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The effect of heavy aromatic sulfur compounds on sulfur in cracked naphtha

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Abstract

The scope of the present study was to elucidate the effect of heavy sulfur compounds, commonly found in the gas oils, on the percentage of sulfur in gasoline range during the Fluid Catalytic Cracking (FCC) process. Five model sulfur compounds commonly found in the gas oils were studied: benzothiophene, 2-methyl-benzothiophene, 3-decyl-thiophene, dibenzothiophene and 4,6-dimethyl-dibenzothiophene. In order to maintain a realistic hydrocarbon environment each one of the heavy sulfur model compounds were diluted in conventional gas oil. Their cracking behaviour were studied using a steamed deactivated FCC catalyst, while the run tests were performed in an automated Short Contact Time Microactivity Test Unit (SCT-MAT) operated at 560 °C and 12 s run time. The experimental results indicated that the long chain alkyl-thiophene (3-decyl-thiophene) is mainly responsible for the increase of sulfur amount in the gasoline range during cracking, through dealkylation and side cracking reactions for the production of thiophene and shorter chain alkyl-thiophenes, respectively. That sulfur compound was also the most reactive one with respect to desulfurization, since it was highly cracked to H_2S and decomposed to S in coke. On contrary, the polycyclic sulfur compounds did not affect the sulfur amount in gasoline, while their reactions were strongly related to their chemical structure. Thus, the main reaction pathway of the alkylated 2-methyl-benzothiophene and 4,6-dibenzothiophene during the FCC process was isomerization, while for benzothiophene and dibenzothiophene alkylation reactions were dominated.

Keywords: Benzothiophene; Dibenzothiophene; FCC gasoline sulfur

1. Introduction

Sulfur is the most abundant heteroatom in crude oils. Generally, the higher the boiling point of the petroleum fraction, the higher its sulfur content. Gas oils represent the feedstock of the Fluid Catalytic Cracking Unit (FCCU), which is the main contributor to the total gasoline pool, and typically their sulfur content is half the sulfur of the total crude oil [1,2]. The main sulfur compounds in gas oils are benzothiophenes, dibenzothiophenes and their alkylated derivatives, which represent the most refractory and stable sulfur compounds [3].

Choudhary et al. [4] analyzed two heavy oils in terms of their sulfur groups content and distribution. In their study they reported that heavy oils can differ appreciably in their total sulfur content and distribution. Benzothiophenes, dibenzothiophenes, benzonaphthothiophenes, and nonaromatic sulfides were the dominating compounds in one of the heavy oils studied, while thiophenes, phenanthrothiophenes, thiophenes with a total of five annulated rings either in compact or extended form, and thiophenes with a total of six annulated rings were also present in much smaller amounts. Brunet et al. [5] made an extensive review on the possible origins of sulfur impurities in FCC gasoline. They reported that in order to identify the origin of the sulfur impurities in FCC gasoline, it is essential to know what are the sulfur compounds present in FCC feedstocks. According to their study the potential sulfur components in these feedstocks are thiophene, benzothiophene, dibenzothiophene, polyaromaticthiophenes and their alkylated derivatives as well as thiols and sulfides.

According to FCC pilot plant results reported by Collet et al. [6], the majority of the feed sulfur after cracking is found in flue

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gases as H_2S (33–55%) and liquid streams, namely gasoline (2–5 wt.%), diesel (18–30 wt.%) and HCO. Valla et al. [7], have studied extensively the sulfur distribution in FCC gasoline product coming from FCC pilot plant and short contact time microactivity test (SCT-MAT) experiments showing that sulfur in cracked gasoline distributes roughly as light mercaptans and disulfides (20 wt.%), thiophene and alkylthiophenes (50 wt.%) and benzothiophene (30 wt.%) depending on the feed sulfur.

