 min using fivefold $AlCl_3$ or $FeCl_3$ (mol/mol S) and zerofold, onefold, or twofold AC. As presented in Table 5, adding AC to the system increases the sulfur removal of the systems, but desulfurization of AC–$FeCl_3$ is of low efficiency, indicating poor sulfur activity or selectivity of AC–$FeCl_3$. Fortunately, the desulfurization efficiency of AC–$AlCl_3$ improves to a great extent in contrast with that of sole $AlCl_3$ (56.6%), showing 72.7 and 84.5% sulfur removal for adding onefold and twofold AC, respectively. Obviously, the ACDS activity in real oil is a bit weaker than that in toluene-rich system. After ACDS experiment of AC–$AlCl_3$, some acylated sulfurs and aromatics are detected by GC–MS, as listed in Table S1, Supporting Information, and their MS spectrums are presented in Figures S7 and S8, Supporting Information, indicating the occurrence of acylation reaction in real oil and identifying the competition of polycyclic aromatics. And, the appearance of pyrolysis oil changes from muddy into transparent liquid as presented in Figure S9, Supporting Information, which may be ascribed to the removal of polycyclic aromatics with ACDS proceeding, and no AC residue is detected in the as-treated oil by HPLC in Figure S10, Supporting Information. Meanwhile, the elemental analysis listed in Table 6 shows that H/C increases after ACDS treatment, and N-content is also decreased, suggesting an improved quality of pyrolysis oil used. Moreover, considering the similarity between ACDS and extractive catalytic ODS (ECODS), that is, realizing desulfurization via improvement of basicity and polarity of thiophenic compounds, so the desulfurization results in real oil between these two methods are compared. As listed in Table 7, the ACDS may be superior to that of ECODS in terms of initial S-content in oils,

Table 6. Elemental Analysis for Real Oil Before and After ACDS

Oils	H/C (mol/mol)	S-Content (ppm)	N-Content (ppm)
Crude oil	1.44	6234	590
Oil after ACDS	1.55	966	120

Note: ACDS conditions: fivefold $AlCl_3$, twofold AC, 303 K, 30 min.

Table 7. Comparison of Desulfurization Performance Between ACDS and ECODS for Real Oil

Real Oils	S-Content (ppm)	Catalyst/Oil (g/g)	O/S (mol/mol)	Temperature (K)	Time (min)	Desulfurization Yield (%)
Pyrolysis oil	6234	0.13	2	303	30	84.5[a]
Diesel	5380	0.50	16	363	60	56.2[b]
Diesel	1078	0.67	40	303	30	71.3[c]

[a] ACDS in this work, catalyst: $AlCl_3$, O-containing reagent: AC.

[b] ECODS in Ref. 26, catalyst: $BmimZnCl_3$, O-containing reagent: H_2O_2.

[c] ECODS in Ref. 27, catalyst: $BmimFeCl_4$, O-containing reagent: H_2O_2.

catalyst amount, reaction condition, and desulfurization performance.[26,27]

Conclusion

ACDS proposed in this article show very good performance for thiophenic compounds under mild conditions, and AC–$AlCl_3$ is found to be the best ACDS material. In *n*-octane oil, DBT, BT, and T can be removed thoroughly by AC–$AlCl_3$ within 30 min. In toluene-rich oil, the desulfurization yields of AC–$AlCl_3$ are reduced slightly at 30 min, specifically, 72.0% for DBT, 97.9% for BT, or 98.2% for T. In this process, AC is the C=O group source, while $AlCl_3$ is both catalyst and adsorbent. For the catalysis of $AlCl_3$ in *n*-octane oil, the reaction rate constants of sulfur acylation are 6.175 and 6.294 L mol^{-1} min^{-1} for DBT and BT, respectively. Meanwhile, for the adsorption of $AlCl_3$ in toluene-rich oil, the sulfur capacity can be enhanced significantly with the help of AC, showing the enhancements from 0 to 27.3 mg S/g for DBT and from 40.3 to 75.4 mg S/g for BT. In real oil, moreover, AC–$AlCl_3$ still shows good desulfurization performance, showing the 84.5% sulfur removal and the improvement of oil quality.

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