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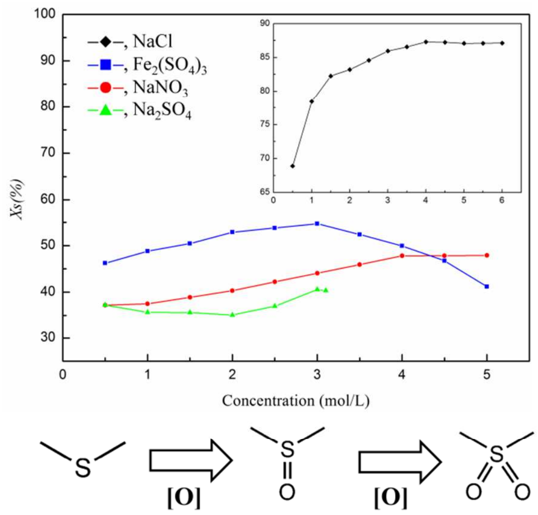

Inorganic salt were used as supporting electrolyte to oxidize organic sulfides and achieve the purpose of deep desulfurization.

Deep desulfurization of condensate gasoline by electrochemical oxidation and solvent extraction

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Abstract

Organic sulfides in liquid fuels have become one of the main sources of serious air pollution. To meet the environmental requirements, deep desulfurization of high sulfur-containing liquid fuels is necessary. In this paper, the combination of electrochemical oxidation and solvent extraction was proposed to reduce the sulfur content in condensate gasoline. FTIR and GC-FPD were utilized to analyze oxidation products and confirm the reaction process. The experimental results indicated that adding supporting electrolyte such as sodium chloride can markedly promote the oxidative desulfurization process. The oxidation products with strong polarity can be extracted by polar solvents effectively. The optimal electrochemical oxidation conditions were as follows: supporting electrolyte, electrolysis temperature, electrolysis time, volume ratio of electrolyte solution to raw oil and stirring rate were 4mol/L NaCl, 298 K, 50min, 3.0, 500 r/min, respectively. After electrochemical oxidation and three-stage extraction, the sulfur content of condensate gasoline decreased from 3478.4 μg/g to 13.1 μg/g and desulfurization efficiency reached 99.62%. Furthermore, the mechanism of electrochemical oxidation and solvent extraction desulfurization has been discussed.

Keywords

Condensate gasoline, Desulfurization, Electrochemical oxidation, Solvent extraction

1 Introduction

Organic sulfides in transportation fuels remain a primary source of air pollution because the burning of sulfur-containing fuels will result in hazy weather and acid rain [1]. With the rapid development of global economy, the demand and output of condensate gasoline increase significantly [2]. Condensate gasoline is widely used as high-quality fuel and chemical raw material in refining and hydrocracking process to produce naphtha, olefins, aromatics, gasoline and any other hydrocarbons [3-5]. However, condensate gasoline contains a large number of organic sulfides, especially mercaptans, which will poison the catalyst, corrosive pipes, and affect product quality [6]. The current specification in many developed countries has defined as that the maximum sulfur content in fuels is must be less than 10 μg/g [7]. The latest environmental regulations in China require that the sulfur content in fuels should be no higher than 50 μg/g from 2014 [8-9]. So removing or converting those organic sulfides to harmless materials is necessary for refiners.

The conventional method for desulfurization process is hydrodesulphurization technology (HDS), which is widely used all around the world. However, high pressure, high temperature, large amount of hydrogen and active catalysts are necessary for HDS [10-11]. In addition, the investment and operation cost of HDS is very high. For these reasons, many non-hydrodesulphurization technologies have been developed, such as oxidation, extraction, adsorption, alkylation, membrane separation, biodesulfurization and their combinations [12-19]. Compared with traditional hydrodesulphurization technology, oxidative desulfurization technology possesses the advantages of mild reaction conditions (ambient temperature and atmospheric pressure), reasonable investment and operation costs, more simple technological process and automatic control. The common oxidants of oxidative desulfurization are H_2O_2, peroxy acid and ionic liquids [20-22].

As a new kind of oxidative desulfurization method, electrochemical oxidative desulfurization has been investigated in recent years. No consumption of oxidants and small amount of wastewater makes this technology with high research values [23]. Chen et al. [24] reported that organic sulfur compounds in coal water slurry could be effectively removed by electrochemical oxidation-extraction in KNO_3 and ionic liquids system. Zhao et al. [25] pointed out sulfides can be removed from coal efficiently by electrochemical oxidation in NaCl solution. Schucker et al. [26] invented an electrochemical oxidative process to remove sulfides from a model hydrocarbon stream. Besides, Wang et al. [27-28] developed an electrochemical desulfurization process to remove organic sulfur compounds in an electrochemical fluidized-bed reactor using particle group anode (i.e. β-PbO_2/C or CeO_2/C). The experimental results showed that the particle group anode could considerably improve the electrochemical catalysis performance and promote the electrochemical oxidation reaction rate of the desulfurization reaction. However, studies of electrochemical oxidative desulfurization are mainly concentrated on coal water slurry. Few researches are focused on the combination of electrochemical oxidation and solvent extraction desulfurization process of liquid fuels, especially for high mercaptan containing condensate gasoline. Related studies on supporting electrolyte and extraction agents in desulfurization process are scarce.