While crude sources are getting heavier and more sour, world wide environmental legislation regarding transportation fuels force the refineries to reduce the sulfur content in gasoline towards 10 ppm by the year 2011 [8]. Typical problems caused by the sulfur compounds are catalyst poisoning and deactivation in processing, corrosion of equipment and the oxidation of sulfur compounds to SO_x when fuel combustion, which causes serious environmental problems [9]. Gasoline from the FCC units makes up about 25–40 wt.% of the gasoline blend stocks and accounts for over 90 wt.% of the sulfur in the entire gasoline pool [10]. Approaches to reducing sulfur content in FCC gasoline include [10]: (1) post-treating product to remove sulfur from FCC gasoline; (2) pre-treating the FCC feed to remove sulfur. A new challenging approach for the in situ desulfurization during the FCC operation using appropriately designed catalytic additives is widely studied nowadays from several scientific groups [11–15]. Albemarle Resolve Technology and Grace Davison's Saturn (GSR) Technology are representative FCC catalyst additives that have been commercialized [10]. However, more research and scientific effort is needed in order to produce more efficient materials. The difficulty to remove sulfur compounds using selective catalyst additives in situ the FCC process is due to the aromatic character of the thiophenic compounds which makes them highly stable [16].

Recently, more fundamental studies are conducted on the reaction mechanism and the kinetics of sulfur compounds during the FCC process, in order to give light on their reactivity and proceed with more efficient materials for their in situ reduction [17–21]. Corma et al. [17] studied the reaction mechanism of sulfur compounds using real gas oil spiked with different sulfur model compounds. In reference to their experimental results thiophene is a very stable molecule, while alkylated thiophenes are more reactive. Benzothiophene follows mainly alkylation reactions for the production of alkyl-benzothiophenes, while alkylated benzothiophenes cracks to lighter alkyl-benzothiophenes but mainly decomposes to coke. Valla et al. [19] and Harding et al. [20] studied the mechanism and also the kinetics of sulfur compounds present in gasoline fraction introducing model sulfur compounds in hexadecane. According to the experimental results of Valla et al. [19] benzothiophene is more reactive than thiophene. However, it does not participate in cracking reactions, while slightly desulfurize. It follows mainly alkylation reactions for the production of heavier alkylated benzothiophenes.

While all the above studies were mainly focused on the reaction mechanism of gasoline sulfur compounds, the aim of the present study was to determine the precursors of sulfur compounds in gasoline range. It is worthy to be noted that Beltran et al. [21] suggested that thiols and mercaptans, could be responsible for the formation of thiophenic species during the FCC process through cyclization and dehydrogenation reactions. Besides, Leflaive et al. [18] have proved that H_2S in combination with the presence of olefins may also react for the formation of thiophenic derivatives. Our scope was to determine the heavy sulfur compounds found in gas oils that may be responsible for the formation of sulfur compounds in FCC gasoline during their cracking. With respect to this scope five sulfur compounds, commonly found in gas oils, were

Table 1
Heavy model sulfur compounds (chemical structure, boiling and melting points)

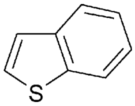
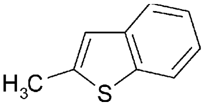
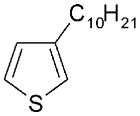
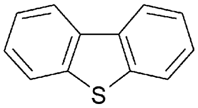
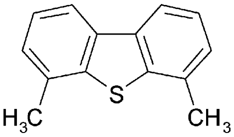
Sulfur model compounds	Chemical structure	Boiling point (°C)	Melting point (°C)
Benzothiophene (Aldrich, 99% purity)		221–222	
2-Methyl-benzothiophene (Aldrich, 97% purity)		~240	47–52
3-Decyl-thiophene (Aldrich, 97% purity)		119–120	
Dibenzothiophene (Aldrich, 99% purity)		332–333	
4,6-Dimethyl-dibenzothiophene (Aldrich, 97% purity)			153–157

Table 2
Reference gas oil properties

Properties	
API	22.8
Density (60 °C) (g/ml)	0.8856
Density (15 °C) (g/ml)	0.916
Specific gravity	0.9169
Sulfur (wt.%)	0.6094
Total nitrogen (wt.%)	0.1497
Average boiling point (°C)	460
ASTM D-1160 (°C)	2 mmHg
IBP	325.9
10%	400.4
20%	425.8
30%	443.3
50%	469.3
70%	498.5
80%	516
90%	541.6
FBP	>584.8

studied in terms of their cracking effect on the sulfur content in gasoline product.

