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Decomposition Mechanism of Organic Sulfide in Heavy Oil during Thermal Reaction

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Abstract: As the proportion of high-sulfur crude oil continues to rise, the transformation behavior of sulfur compounds during delayed coking is of considerable significance for clean fuel production and for controlling the sulfur content of petroleum coke. In this work, model crude oil systems were constructed using liquid paraffin as the saturate fraction and p-xylene as the aromatic fraction, with thiophene and benzothiophene added separately. Thermal reaction experiments were conducted at 500 °C for 3 h. Gas chromatography with sulfur chemiluminescence detection (GC-SCD) was used for qualitative and quantitative analysis of the sulfur composition in gas- and liquid-phase products, and the transformation pathways of sulfur compounds were inferred in conjunction with free-radical reaction mechanisms. The results show that H_2S predominates in the gas-phase sulfur in both systems, and that the liquid phase contains, in addition to unreacted sulfur compounds, a substantial variety of newly formed sulfur compounds. These findings demonstrate that the thermal reactions in both systems follow a free-radical mechanism centered on C–S bond activation. Furthermore, benzothiophene is converted from a readily desulfurized small molecule into sulfur compounds that are more prone to condensation and coke formation. The results provide a molecular-level basis for regulating the transformation of thiophene-type sulfur compounds and for low-sulfur clean processing in heavy oil thermal reactions.

Keywords: Thiophene; Benzothiophene; Thermal Reaction; Sulfur Compound Transformation; Free-radical Mechanism.

1. Introduction

In recent years, as human exploitation of petroleum resources has continued to increase, crude oil resources around the world have been steadily declining, and crude oil quality has been deteriorating. A large proportion of crude oil is high-sulfur crude oil with sulfur content ≥2% [1]. As a result, the output of vacuum residue processed by China's refining and petrochemical units has increased year by year, making the upgrading and cleaning of heavy oil a major problem and challenge facing China's refining and petrochemical enterprises.

The processing of residue is a highly systematic process involving many refining technologies [2,3], among which delayed coking is a very important residue processing process. China's delayed coking capacity ranks second in the world. The average API gravity of world crude oil is projected to decline from 33.3 in 2009 to 32.9 in 2030, and the average sulfur content is projected to increase from 1.11% in 2009 to 1.22% in 2030. In heavy oil processing, the presence of sulfur has a crucial impact on petroleum processing quality. Sulfur can cause corrosion of refining and petrochemical equipment, poisoning and deactivation of catalysts, and environmental pollution. Out of consideration for environmental friendliness, countries around the world have set higher requirements for the quality of products from petroleum processing, especially the sulfur content in products. Many countries have implemented corresponding product sulfur standards, imposing stricter management and quality requirements on fuel oils [4-6].

On the other hand, due to the increasing proportion of high-sulfur crude oil and the deterioration of its quality, the sulfur content of petroleum coke, the main by-product of the delayed coking process, has also continued to increase. Petroleum coke is characterized by high carbon and low ash content and can be classified into low-sulfur coke, medium-sulfur coke, and high-sulfur coke [7-9]. Low- and medium-sulfur coke can be used as fuel for the production of carbonaceous materials. Because sulfur causes irreversible damage and pollution to the environment, high-sulfur coke cannot be directly used for combustion power generation either [10-12]. Therefore, reducing the sulfur content of gasoline, diesel, and petroleum coke has important energy and environmental value [13].

The thermal reaction process of heavy oil is extremely complex. References [14-17] indicate that two basic reactions mainly occur in the thermal reaction process of heavy oil, namely cracking reactions and condensation reactions, both of which follow the free radical reaction mechanism. In order to gain a deeper understanding at the molecular level of the conversion and distribution patterns of sulfur compounds in the heavy oil thermal reaction process, relatively simple model compounds are used to replace the complex heavy oil system, so as to realize research on the conversion and distribution patterns of sulfur compounds in the thermal reaction process of model compounds. Sulfur compounds in heavy oil are mainly thiophene-type sulfur compounds. Therefore, clarifying the conversion patterns of thiophene-type sulfur compounds in the thermal reaction process is of great significance for the low-sulfur cleaning of energy and for supporting the realization of national clean energy goals [18-19].