In this paper, the combination of electrochemical oxidation and solvent extraction was used to remove organic sulfides from high sulfur-containing condensate gasoline (sulfur content: 3478.4 μg/g). Four kinds of inorganic salt were used as supporting electrolyte in 10% H_2SO_4 solution with a constant current of 500 mA in electrochemical oxidation. Several kinds of extractants were used to remove oxidation products of organic sulfides in the extraction process. In addition, the optimal desulfurization conditions of condensate gasoline were also been studied.

2 Experimental

2.1 Chemical Materials

The sample of condensate gasoline (density: 732.0 kg/m^3, sulfur content: 3478.4 μg/g) was supplied by PetroChina Southwest Oil and Gasfield Company. NaCl (AR, 99.5%), $NaSO_4$ (AR, 99.0%), $NaNO_3$ (AR, 99.0%), $Fe(SO_4)_3$ (AR), H_2SO_4 (AR, 98.0%), $C_{16}H_{35}N{\bullet}H_2SO_4$ (Tetrabutyl Ammonium Hydrogen Sulfate) (LR, 99.0%), N-methyl-2-pyrrolidone (NMP) (AR, 99.0%), Methanol (AR, 99.5%), Acetonitrile (AR, 99.0%), Polyethylene glycol 400 (PEG400) (AR), N-Formylmorpholine (NFM) (AR, 99.0%) were purchased from Chengdu Kelong Chemical Co., Ltd. All reagents were used without any further purification. All solutions were prepared in ultrapure water (electrical resistant: 18.25 MΩ•cm).

2.2 Experimental Methods

The desulfurization process of condensate gasoline was divided into two steps, electrochemical oxidation and solvent extraction. As shown in Figure 1, the electrochemical oxidation experiments of condensate gasoline were carried out in an electrolytic cell with 10% H_2SO_4 solution as electrolyte solution and the current was constant 500 mA. Two graphite electrodes with dimension of 20 mm × 20 mm were work as anode and cathode, respectively. The space between two electrodes was 2.5 cm. Different concentrations of inorganic salt (such as NaCl, Na_2SO_4, $NaNO_3$ and $Fe_2(SO_4)_3$) were added in electrolyte solution to work as supporting electrolyte. A small amount of phase transfer catalysts ($C_{16}H_{35}N{\bullet}H_2SO_4$, 0.1 mol/L) were added in electrolyte solution to promote the oxidizing reaction on the phase interface.

10 ml condensate gasoline was mixed with an amount of prescribed electrolyte solution and then put into the electrolytic cell under atmospheric pressure. After electrochemical oxidation and a few minutes' standing, oil and electrolyte were layered. The upper condensate gasoline was separated by separating funnel and the organic sulfur (oxidation products) was removed by solvent extraction. The desulfured condensate gasoline and extracting agents were collected and prepared for further analysis. Meanwhile, the optimal conditions of electrochemical oxidation and solvent extraction desulfurization were examined.

Figure 1. The sketch of electrochemical desulfurization experimental setup

(1-potentiostat, 2-anode, 3-electrolysis cell, 4-raw oil, 5-electrolyte solution, 6-magnetic stir bars, 7-thermostatic magnetic stirring water bath, 8-cathode)

2.3 Analysis Methods

The total sulfur content of condensate gasoline before and after desulfurization tests were determined by WKL-3000 sulfur-chlorine analyzer (Taizhou Guochang Analytical Instruments Co., Ltd.). Both the accuracy and relative error of sulfur-chlorine analyzer were ≤ 5%. The condensate gasoline before and after electrochemical oxidation was analyzed by Fourier transforms infrared spectra (FTIR) (Beijing Beifen-Ruili Analytical Instruments Co., Ltd.). The conversions of organic sulfides in condensate gasoline were analyzed by using GC-FPD (GC-9790II, Zhejiang Fuli Analytical Instrument Co., Ltd.) with a DM-PLOT S capillary column (30 m × 0.53 mm × 20.00 μm). The injector temperature was 513 K, and the detector temperature was 533 K. The column temperature was programmed from 313 K (maintained for 2 min) to 493 K at 5 K/min, and the carrier gas was nitrogen. In addition, the total desulfurization efficiency (X_S) of condensate gasoline was calculated as follows:

$$Xs = \frac{S_0 - S_T}{S_0} \times 100\%$$

Where X_S was the desulfurization efficiency (%) of condensate gasoline, S_0 and S_T were the sulfur content (μg/g) of raw oil and products, respectively. All data (error ≤ 5%) were presented as the average of two replicates in each treatment.

