



# Acylation desulfurization of heavy cracking oil as a supplementary oil upgrading pathway



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## ABSTRACT

Acylation reaction is used to enhance the basicity and polarity of the thiophenes and thus promote their adsorptive removability by Lewis acid, forming an acylation desulfurization (ADS) process for the refractory sulfurs. The ADS performance of six acylating reagents (ARs) was assessed for heavy cracking oil and light oil at 303 K with  $\text{AlCl}_3$  as the catalyst, and the influence of ADS on the oil quality was also studied. The results show that ADS is efficient to remove the thiophenes, but less efficient for the removal of mercaptans and thioethers in light oil. S-removal rate of 90.9% was achieved for heavy cracking oil with acetyl bromide (AB)- $\text{AlCl}_3$  (AB/S = 2/1;  $\text{AlCl}_3/\text{S} = 5/1$ ) in 0.5 h. The coexistent olefins and aromatics can slightly deteriorate the ADS performance and influence the oil properties. ADS might be used as a promising sulfur separating strategy for the cracking oil.

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## 1. Introduction

High sulfur (S-) content oil can cause serious air pollution and other environmental problems, and thus the S-content is being limited to a very low level, e.g. 10 ppm in many countries [1,2]. Hydrodesulfurization (HDS) is the conventional desulfurization process, which is however confronted with the challenge of the harsh conditions for the deep removal of thiophenes [3–6], e.g. benzothiophene (BT), dibenzothiophene (DBT) and their alkyl substituted derivatives, as well as the resulting influence on the oil compositions and quality.

Toward efficient desulfurization with high oil yield, it is advantageous to separate the refractory sulfurs first from the cracking oils via various separation methods, such as extraction [7–9], complexation [10,11] and adsorption [1,2,12,13], and then treat the resultant S-rich oil with a dedicated HDS process. The performance of these separation approaches is highly dependent on the physicochemical interaction between S-compounds (a Lewis base) and separating reagents (Lewis acid), and can be interpreted by the HSAB theory [14]. To enhance such interaction, many efforts have been tried to increase the acidity and/or softness of the extractants or adsorbents by various approaches, e.g. (1) by incorporating additional  $\text{AlCl}_3$  to the neutral ionic liquid [BMIM][ $\text{AlCl}_4$ ], forming a new ionic liquid with stronger Lewis acidity [15]; (2) by modifying the conventional adsorbents like active carbon and zeolite with soft Lewis acids, e.g.  $\text{Ni}^{2+}$ ,  $\text{Cu}^+$  and  $\text{Ag}^+$  to form additional  $\pi$ -complexation with thiophenes [2,16–18]; (3) by using a carbonium pseudo IL that offers a much higher acidity than conventional

imidazolium, ammonium, or phosphonium based ILs with the same anion [19]. In contrast to the above strategy, increasing the basicity of thiophenes is also advantageous for their efficient removal through extraction or adsorption. For example, all sulfones as oxidative products of thiophenes are much easier to be removed by a conventional adsorbent or extractant due to their higher polarity and basicity arising from the sulfoxide group ( $\text{S}=\text{O}$ ) [20–22]. Toward this direction, we proposed an acylation desulfurization (ADS) [23] method, whereby a carbonyl group ( $\text{C}=\text{O}$ ) is grafted to the thiophenic molecules via acylation reaction, and the resulting O-containing sulfurs are removed in situ by the Lewis acid catalyst used e.g.  $\text{AlCl}_3$  or  $\text{FeCl}_3$ . The desulfurization performance of ADS is excellent for model oil and effective for heavy cracking oil. In order to explore its practical applicability, more detailed work is needed for real oil (RO) so as to elucidate (1) its effectiveness for different species of S-compounds; (2) the workability of different ARs; (3) the impact of the coexisting aromatics in the feed oil; and (4) its influence on the oil quality.