Based on the actual compositional characteristics of crude oil, this paper establishes a simulated system with liquid paraffin and xylene as the main components, and adds thiophene and benzothiophene sulfur compounds to the system. By studying the distribution patterns of sulfur compounds in the products after thermal reaction, the conversion patterns of sulfur compounds with different structures in the thermal reaction process are investigated, and the conversion mechanism of sulfur compounds in the

thermal reaction process is clarified.

2. Experimental Section

2.1. Thermal Reaction Experimental Apparatus and Experimental Procedure

According to the model system in the literature [20], this paper uses liquid paraffin as the saturate fraction of the model compounds and p-xylene as the aromatic fraction of the model compounds, and adds different contents of thiophene and benzothiophene to establish a crude oil simulation system. The sulfur composition of the gas and liquid phase products during the thermal reaction process was studied by chromatography, and the possible conversion pathways of sulfur compounds in the thermal reaction process were inferred based on the product composition and characteristics. The specific procedure is as follows: first, a certain mass of model oil was weighed and placed in a beaker, heated in a heating mantle and stirred until uniformly mixed. After 1 h, it was poured hot into a high-pressure reactor. The air in the reactor was replaced three times with N2, and the airtightness of the apparatus was checked at the same time. Then the reaction temperature was set, heating was started, and timing began when the temperature in the reactor reached the target temperature and stabilized. After 3 h, the heating was turned off and the reaction ended. After cooling to room temperature, the gas outlet valve was opened and the reaction gas was collected in an aluminum foil gas bag. The reactor was opened, and the liquid product produced by the reaction was withdrawn with a dropper for testing sulfur content and sulfur distribution.

2.2. Analytical Methods for Products of the Thermal Reaction Process

2.2.1. Analysis of Sulfur Compounds in Gas-phase Products

An aluminum foil gas bag was connected to the exhaust valve of the high-pressure autoclave to collect gas-phase products. A gas chromatograph was used to analyze sulfur composition information, and qualitative and quantitative analysis of gas-phase products was carried out according to the retention times of substances in the standard gas. Sulfur-containing compounds were analyzed and characterized by GC-SCD. The chromatographic operating conditions were as follows: the column was an HP-PONA column with dimensions of 60 m × 320 μm × 4.2 μm; the inlet temperature was 250 °C; the detector temperature was 280 °C; the oven initial temperature was 35 °C, increased to 230 °C at a rate of 10 °C/min, and held for 15 min.

2.2.2. Analysis of Sulfur Composition in Liquid-phase Products

The sulfur composition of the liquid-phase products after thermal reaction was analyzed by gas chromatography equipped with a sulfur chemiluminescence detector (SCD). The chromatographic operating conditions were as follows: the column was an HP-PONA column with dimensions of 50 m × 200 μm × 0.5 μm; gasoline method: inlet temperature 250 °C; detector temperature 250 °C; oven initial temperature 35 °C, increased to 180 °C at a rate of 2 °C/min, and held for 72.5 min.

3. Experimental Results and Discussion

3.1. Investigation of the Conversion Mechanism of the Thiophene Model System in the Thermal Reaction Process

3.1.1. Composition Analysis of Thermal Reaction Products of the Thiophene Model System

An appropriate amount of the prepared thiophene model compound was poured into a high-pressure reactor, preparations before reaction were carried out according to the above experimental method, and the reaction temperature was set to 500 °C with a reaction time of 3 h. After the reaction ended, the gas and liquid components were collected for sulfur type testing. The sulfur conversion distributions in the collected gas and liquid components are shown in Fig. 1 and Fig. 2.