3 Results and discussion

3.1 Supporting Electrolyte

It is inefficient to use H_2O directly in electrochemical oxidation desulfurization test, though H_2O can be oxidized at anode to produce hydroxyl radical [23]. In our experiments, the desulfurization efficiency of blank group (direct electrochemical oxidized by 10% H_2SO_4 solution and extracted by NMP) was only 35.08%, slightly higher than direct extraction by NMP (desulfurization efficiency: 34.63%). So it is necessary add supporting electrolyte, which served as not only conducting medium but also electrochemical catalysts, in electrochemical oxidative desulfurization process [27]. The influence of different supporting electrolytes on the electrochemical oxidative desulfurization efficiency was shown in Figure 2. It can be seen from the diagram that all supporting electrolytes can enhance the electrochemical oxidative desulfurization process, the desulfurization effect of NaCl was better than Na_2SO_4, $NaNO_3$ and $Fe_2(SO_4)_3$. This was because Cl^- can be oxidized at anode to produce highly reactive oxidants (such as ClO^-) to promote oxidative desulfurization [25]. Besides, Na^+ and NO_3^- has no significant effect on desulfurization as the slow raised of the desulfurization efficiency was came from the increase of the conductivity with the adding of Na_2SO_4 and $NaNO_3$.

In Figure 2, the desulfurization efficiency first increased markedly with the increasing of NaCl concentration, till the concentration rose to 4 mol/L. After then, the desulfurization efficiency almost remains the same. For Fe^{3+}, though the increasing trend became slower than NaCl, it still has a general desulfurization effect. This result can be explained that the polyvalent metal ion (such as Fe^{3+}) possesses a special oxidation-reduction cycle in the electrochemical process which can partly promote the desulfurization reaction [23]. However, too much $Fe_2(SO_4)_3$ (more than 3 mol/L in Figure 2) increased the viscosity of electrolyte solution, which will weaken the mass transfer and then finally lead to a decrease of desulfurization efficiency. Based on the above experimental results and discussion, the optimal supporting electrolyte was NaCl and the concentration of NaCl was 4 mol/L.

Figure 2. Effect of electrolyte concentration on electrochemical desulfurization

(─◆─, NaCl; ─■─, $Fe_2(SO_4)_3$; ─●─$NaNO_3$; ─▲─, Na_2SO_4)

(Experimental conditions: electrolysis temperature: 298 K, electrolysis time: 60 min, volume ratio of electrolyte to oil: 3.0, stirring rate: 500 r/min, extractant: NMP)

3.2 Electrolysis Temperature

Electrolysis temperature was a very important factor in oxidative desulfurization as it affects not only the reaction rate but also the mass transfer rate [29]. The effect of electrolysis temperature on desulfurization was shown in Figure 3(a). The desulfurization efficiency decreased tardily with the increase of electrolysis temperature. The *Xs%* kept more than 80% even when the temperature rose to 350 K. This was because that the electrochemical oxidation reaction released heat, and raised system temperature, which restrained the desulfurization reaction [30]. Furthermore, high temperature was beneficial to the oxygen evolution from water, which would result in a loss of energy. Considering the desulfurization efficiency and economic efficiency, 298 K (ambient temperature) was a suitable reaction temperature.

3.3 Electrolysis Time

Another important technical parameter for oxidative reactions was electrolysis time, which reflects the oxidative reaction efficiency and determines the experimental energy consumption [31]. The effect of electrolysis time on desulfurization efficiency was shown in Figure 3(b). When the electrolysis time was less than 50 min, extending reaction time could improve the desulfurization efficiency effectively. But when the time exceeded 50 min, the desulfurization efficiency almost unchanged, which means that most of the organic sulfides can be oxidized in 50 min. Furthermore, longer reaction time will lead to a lot of power consumption which will reduce the current efficiency. Consequently, 50 min was the optimal reaction time.

3.4 Volume Ratio of Electrolyte Solution to Raw Oil

The electrolyte solution and condensate gasoline in electrolysis cell are two phases, which means the volume ratio of electrolyte solution to raw oil should be discussed for improving their mass transfer and reaction rate [32]. In Figure 3(c), the desulfurization efficiency grew very quickly with the increasing of the volume ratio, which could be explained reasonably as that the increasing of electrolyte volume provided more oxidants (such as hydroxyl radical and hypochlorite anion) which generated at anode by H_2O or Cl^- to oxidize the organic sulfides in electrolyte solution. However, too much electrolyte solution will lead to oxygen evolution on anode, which will reduce the current efficiency and economic efficiency, therefore, 3.0 was a suitable volume ratio of electrolyte solution to raw oil in the experiments, and the desulfurization efficiency could reach 87.35% at that point.