2. Experimental

Five heavy aromatic model sulfur compounds were studied: benzothiophene, 2-methyl-benzothiophene, 3-decyl-thiophene, dibenzothiophene and 4,6-dimethyl-dibenzothiophene. The chemical structure and some physical properties of the above components are shown in Table 1. In order to isolate the cracking behaviour of the above heavy sulfur compounds from the numerous and complicated catalytic cracking reactions of hydrocarbons and other sulfur compounds in the feed and simultaneously to maintain a realistic hydrocarbon environment, each of the above model components were diluted in real gas oil with a medium sulfur content. The properties of the gas oil are shown in Table 2, while the concentrations of the diluted model compounds in the gas oil are presented in Table 3.

A commercial catalyst coded as Cat(B) (supplied by the catalyst vendor Albemarle) was used for the catalytic tests, after steam deactivation at 788 °C for 9 h and 100% steam. The steamed catalyst had 200 m^2/g total surface area and 24.4 Å UCS [12].

All the experiments were performed in a fully automated short contact time microactivity test unit (SCT-MAT) operating at 560 °C and 12 s run time. Details of the unit can be found elsewhere [22,23]. The catalyst to oil ratio has been varied, by changing the catalyst amount.

The gaseous products were analyzed by a Refinery Gas GC Analyzer (HP-5890), equipped with four columns and two detectors (TCD and FID). Simulated distillation procedures (GC: Varian 3400 with MEGAPORE OV-101 column) were applied for measuring the conversion of liquid products. The hydrocarbons in gasoline range were analyzed by a Capillary Gas Chromatograph (HP 5880 A), while an Elemental Analyzer (LECO CHN-800 model) was used for measuring the coke deposited on the catalyst after the tests.

The qualitative and quantitative determination of the total sulfur, as well as the individual sulfur compounds in liquid products were determined by GC (HP 6890 plus) connected to a Sulfur Chemiluminescence Detector-SCD (Sievers model 355). The sulfur amount in coke was determined by an Elemental Analyser (CHNS LECO-932). Sulfur conversion was expressed as the percentage of sulfur feed converted to a particular sulfur compound or product cut. Thus, upon reaction feed sulfur was distributed into gases (dry gas and LPG) as H_2S, liquid product and coke. The amount of H_2S in the gaseous products was determined by subtraction assuming 100% sulfur balance. However, due to analytical restrictions the measurements of sulfur in coke were approximate and indicative. For that reason the exact values of sulfur in coke are not given. Instead the desulfurization reactions are discussed due to the indicative measurements.

3. Results and discussion

3.1. Benzothiophene cracking

The introduction of benzothiophene (BTH) in the gas oil caused minor to zero differences in the yields of the primary FCC products, compared to the gas oil cracking. Thus, the addition of benzothiophene in the gas oil caused a minor increase in the gasoline yield. The minor effect of the addition of benzothiophene to the overall product yields was expected, if we consider the very low amount of the specific model compounds introduced in the gas oil.

In Table 4 the distribution of benzothiophene to other sulfur compounds after cracking, at constant gas oil conversion 65 wt.% is shown. The overall conversion of benzothiophene is up to 42 wt.%. However, as it is shown in Table 4 benzothiophene cracking does not influence the percentage of sulfur compounds in the gasoline range. In Fig. 1 the delta concentrations of gasoline sulfur compounds after cracking of benzothiophene + gas oil mixture compared to gas oil cracking is presented. Minor to zero deltas were observed. On contrary, 23 wt.% is converted to sulfur compounds accumulated in the

Table 3
Model sulfur compounds concentrations and total sulfur in the gas oil + model compounds feeds

Model sulfur compounds	Sulfur compounds concentration in the gas oil (ppm)	Total sulfur in gas oil + sulfur compound feed (wt.%)
Benzothiophene	2285	0.835
2-Methyl-benzothiophene	2410	0.841
3-C_{10}-thiophene	2140	0.819
Dibenzothiophene	2240	0.824
4,6-Dimethyl-dibenzothiophene	2170	0.817