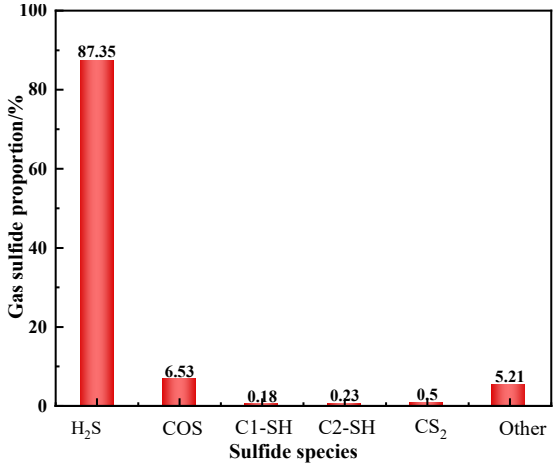


Fig 1. Gas-phase products of the thermal reaction of the thiophene model compound

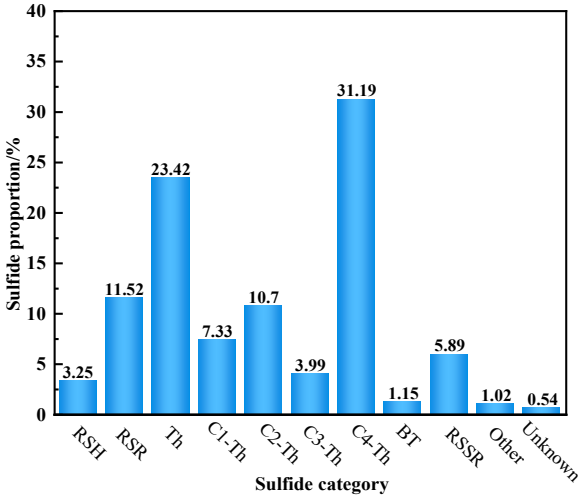


Fig 2. Sulfur distribution in the liquid-phase products of the thermal reaction of the thiophene model compound

As shown in Fig. 1 and Fig. 2, a total of four sulfur compounds were detected in the gas products of the thiophene model compound, among which most of the gaseous sulfur compounds were H2S, with its proportion being more than ten times or even several tens of times that of the other sulfur compounds. YAN et al. [21] found in pyrolysis experiments of the 2-methylthiothiophene model compound using TPD-MS that the release intensity of H2S in the gas products was significantly higher than that of COS, CS2, and other sulfur compounds. During the thermal reaction process, thiophene

undergoes C–S bond cleavage to generate SH radical fragments, which subsequently combine with free hydrogen to form H2S [22-23]; hydrogen transfer reactions of other substances in the thermal reaction system provide free hydrogen for the C–S bond cleavage. Carbonyl sulfide (COS) may be formed by the combination of sulfur-containing radicals with some oxygen-containing groups in the thermal reaction system [24]. CS2 may be formed by the combination of CS radicals generated during the thermal conversion of thiophene with S radicals.

Apart from unreacted thiophene, the sulfur compounds in the liquid products were mainly alkyl-type thiophenes, such as 2-methylthiophene, 3-methylthiophene, and some dimethylthiophenes. There were also some benzothiophene-type sulfur compounds as well as small amounts of hydrogen sulfide, thiols, carbon disulfide, thioethers, and disulfides. After the reaction ended, while opening the reactor to collect the products, a trace amount of carbon black was found at the bottom of the reactor. The appearance of carbon black indicates that during the thermal cracking of the thiophene model compound, some components underwent condensation reactions to form a small amount of coke. Zhu Genquan [25], Wu Chuanpeng [26], and Corma [27], in summarizing the conversion patterns of thiophene-type sulfur compounds, all observed the phenomenon of coke formation via condensation reactions of thiophene-type sulfur compounds. In the thermal reaction process of the model compounds, besides the thermal conversion reactions of sulfur compounds, the solvents liquid paraffin and p-xylene also undergo thermal conversion reactions.