3.5 Stirring Rate

Stirring rate effect the degree of mixing of raw oil and electrolyte solution in electrochemical oxidation process. As long as sulfur-containing compounds contacted with anode or active oxidants easily, the desulfurization efficiency could be high, especially for contact effect between oil and water phase [23]. It can be inferred from Figure 3(d) that the desulfurization efficiency raised with the increasing of stirring rate. When the stirring rate was 0 r/min (without stirring), the desulfurization efficiency was 72.82%, much higher than direct extraction by NMP (desulfurization efficiency: 34.63%). This result revealed that the oxidization reaction will occur after passing an electric current. And the desulfurization efficiency of electrochemical oxidation–extraction process is much higher than direct extraction. When the stirring rate exceeded 500 r/min, condensate gasoline and electrolyte solution mixed uniformly, the desulfurization efficiency reached 87.35%. Although continue increasing the stirring rate can promote the mass transfer rate and increase the desulfurization efficiency, the rate of increment was too small. Considering the energy consumption and economy, 500 r/min was the optimal stirring rate.

Figure 3. Effect of Operating Conditions of Electrochemical Oxidation

(a) Electrolysis Temperature (electrolysis time: 60 min, V (electrolyte solution): V (raw oil) = 3.0, stirring rate: 500 r/min).

(b) Electrolysis Time (electrolysis temperature: 298 K, V (electrolyte solution): V (raw oil) = 3.0, stirring rate: 500 r/min).

(c) V (electrolyte solution): V (raw oil) (electrolysis time: 50 min, electrolysis temperature: 298 K, stirring rate: 500 r/min).

(d) Stirring Rate (electrolysis temperature: 298 K, electrolysis time: 50 min, V (electrolyte solution): V (raw oil) = 3.0).

Other common reaction conditions: supporting electrolyte: 4 mol/L NaCl, extractant: NMP.

3.6 Extraction Solvents and Extraction Times

It can be deduce that the extraction of the organic sulfides depends markedly on the nature of organic sulfides especially their partition coefficient, solubility and polarity [33]. After electrochemical oxidation, the organic sulfides in condensate gasoline have been translated to sulfoxide and sulfone. Those oxidation products with strong polarity and high boiling point can be extracted by polar solvents very easily [34]. The extraction desulfurization effect of different polar solvents was shown in Table 1 and Figure 4(a). In the extraction process of oxidized condensate gasoline, all solvents can effectively extract the oxidized sulfur compounds from condensate gasoline. The extraction effect declined in the order: NMP > Acetonitrile > NFM > Methanol > PEG400. However, in the direct extraction process of condensate gasoline, all solvents cannot extract organic sulfides effectively. These results showed that the combination of electrochemical oxidation and solvent extraction can remove organic sulfides more efficient than direct extraction. Besides, the yield loss of condensate gasoline was mainly caused by the extraction process. The electrochemical oxidation process did not result in a condensate gasoline yield loss. Moreover, NMP was the most effective solvent among five polar solvents.

In order to achieve deep desulfurization effect and obtain clean fuel, multistage extraction was performed for the reduction of sulfur content of liquid fuels to considerably negligible amount [35]. As can be observed in Figure 4(b), all solvents exhibited excellent extraction behavior within three extraction stages. Among the five polar solvents, NMP possess the best extraction desulfurization effect.

Table 1. Sulfur contents and volume yield in different extraction solvents after oxidation

Figure 4. Effect of (a) Extraction Solvents and (b) Extraction Times

(Oxidative conditions: supporting electrolyte, 4 mol/L NaCl, electrolysis temperature: 298 K, electrolysis time: 50 min, volume ratio of electrolyte to oil: 3.0, stirring rate: 500 r/min)

The optimum operating conditions of electrochemical oxidation were summarized as follows: supporting electrolyte: 4 mol/L NaCl, electrolysis temperature: 298 K, electrolysis time: 50 min, V (electrolyte solution): V (raw oil) = 3.0, stirring rate: 500 r/min. After three-stage extraction by NMP, the desulfurization efficiency reached 99.62% and the sulfur content of condensate gasoline decreased from 3478.4 μg/g to 13.1 μg/g. The sulfur content of condensate gasoline has already met the definite requirement of low sulfur fuels (e.g., < 10~50 μg/g) [1, 4, 35].