Table 4
Weight percentage sulfur distribution of the model compound after cracking (SCT-MAT, feed conversion 65 wt.%, steamed (B))

wt.% sulfur distribution	BTH	3MEBTH	3DTH	DBTH	4,6DMDBTH
To sulfur compounds in gasoline	–	4.7	13.9	0.4	0.7
To thiophene		0.5	5.3		
To tetrahydrothiophene			2.5		
To alkylated thiophenes			5.1		0.7
To benzothiophene		4.2	1.0	0.4	
To sulfur compounds in LCO	23.0	38.8	10.7	26.5	31.0
To C_1-benzothiophenes	18.2	32.0[a]			
To C_2-benzothiophenes	4.4	6.8			
To C_3-benzothiophenes	0.4		6.5		
To dibenzothiophene					
To C_1-dibenzothiophenes			4.2	16.0	5.3
To C_2-dibenzothiophenes				10.5	25.0[a]
To sulfur compounds in HCO	–	1.5	3.3	8.0	3.2
Total conversion	42.0	45.0	81.0	37.0	45.5

[a] Isomers.

Light Cycle Oil (LCO). Thus, 18.2 and 4.4 wt.% of benzothiophene is converted to C_1-benzothiophenes and C_2-benzothiophenes, respectively, through alkylation reactions. Indicatively, the concentration of C_1-benzothiophenes before and after the introduction of benzothiophene in the gas oil versus gas oil conversions is shown in Fig. 2. Obviously, the remaining 19 wt.% of the converted benzothiophene is desulfurized to H_2S and decomposed to S in coke. Benzothiophene desulfurization to H_2S is quite difficult [19], since as it has been suggested in literature, it premises the saturation of the thiophenic ring through hydrogen transfer reactions followed by cracking for the production of H_2S and hydrocarbons. Consequently, and based on indicative measurements of H_2S and S in coke after benzothiophene cracking, it is proposed that benzothiophene desulfurization takes place mainly through polymerization and condensation reactions, which result to S deposition on catalyst [19]. It is worthy to be noted, that Corma et al. [17] was led to comparatively results about benzothiophene reactions through their study. They suggested that only a small amount of benzothiophene could be hydrogenated with the saturated ring opened in a consecutive step. The main reactions that they could confirm were its alkylation for the production of C_1–C_3 benzothiophenes [17]. Our group has also performed an extensive study on the reaction mechanism and kinetics of benzothiophene [19]. With respect to the experimental results of that study, it was also suggested that its primary reaction is alkylation to heavier alkylated benzothiophenes and mainly C_1-benzothiophenes, while it decomposes through polymerization and condensation reactions to coke.

Considering the above results, two are the main reaction pathways of benzothiophene: Alkylation to heavier sulfur compounds out of the gasoline range and mainly methylbenzothiophenes and desulfurizarion with S deposition in coke, possible through polymerization and condensation reactions (Scheme 1).

3.2. 2-Methyl-benzothiophene cracking

The yields of the primary FCC products were not affected by the incorporation of 2410 ppm sulfur of 2-methyl-benzothiophene (2MEBTH) in the gas oil. Just minor increase in gasoline yield and a minor decrease in LPG yield was observed. As in

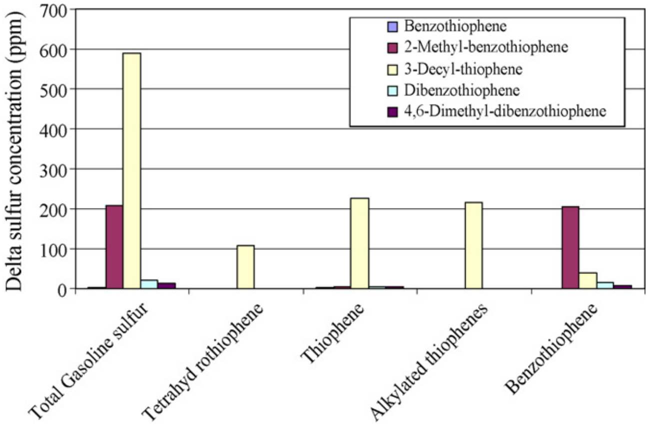


Fig. 1. Delta concentrations of gasoline sulfur compounds after cracking of gas oil + model compounds mixtures compared to gas oil cracking at constant 65 wt.% conversion.