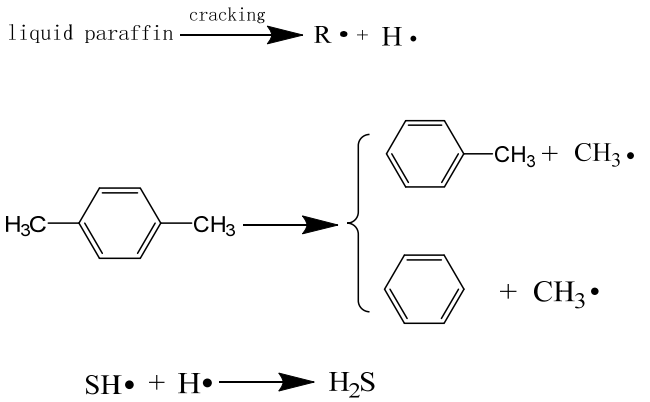


Fig 3. Possible Reaction Paths of Solvothermal Reaction in Model Compounds

Therefore, the thermal conversion pathways of the solvents are analyzed first: paraffin is an alkane substance with a high carbon number, and during the thermal reaction process it undergoes free radical dehydrogenation reactions or chain scission reactions, generating a series of alkanes, alkenes, and hydrogen radicals. In particular, when the dehydrogenation reaction of paraffin generates olefins with C6 or more, these olefins undergo aromatization reactions to form substances containing benzene ring structures [18]. p-Xylene follows the free radical thermal cracking mechanism during the thermal reaction process. Because the benzene ring has high structural stability, the degree of ring-opening reaction of the benzene ring in p-xylene during the thermal reaction process is relatively small, and it tends to undergo side-chain cleavage and dehydrogenation reactions. Cleavage of the side-chain methyl C–C bond of p-xylene can generate benzyl radicals or benzene rings. The thermal conversion pathways of the solvents are shown in Fig. 3. Through preliminary literature research, it was found that few previous studies have explored the thermal reaction conversion pathways of model compounds. Therefore, deducing the reaction pathways of the model compounds based on the gas-phase and liquid-phase products detected by chromatography is of certain significance.

3.1.2. Formation Mechanism Analysis of H2S

The formation of H2S mainly originates from two parts. One part is the direct cleavage of the C–S bond of the thiophene ring, with the SH radical reacting with H radicals in the system to form H2S; the other part may originate from the C=C double bond of the thiophene ring accepting H· generated from paraffin chain scission or dehydrogenation reactions of other substances in the system, whereby the double bond is saturated to form tetrahydrothiophene, and tetrahydrothiophene undergoes high-temperature cracking to generate H2S.

3.1.3. Formation Mechanism Analysis of Thiols and Thioethers

Through compositional analysis of the liquid products, it was found that the thiols in the liquid products were mainly ethanethiol, allyl mercaptan, and 3-methyl-2-butanethiol. The formation pathway of ethanethiol may be that the C–S bond of tetrahydrothiophene first cleaves to generate butanethiol; according to bond energy theory analysis of the structure of butanethiol, the C–C bond located in the middle of the butanethiol molecular structure is prone to cleavage, generating ethanethiol and ethane. The formation pathway of allyl mercaptan may be that thiophene accepts free hydrogen generated in the system, one of the C=C bonds is first saturated, and then the C–S bond connected to the double bond is broken, generating allyl mercaptan. The formation pathway of 3-methyl-2-butanethiol is that the thiophene ring is saturated by hydrogen radicals, the C–S bond cleaves to generate butanethiol, and butanethiol undergoes free radical reactions with free methyl radicals in the reaction system to generate methylbutanethiol. The formation pathway of thiols with more than 4 carbon atoms is the cleavage of the C–S bond of alkylthiophenes generated in the system. The main formation pathway of thioethers in the liquid products is that the double bond of thiophene is saturated and the C–C bond at the β position cleaves. The formation pathways of other thioethers are roughly that thiophene first undergoes double bond saturation, then C–C bonds at different positions cleave, or chain reactions with free methyl, ethyl, and other radicals in the system occur to generate them. The formation pathway of thioethers with more than 4 carbon atoms is the cleavage of the C–C bond of alkylthiophenes.

3.1.4. Formation Mechanism Analysis of Alkylthiophenes

The main sulfur compounds in the liquid-phase products are alkylthiophenes, including C1, C2, C3, and C4 thiophenes. The main formation pathway is that methyl radicals, ethyl radicals, and propyl radicals in the system attack the thiophene ring, generating thiophene-type sulfur compounds with methyl groups at different positions.