3.7 FTIR and GC-FPD Analysis

To make clear the desulfurization mechanism of electrochemical oxidation and solvent extraction, correlation analysis has been performed. The FTIR spectra of condensate gasoline before and after electrochemical oxidation were shown in Figure 5. This diagram illustrated the conversion of organic sulfides in electrochemical oxidation process. The peaks of 1303cm^{-1} and 1159cm^{-1} (-SO_2), 1050cm^{-1} (-SO) and 579 cm^{-1} (-C-Cl) were observed in condensate gasoline after electrochemical oxidation. According to previous researches [21, 36, 37, 38], those peaks were the characteristic peaks of sulfoxide and sulfone. These results indicated that organic sulfides have been successfully oxidized to sulfoxide and sulfone in electrochemical oxidation process. Besides, carbon-chlorine bond was also observed after electrochemical oxidation, this is because a part of organic sulfides which with weak reductive (such as mercaptans) can react with ClO^- and Cl_2 to sulfonyl chloride compounds [39].

The GC-FPD chromatograms of raw and oxidized condensate gasoline after NMP extraction were presented in Figure 6. It can confirm from this diagram that the main organic sulfides in condensate gasoline were mercaptans, only a part of organic sulfides had been removed by direct extraction. However, after electrochemical oxidation-extraction, almost all organic sulfides have been removed. This consequence proved that most organic sulfides in condensate gasoline were nonpolarity or weak polarity, which cannot dissolve in polar solvents. After electrochemical oxidation, organic sulfides were transformed into the corresponding oxidation products, those oxidation products were easily dissolved in polar solvents.

Figure 5. FTIR spectra of condensate gasoline before and after electrochemical oxidation

Figure 6. GC-FPD chromatograms of condensate gasoline before and after desulfurization

(A: Raw oil, B: Direct extraction, C: Electrochemical oxidation-extraction)

In addition, the existence of ClO^{-} was demonstrated by an indicator. After oxidation, a few drops of methyl orange were added to the electrolyte solution. The color of the electrolyte immediately turned to red and soon faded. This result indicated that large amounts of ClO^{-} had been generated after electrochemical oxidation.

3.8 The Reaction Process of Electrochemical Oxidative and Solvent Extraction Desulfurization

After electrochemical oxidation under the best operating condition, S=O and O=S=O were detected by FT-IR, this result proved that the final oxidative products of organic sulfides were sulfoxide and sulfone. The GC-FPD analyses indicated that only by oxidation can those organic sulfides be effectively removes by polar solvents. Furthermore, the appeared of ClO^{-} showed that those anion play the role of oxidants. Based on the above analyses and previous researches [24, 36, 39, 40, 41, 42], a possible desulfurization reaction process of condensate gasoline by electrochemical oxidation and solvent extraction was brief description in Figure 7.

Firstly, high-activity oxidative medium (such as hydroxyl radical and hypochlorite anion) was obtained by electrochemical oxidation of H_2O and Cl^- at anode. Secondly, the oxidative medium will oxidize the sulphur atom to S=O and O=S=O at the phase interface between electrolyte solution and condensate gasoline. It will significantly increase the polarity of sulfide molecules. At the same time, those oxidative medium will be deoxidized and then participate in the next reaction. Finally, the oxidation products of organic sulfides were extracted by polar solvents and completely separated from condensate gasoline.

Figure 7. Mechanism of the desulfurization process

4 Conclusions

In this paper, the remove of organic sulfides from condensate gasoline through the combination of electrochemical oxidation and solvent extraction has been systematically studied, and the following results obtained.

(1) As a new kind of desulfurization methods, electrochemical oxidative desulfurization can efficiently reduce the organic sulfur content at room temperature and atmospheric pressure. Adding supporting electrolyte such as sodium chloride will promote oxidative desulfurization significantly.

(2) The electrochemical oxidation of organic sulfides was an indirect oxidation process and no conventional oxidants were used. The oxidation products with strong polarity can be

extracted by polar solvents very easily. Among all polar solvents in the experiment, NMP has the best extraction desulfurization effect.

(3) After electrochemical oxidation under the optimum operating conditions (supporting electrolyte: 4 mol/L NaCl, electrolysis temperature: 298 K, electrolysis time: 50 min, V (electrolyte solution): V (raw oil) = 3.0, stirring rate: 500 r/min) and three-stage extraction by NMP, the desulfurization efficiency reached 99.62% and the sulfur content of condensate gasoline decreased from 3478.4 μg/g to 13.1 μg/g. The product has already met the definite requirement of low sulfur fuels.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. *b* These authors contributed equally.

Notes

The authors declare no competing financial interest.