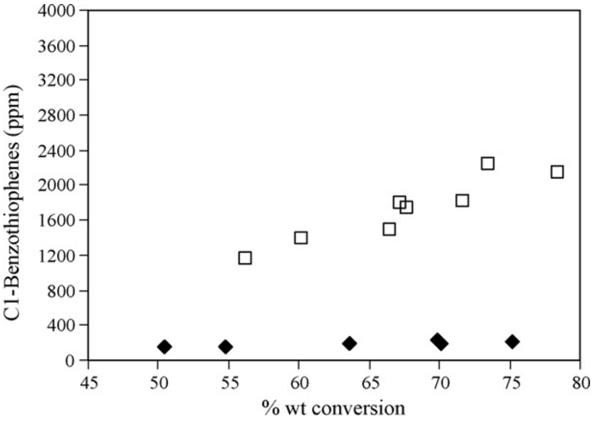


Fig. 2. C_1-benzothiophenes concentration after cracking of gas oil and gas oil + benzothiophene mixture: (◆) gas oil, (□) gas oil + benzothiophene.

Benzothiophene → Alkylated benzothiophenes
Short chain alkyl benzothiophenes → Isomers
Alkylated thiophenes → Thiophene, Alkylated thiophenes, Tetrahydrothiphene, Benzothiophene, Alkylated benzothiophenes
Dibenzothiophene → Alkylated dibenzothiophenes
Alkylated dibenzothiophenes → Isomers

Scheme 1. Reaction pathways of heavy sulfur species under the FCC conditions.

the case of benzothiophene, the small amount of 2-methyl-benzothiophene added in the gas oil, did not expect to cause considerable differences to the yields of the primary FCC products.

The overall conversion of 2-methyl-benzothiophene to other sulfur compounds at constant 65 wt.% gas oil conversion is presented in Table 4. The overall 2-methyl-benzothiophene conversion is 45 wt.%. However, only a small portion is converted to sulfur compounds in gasoline range. Specifically, 4.2 wt.% of 2-methyl-benzothiophene is converted to benzothiophene possible through dealkylation reactions. The delta concentrations of gasoline sulfur compounds after cracking of gas oil + 2-methyl-benzothiophene mixture compared to gas oil cracking is shown in Fig. 1. The higher portion of 2-methyl-benzothiophene (39 wt.%) is transformed to other methyl-benzothiophenes through isomerization reaction (Table 4). In Fig. 3 the increase of the concentration of methyl-benzothiophenes isomers (except 2-methyl-benzothiophene) after the incorporation of the model compound in the gas oil is shown. Besides, some portion is converted to C_2-benzothiophenes through alkylation reactions. Consequently, 2-methyl-benzothiophene is a particularly stable sulfur compound, which is not actually converted, but mainly isomerizes to other C_1-benzothiophenes. A small portion is participated in alkylation reactions for the production of C_2-benzothiophenes, while a minor portion is dealkylated for the production of benzothiophene. Considering that benzothiophene is the final sulfur component in gasoline range, cracking of C_1-benzothiophenes has minor effects on the sulfur content in gasoline.

3.3. 3-Decyl-thiophene cracking

Minor effects on the primary FCC products were observed after cracking of gas oil + 3-decyl-thiophene (3DTH) mixture compared to gas oil cracking. Thus, gasoline yield was slightly increased comparing the results at constant 65 wt.% conversion. As with the above sulfur compounds studied, no significant difference in the primary FCC products was expected considering the small amount of 3-decyl-thiophene added in the gas oil.

The overall 3-decyl-thiophene conversion is high, 81 wt.% as it is presented in Table 4. Its cracking under the FCC conditions affects strongly the sulfur percentage in gasoline range, since it is converted to lower boiling point sulfur compounds accumulated to the specific FCC product. Thus, 5 wt.% more thiophene is found in gasoline after cracking of gas oil + 3-decyl-thiophene compared to gas oil cracking, possible due to dealkylation reactions. The increase in thiophene concentration compared to gas oil cracking results is shown in Fig. 4. The amounts of C_1-thiophenes and the C_2-thiophenes were also increased by almost 3 and 2 wt.%, respectively due to side chain cracking reactions, while benzothiophene was increased by 1 wt.%, possibly through cyclization of the long chain alkyl-thiophene. The increase in