3.1.5. Formation Mechanism Analysis of Benzothiophene-Type Sulfur Compounds

The formation pathway of BT may be that thiophene directly undergoes polycondensation and polymerization reactions with benzene rings in the system, changing from the original monocyclic structure to polycyclic sulfurated aromatic hydrocarbons. The formation pathway of

alkylbenzothiophenes is the combination of benzothiophene with free methyl radicals in the system.

In summary, the reactions of thiophene during the thermal reaction follow the free radical reaction mechanism, undergoing a series of reactions such as ring-opening chain scission, dehydrogenation, condensation, and alkylation. The thermal reaction pathways of thiophene are shown in Fig. 4 and Fig. 5.

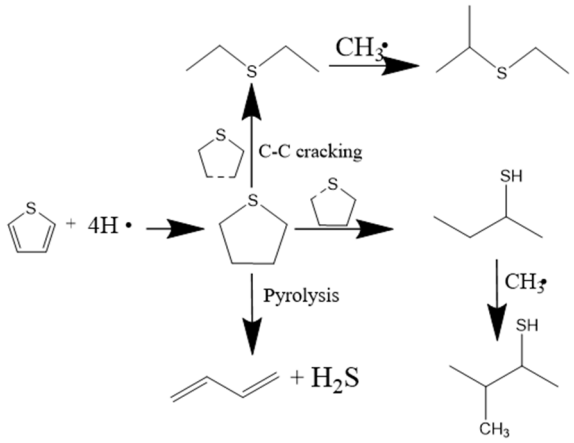


Fig 4. Possible Reaction Paths of Thiophene to tetrahydrothiophene

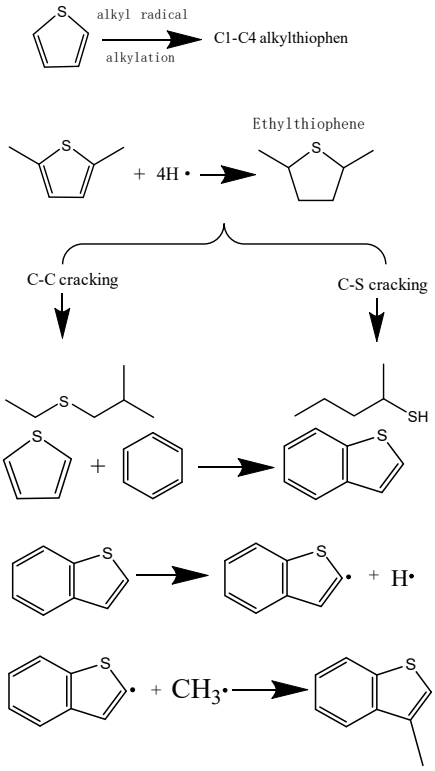


Fig 5. Alkylation of Thiophene and Possible Reaction Paths of Products

3.2. Investigation of the Conversion Mechanism of the Benzothiophene Model System in the Thermal Reaction Process

3.2.1. Composition Analysis of Thermal Reaction Products of the Benzothiophene Model System

An appropriate amount of the prepared benzothiophene model compound was poured into a high-pressure reactor. Preparations before the reaction were carried out according to the above experimental method, and the reaction temperature was set to 500 °C with a reaction time of 3 h. After the reaction ended, the gas and liquid components were collected for sulfur type testing. The sulfur conversion distributions in the collected gas and liquid components are shown in Fig. 6 and Fig. 7.