## 2. Experiment

### 2.1. Materials

Acetyl chloride (AC, >99%) was purchased from Sinopharm Chemical Reagent. Propionyl chloride (PC, >99%), butyryl chloride (BC, >99%), propionic anhydride (PA, >99%), butyric anhydride (BA, >99%) were bought from Aladdin Chemistry. Acetyl bromide (AB, >98%) was purchased from Alfa Aesar. Aluminum chloride anhydrous ( $\text{AlCl}_3$ , >99%) was made by Shantou Xilong Chemical. All the reagents are used as received without further purification. Two kinds of oils were used in

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the study, i.e., heavy cracking oil from Puyang Petrochemical, and light oil from Chemical Research Institute of Daqing.

## 2.2. Oil analysis

Some physical properties and chemical compositions of the ROs were determined, including density, viscosity, boiling point–distillation curves, sulfur species and their distribution, S-content, N-content, and H/C ratio, etc. The density and viscosity at 293 K were measured respectively by Anton Paar DMA 5000 densimeter and Anton Paar AMVn viscosimeter. The simulated boiling point–distillation curve was measured and calculated by the SH/T 5008 method for the heavy cracking oil and its upper layer product, and ASTM D7169 method for the bottom layer product of desulfurized heavy cracking oil. The hydrocarbon ratio (H/C) was obtained by elemental analysis using EuroEA Elemental Analyzer.

The total S-content and N-content of ROs were measured by sulfur and nitrogen analyzer (KY-3000SN, China) Analysis details: high-purity Ar and O<sub>2</sub> as carrier gas; flow rate (Ar) = 170 mL · min<sup>-1</sup>, flow rate (O<sub>2</sub>) = 290 mL · min<sup>-1</sup>; furnace temperature = 1303 K; injection volume = 4 μL with its minimum detectable S-content being about 0.3 ppm. For each sample, the S-content analysis was repeated three times to get an average value. The maximum relative errors were within 3% when the S-content of the sample is more than 10 ppm and 15% when the S-content is less than 10 ppm, respectively. External standard method was used in this work and the standard curve was calibrated beforehand by samples with known S-content.

The S-compound distribution in RO was analyzed directly by Gas Chromatography–Sulfur Chemiluminescence Detector (GC–SCD, Agilent Gas Chromatograph 7890 equipped with SCD). Analysis details of GC: High-purity N<sub>2</sub> as carrier gas; column flow rate (N<sub>2</sub>) = 0.8 mL · min<sup>-1</sup>; HP-1MS column (30 m × 0.32 mm × 0.25 μm) was used. The column temperature was first set at 303 K and retained for 10 min and then the temperature was heated to 573 K at an increasing rate of 10 K · min<sup>-1</sup> and kept at 573 K for 20 min. Analysis details of SCD: temperature of burner = 1073 K; flow rate (H<sub>2</sub>) = 40 mL · min<sup>-1</sup>; flow rate (air) = 40 mL · min<sup>-1</sup>; and split ratio = 50:1.

## 2.3. ADS experiment

The ADS materials used are physical mixtures of Lewis acid AlCl<sub>3</sub> and different ARs, including AC, BC, PC, BA, PA and AB. To the RO, specific amount of AR like AC and Lewis acid like AlCl<sub>3</sub> was added in turn with vigorous magnetic stirring for a period of time at 303 K. The reaction was then stopped and the oil was separated into two phases by centrifugation. For the heavy cracking oil, the upper phase was colorless and transparent after water washing, and the bottom phase was a viscous black liquid after being treated as follows: (1) pouring out the upper phase by decantation, (2) adding HCl aqueous solution and CH<sub>2</sub>Cl<sub>2</sub> to the residue bottom phase with vigorous stirring for 10 min, (3) collecting the CH<sub>2</sub>Cl<sub>2</sub> layer and removing CH<sub>2</sub>Cl<sub>2</sub> by vacuum vaporization at 323 K. As such, the ADS materials added are removed while the S-compounds remained in the bottom oil phase. The as-treated oils were used for the analysis, characterization, and identification of the acylated products.

For continuous sampling experiment, 20 ml RO was used, and five samples (0.2 mL for each) at different times (10, 20, 30, 60 and 120 min) were taken out from the upper layer for S-content analysis.