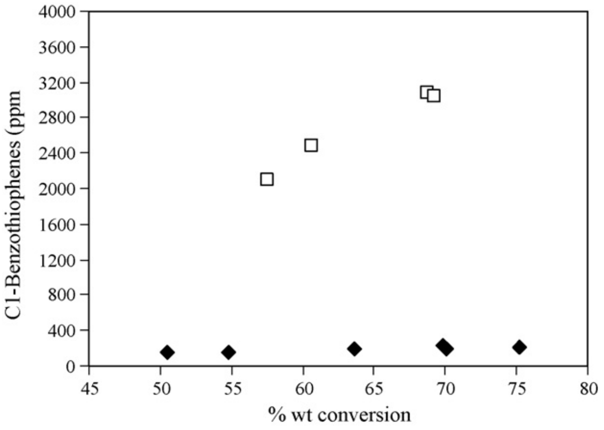


Fig. 3. C_1-benzothiophenes concentration after cracking of gas oil and gas oil + 2-C_1-benzothiophene mixture: (◆) gas oil, (□) gas oil + 2-C_1-benzothiophene.

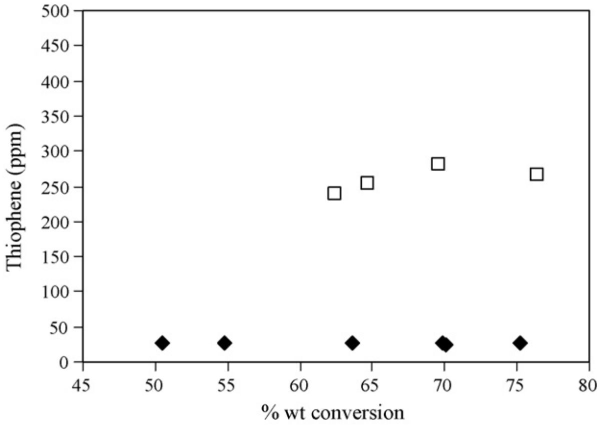


Fig. 4. Thiophene concentration after cracking of gas oil and gas oil + 3-C_{10}-benzothiophene mixture: (◆) gas oil, (□) gas oil + 3-C_{10}-thiophene.

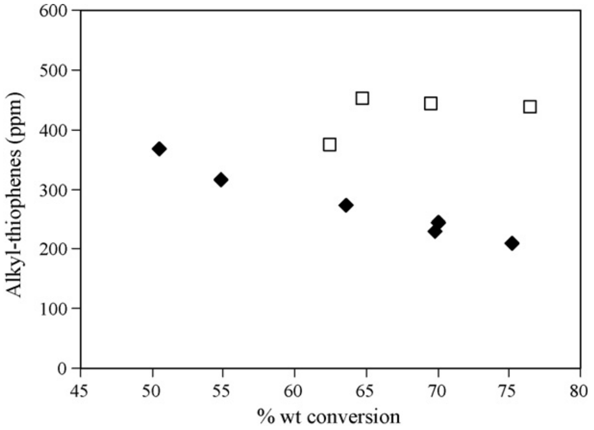


Fig. 5. Alkyl-thiophenes concentration after cracking of gas oil and gas oil + $3C_{10}$-benzothiophene mixture: (◆) gas oil, (□) gas oil + $3-C_{10}$-thiophene.

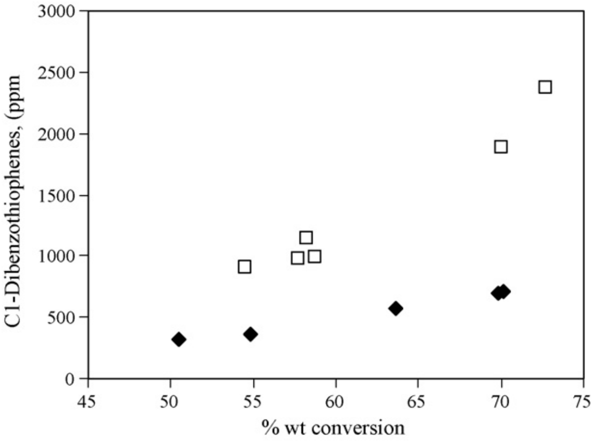


Fig. 6. C_1-dibenzothiophenes concentration after cracking of gas oil and gas oil + dibenzothiophene mixture: (◆) gas oil, (□) gas oil + dibenzothiophene.

alkyl-thiophenes concentration is shown in Fig. 5. Besides, higher amounts of tetrahydrothiophene were detected, which indicates that dealkylation and hydrogen transfer reactions took place. The overall delta concentrations of gasoline sulfur compounds concentrations after gas oil + 3-decyl-thiophene cracking at constant 65 wt.% is shown in Fig. 1.