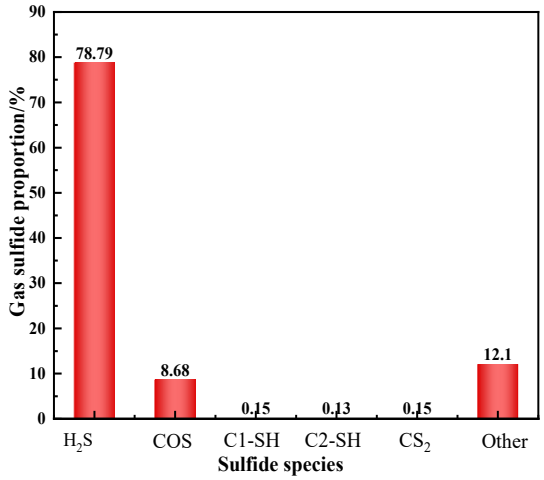


Fig 6. Distribution of gas-phase products from the thermal reaction of the benzothiophene system

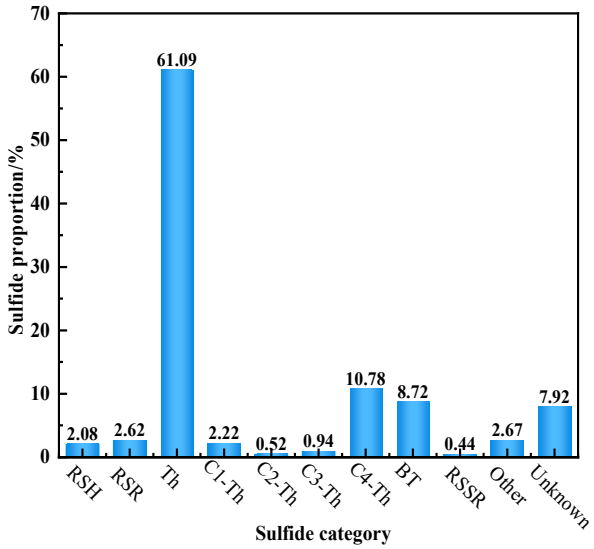


Fig 7. Sulfur distribution in the liquid-phase products of the thermal reaction of the benzothiophene system

As can be seen from Fig. 6, during the thermal reaction of the benzothiophene model compound, most of the sulfur compounds in the gas were H2S, along with small amounts of carbonyl sulfide, thiophene, and trace amounts of methanethiol, ethanethiol, and CS2. The main source of H2S is that the C–S bond of benzothiophene is attacked by hydrogen radicals in the system, undergoes bond cleavage to produce SH radicals, and the SH radicals combine with hydrogen radicals to form H2S. The formation of carbonyl sulfide is mainly due to the homolytic cleavage of C–S bonds and hydrogen transfer reactions of thiophene-type sulfur compounds during the thermal reaction process, with various sulfur-containing radical intermediates generated combining with oxygen-containing groups in the system. As shown in Fig. 7, the sulfur compounds in the liquid products were mainly thiophene-type and their derived sulfur compounds and alkylbenzothiophene-type compounds, accompanied by small amounts of thiols, thioethers, and hydrogen sulfide conversion products. The relative content of thiophene reached 61.09%, indicating that during the thermal cracking of benzothiophene, ring-opening reactions mainly occur to

generate thiophene, and thiophene reacts with free CH3·, CH3CH2·, and CH3CH2CH2· in the system to generate alkylthiophenes with different carbon numbers. BT also undergoes alkylation reactions with free methyl, ethyl, and propyl radicals to generate alkylbenzothiophenes. As can be seen from the above figures, compared with the thermal conversion process of the thiophene model compound, the small-molecule sulfur compounds generated during the thermal conversion of benzothiophene decreased, and most were converted into cyclic sulfur compounds such as thiophene, with a conversion ratio of 75.55%.

3.2.2. Formation Mechanism Analysis of Thiols and Thioethers

Most of the thiols and thioethers generated during the thermal conversion of the benzothiophene model compound were C3–C6 products. Because the benzene ring of benzothiophene has high stability and is not prone to ring opening during the thermal reaction process, the small-molecule thiols and thioethers generated by the reaction roughly all originate from benzothiophene undergoing hydrogen transfer reactions to generate dihydrobenzothiophene, which then undergoes ring-opening cracking to generate intermediate products of thioethers or thiols.

3.2.3. Formation Mechanism Analysis of Thiophene and Alkylthiophenes

Benzothiophene undergoes saturation and ring-opening reactions to generate thiophene, and then thiophene undergoes alkylation reactions to generate alkylthiophenes.