## 3. Results and discussion

### 3.1. Oil composition and quality indices

Some physical properties and indices of the heavy cracking oil are as follows: density (293 K) = 0.8915 g · cm<sup>-3</sup>, viscosity (293 K) = 5.0631 mm<sup>2</sup> · s<sup>-1</sup>, H-content = 10.34 wt.%, C-content = 86.00 wt.%, S-content = 6234 ppm, N-content = 590 ppm. The heavy cracking oil

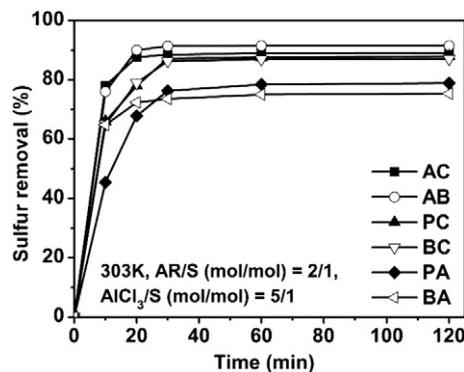


Fig. 1. Effect of reaction time and ARs on the sulfur removal.

is found to be composed of various alkanes and polycyclic aromatics and some olefins with average carbon number 15. Its S-content is quite high and most of them are alkylated derivatives of BT and DBT, which are hardly removed by the conventional HDS process. In contrast, the light oil is mainly composed of various alkanes and olefins and a little aromatics with average carbon number 8. Its S-content and N-content are relatively low, being 541 ppm and 86 ppm, respectively. The main S-compounds are various mercaptans and thioethers, while the polycyclic thiophenes are negligible. The detailed components of the heavy cracking oil and light oil as well as their sulfur species detected are presented in the supporting materials.

### 3.2. The ADS performance for heavy cracking oil

In the ADS experiments for model oils, the usage of AR and AlCl<sub>3</sub> are fixed as AR (AC, PC, BC, PA, BA or AB)/S = 2/1 and AlCl<sub>3</sub>/S = 5/1, respectively, on a mole basis. As shown in Fig. 1, the ADS reaction is a fast process, and the equilibrium can be reached within 0.5 h. The overall sulfur removal efficiency is promising being about 72% as the worst for BA–AlCl<sub>3</sub> and ca. 90% as the best for AB–AlCl<sub>3</sub> and AC–AlCl<sub>3</sub>. The acyl halides (AC, AB, PC, BC) shows better desulfurization performance than acid anhydrides (PA, BA) due to the competitive complexation between AlCl<sub>3</sub> and the resulting carboxylic acids and thus the lowering catalysis of the Lewis acid in the latter case.

The total S-content, the distribution of the residue S-species in the as-treated oil was compared with the original one. As shown in Fig. 2, all thiophene (T) and its derivatives and almost all BT and its derivatives with shorter alkyl substitutes are removed, which justified the effectiveness of the present process for the removal of thiophenes. But about 25% DBTs derivatives still remain in the upper layer product as estimated from the variations of the total S-content and the peak areas of all DBTs identified by GC–SCD, which may be ascribed to their weak

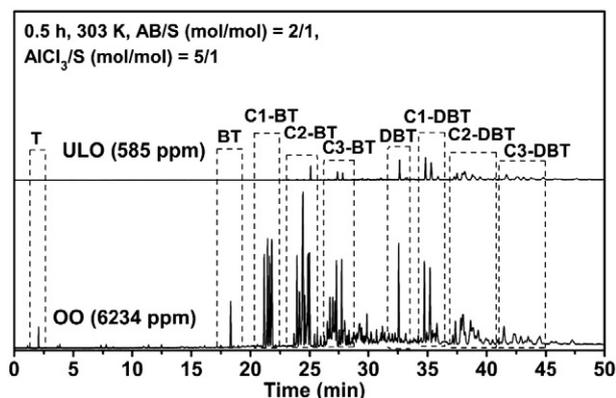


Fig. 2. Sulfur distribution of the heavy cracking oil before and after ADS treatment with AB–AlCl<sub>3</sub>.

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