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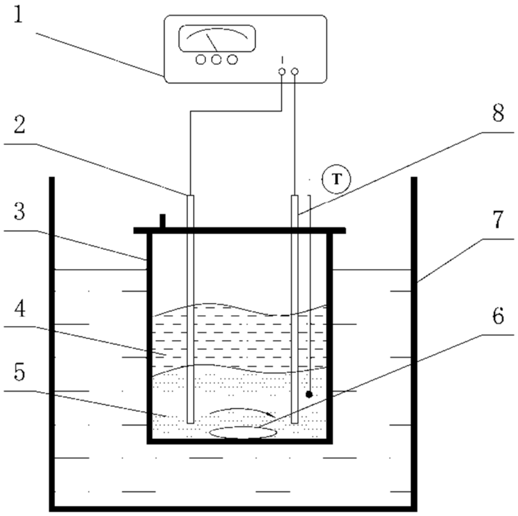

Figure 1. The sketch of electrochemical desulfurization experimental setup

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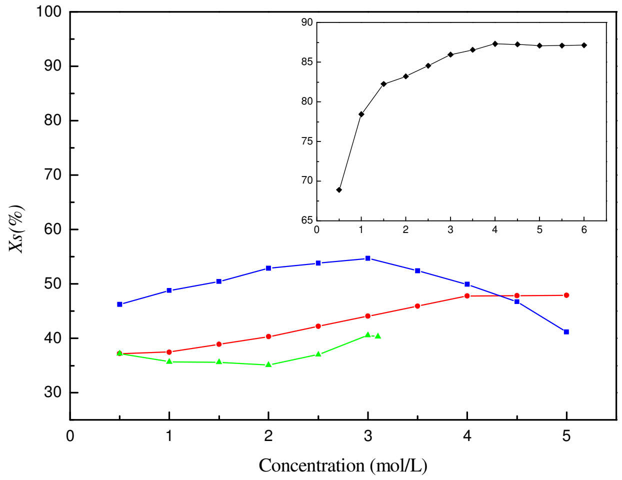
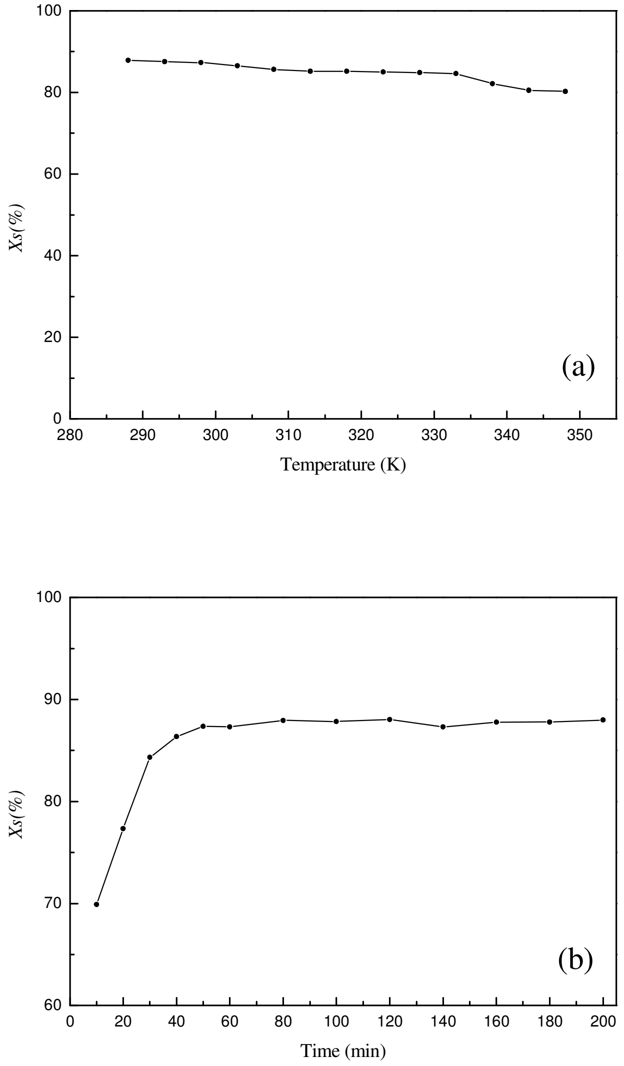


Figure 2. Effect of electrolyte concentration on electrochemical desulfurization

(—◆—, NaCl; —■—, $Fe_2(SO_4)_3$; —●—$NaNO_3$; —▲—, Na_2SO_4)