3.2.4. Formation Mechanism Analysis of Alkylbenzothiophenes

The dihydrobenzothiophene generated by the hydrogen transfer reaction of benzothiophene in Section 5.3.2.1 above undergoes ring-opening cracking to generate intermediate products, which can undergo alkylation reactions with free BT in the system to generate alkylbenzothiophenes; another pathway is that some benzothiophene in the system is attacked by free methyl radicals, ethyl radicals, and propyl radicals, undergoing free radical reactions to generate alkylbenzothiophenes.

In summary, based on the types and distribution characteristics of the gas and liquid products, the thermal reaction conversion pathways of the benzothiophene model compound are inferred as shown in Fig. 8, and Fig. 9.

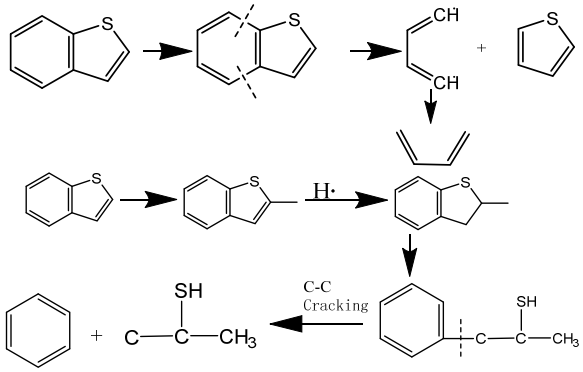


Fig 8. Possible Reaction Paths of Benzothiophene to Thiophene and Benzothiophene after Ring Opening

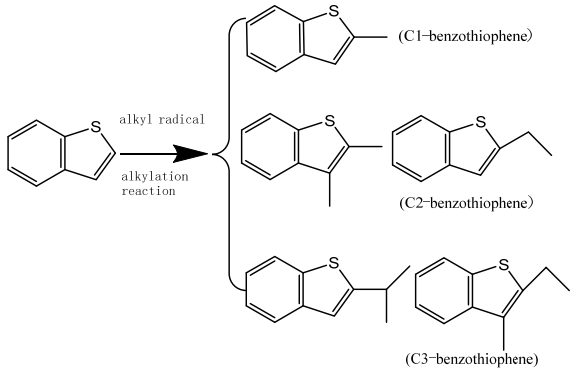


Fig 9. Possible Paths of Alkylation of Benzothiophene

3.3. Comparative Analysis of the Cracking Mechanisms of Thiophene and Benzothiophene

Thiophene and benzothiophene both belong to the class of thiophene-type sulfur-containing model compounds. Their cracking and desulfurization behaviors are both centered on C–S bond activation, but the fusion of the benzene ring significantly changes the electronic structure, adsorption configuration, and reaction selectivity of the molecule, causing the two to exhibit systematic differences in reaction pathways, product distribution, and coking tendency.

3.3.1. Analysis of Common Features of the Reaction Mechanisms

The cracking of both is not a simple thermal scission process, but requires hydrogen transfer to achieve activation of the C–S bond. The aromaticity of the thiophene ring and the benzothiophene ring gives the C–S bond a relatively high cleavage energy barrier, and the efficiency of direct pyrolysis is limited; the hydrogen transfer effect of hydrocarbon hydrogen donors or catalysts in the system can first hydrogenate and saturate the sulfur-containing ring system, reducing the C–S bond order and promoting ring opening, and then S–H radical fragments combine with free hydrogen to generate H_2S. At the same time, both are prone to alkylation side reactions with olefins and hydrocarbon fragments in the system: thiophene undergoes alkylation to generate light alkylthiophenes such as methylthiophene and dimethylthiophene, while benzothiophene undergoes alkylation to generate alkylbenzothiophenes, causing the boiling points of sulfur compounds to increase and to migrate toward heavy fractions. In addition, under inert thermal reaction conditions, both have relatively high thermal stability, the selectivity of simple desulfurization is limited, and side reactions such as polymerization and condensation occur in parallel, constituting the chemical source of coke deposition.