(Experimental conditions: electrolysis temperature: 298 K, electrolysis time: 60 min, volume ratio of electrolyte to oil: 3.0, stirring rate: 500 r/min, extractant: NMP)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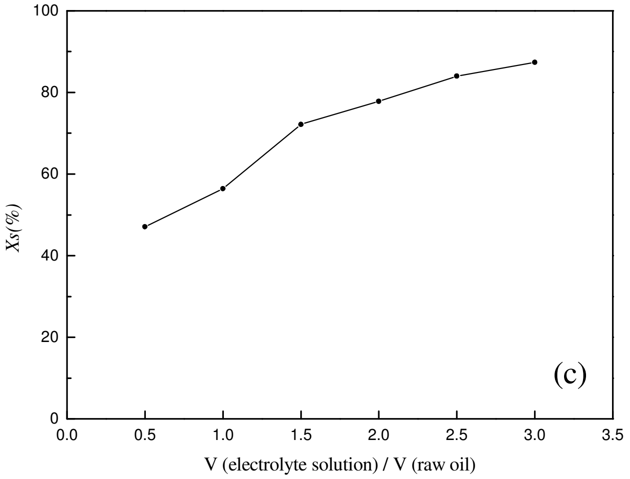
40
60
80
100
120
140
160
180
200
Time (min)
(b)



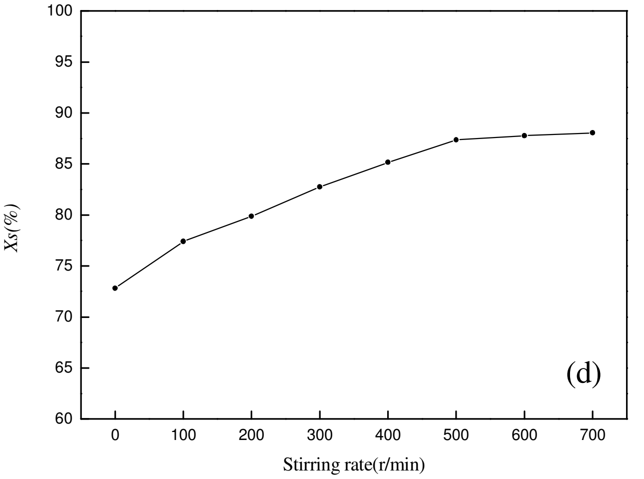


Figure 3. Effect of Operating Conditions of Electrochemical Oxidation

(a) Electrolysis Temperature (electrolysis time: 60 min, V (electrolyte solution): V (raw oil) = 3.0, stirring rate: 500 r/min).

(b) Electrolysis Time (electrolysis temperature: 298 K, V (electrolyte solution): V (raw oil) = 3.0, stirring rate: 500 r/min).

(c) V (electrolyte solution): V (raw oil) (electrolysis time: 50 min, electrolysis temperature: 298 K, stirring rate: 500 r/min).

(d) Stirring Rate (electrolysis temperature: 298 K, electrolysis time: 50 min, V (electrolyte solution): V (raw oil) = 3.0).

Other common reaction conditions: supporting electrolyte: 4 mol/L NaCl, extractant: NMP.

Table 1. Sulfur contents and volume yield in different extraction solvents after oxidation

extraction solvents	density (kg/m^3)	S-content (μg/g)	X_S (%)	volume yield (%)
NMP	1028	440.0	87.35	86
Methanol	791	759.7	78.16	90
Acetonitrile	786	719.3	79.32	90
NFM	1142	741.6	78.68	89
PEG400	1125	1349.3	61.21	92

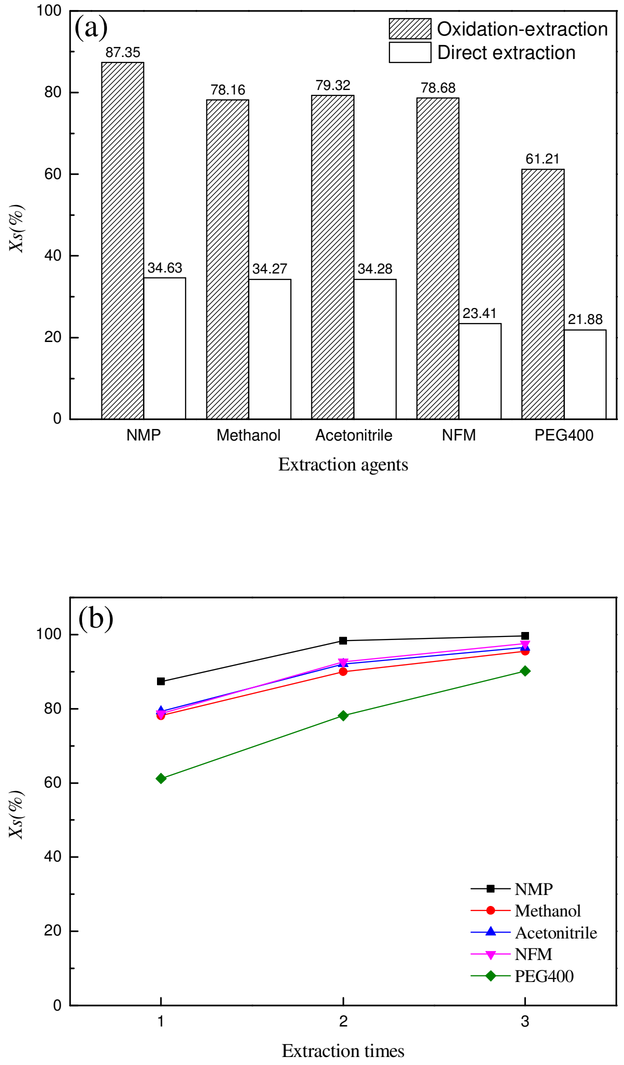


Figure 4. Effect of (a) Extraction Solvents and (b) Extraction Times

(Oxidative conditions: supporting electrolyte, 4 mol/L NaCl, electrolysis temperature: 298 K, electrolysis time: 50 min, volume ratio of electrolyte to oil: 3.0, stirring rate: 500 r/min)

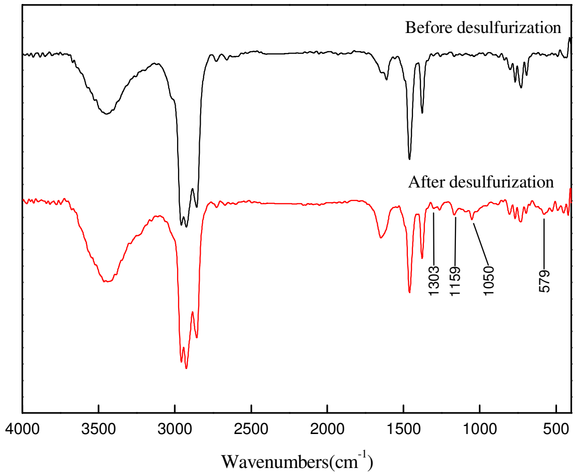


Figure 5. FTIR spectra of condensate gasoline before and after electrochemical oxidation

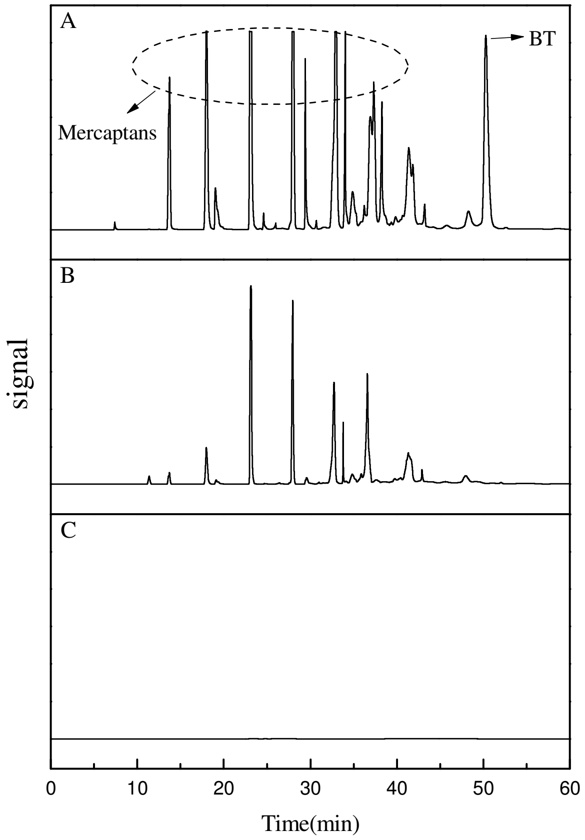


Figure 6. GC-FPD chromatograms of condensate gasoline before and after desulfurization

(A: Raw oil, B: Direct extraction, C: Electrochemical oxidation-extraction)

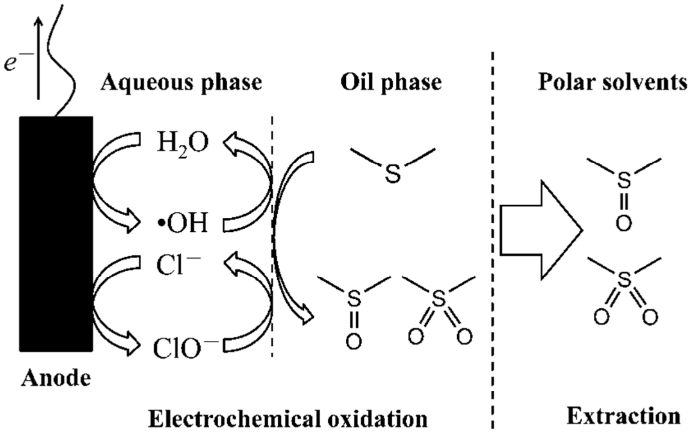


Figure 7. Mechanism of the desulfurization process