3.3.2. Differences in Reaction Pathways and Selectivity

The cracking of thiophene is dominated by the pathway of C–S bond cleavage for desulfurization. Under thermal reaction conditions of 500 °C and 3 h, H_2S was absolutely dominant among the gas-phase sulfur compounds, with its content being more than ten to several tens of times that of the remaining sulfur compounds such as COS and CS_2, indicating that hydrodesulfurization of SH radical fragments is the main channel for thiophene conversion; COS can be generated by the combination of sulfur-containing radicals with oxygen-containing groups in the system, and CS_2 can be generated by the combination of CS radicals with S radicals. Apart from unreacted thiophene, the liquid phase was mainly alkylthiophenes such as 2-methylthiophene, 3-

methylthiophene, and dimethylthiophene, accompanied by benzothiophene-type compounds, thiols, thioethers, and disulfides, while the trace amount of carbon black at the bottom of the reactor indicates that thiophene undergoes polymerization/polycondensation and deep cracking side reactions at high temperature, that is, desulfurization and coking constitute a competition.

The conversion of benzothiophene, by contrast, is dominated by alkylation-induced weight increase, and direct ring-opening desulfurization is not its main destination. The reactivity of benzothiophene is significantly higher than that of thiophene: in FCC model compound studies, thiophene is extremely stable in the gasoline fraction, whereas benzothiophene is more readily involved in conversion; it preferentially undergoes alkylation with hydrocarbon fragments, generating higher-boiling alkylbenzothiophenes that are enriched in the diesel and higher fractions, and some undergo polymerization and condensation to form coke. In hydrogenation catalytic systems, influenced by the probability of directional hydrogenation and the ease of adsorption on active centers, the conversion order can show the pattern benzothiophene > thiophene > dibenzothiophene.

3.3.3. Correlation Between Product Sulfur Distribution and Coking Behavior

From the perspective of sulfur conversion pathways, the thiophene system is dominated by gas-phase H_2S removal, and the liquid-phase sulfur mainly remains as unreacted thiophene and light alkylthiophenes, with sulfur tending to remain in the gasoline fraction or transfer to the gas phase; the benzothiophene system, because alkylation dominates, has sulfur compounds enriched toward diesel and heavy fractions as the boiling point increases, and the contribution of gaseous desulfurization is relatively low. It is worth noting that the detection of benzothiophene-type sulfur compounds in the liquid products above implies that thiophene can be converted into benzothiophene-type intermediates through aromatization/condensation pathways at 500 °C, and the generated benzothiophene, due to its higher activity, can further undergo alkylation or condensation, ultimately contributing to heavy sulfur and bottom carbon black. It can thus be seen that the core contradiction in thiophene cracking is the competition between desulfurization to produce H_2S and condensation to form coke, while the core destination of benzothiophene cracking is alkylation and condensation. The introduction of the benzene ring transforms benzothiophene from a desulfurizable small molecule into a reaction intermediate that is more prone to condensation and more prone to coke formation.

4. Conclusion

Under thermal reaction conditions, after cracking, thiophene gave gas-phase products dominated by H_2S and liquid-phase products mainly consisting of alkylthiophenes accompanied by benzothiophene-type compounds, thiols, and thioethers, following the free radical mechanism, with desulfurization competing with coking. The gas-phase products of the benzothiophene system were also dominated by H_2S, and the liquid phase was dominated by thiophene-type compounds and alkylbenzothiophenes (thiophene accounted for 61.09%, and the conversion of benzothiophene to thiophene-type compounds reached 75.55%), with hydrogen transfer, saturation, ring opening, and benzene removal to form thiophene as the dominant pathway. Both are centered on C–S bond activation, require hydrogen transfer participation, and are prone to alkylation; however, thiophene tends to transfer sulfur to the gas phase via desulfurization, whereas benzothiophene, owing to benzene ring fusion, is more reactive and more prone to condensation and coke formation. Benzothiophene-type sulfur compounds were detected in the thiophene system, indicating that thiophene can undergo aromatization–condensation–coking conversion. This study reveals the desulfurization–condensation–coking conversion route of thiophene-type sulfur compounds during thermal reaction.

Acknowledgments

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