Almost 11 wt.% of 3-decyl-thiophene was converted to sulfur compounds in the LCO range and distributed to C_3-benzothiophenes and heavier C_1-dibenzothiophenes, through cyclization reaction followed by side chain cracking.

However, the higher portion of 3-decyl-thiophene (53 wt.%) was desulfurized to H_2S and S in coke, indicating that the long chain alkyl-thiophenes are very reactive. Hydrogen transfer reactions may be the pathway of H_2S production, while polymerization and condensation reaction of the long chain alkyl-thiophene may lead to S deposition in coke.

The reactions of 3-decyl-thiophene can be classified to dealkylation for the production of thiophene, side chain cracking for the production of shorter chain alkyl-thiophenes, cyclization and side cracking for the production of alkyl-benzothiophenes or alkyl-dibenzothiophenes and desulfurization reactions for the production of H_2S and S in coke. Considering the above results, cracking of decyl-thiophene, thus cracking of alkylated thiophenes, is responsible for the increase of sulfur content in gasoline range, through the dealkylation and side chain cracking reactions (Scheme 1). The high reactivity of alkyl-thiophenes has been also reported in the literature by Corma et al. [17] and Leflaive et al. [18], where other, lighter alkyl-thiophenes, were studied.

3.4. Dibenzothiophene cracking

As in the above cases, the introduction of 2240 ppm of dibenzothiophene (DBTH) in the gas oil did not affect the yields of the FCC primary products, compared to the gas oil cracking results.

The overall conversion of dibenzothiophene, was 37 wt.% for constant gas oil conversion (Table 4). Dibenzothiophene does not influence the sulfur amount of the gasoline range, since only benzothiophene appeared to increase by only 0.4 wt.% compared to its concentration after gas oil cracking. Delta concentrations of gasoline sulfur are presented in Fig. 1. However, 34.5 wt.% of the polycyclic sulfur compound was transformed to the LCO range. Specifically, 16 wt.% was converted to C_1-dibenzothiophenes and 10.5 wt.% was converted to C_2-dibenzothiophenes through alkylation reactions. The effect of dibenzothiophene to the concentration of C_1-dibenzothiophenes is shown in Fig. 6. Almost 8 wt.% of dibenzothiophene was converted to heavier sulfur compounds accumulated in the HCO range. The desulfurization of dibenzothiophene was difficult, since only 1.6 wt.% was decomposed to H_2S and S in coke. Consequently, the dominant reaction of dibenzothiophene under the FCC conditions is alkylation to heavier dibenzothiophenic compounds (Scheme 1).

3.5. 4,6-Dimethyl-dibenzothiophene cracking

Similarly with the results of the above model sulfur compounds, the introduction of 4,6-dimethyl-dibenzothiophene (4,6DMDBTH) to the gas oil, caused minor effects on the primary FCC products.

The overall conversion of 4,6-dimethyl-dibenzothiophene is high, as it is indicated in Table 4, higher than 45 wt.%, for constant gas oil conversion 65 wt.%. However, it was observed that it participates mainly to isomerization reactions for the production of other C_2-dibenzothiophenes. Its cracking does not influence the percentage of sulfur in gasoline range, except of a small increase of benzothiophene (0.7 wt.%). Besides, only a small portion of the compound is converted to C_1-dibenzothiophenes to the LCO range. In literature the hydrodesulfurization of this specific sulfur compound is widely studied, since it has been found to be one of the most stable sulfur compounds due to steric hindrance of the substitutions at 4- and 6-positions [3]. Considering the overall conversion of 4,6-dimethyl-dibenzothiophene and its conversion to sulfur compounds in gasoline, LCO and HCO fractions the remaining 10.5 wt.% was obviously transformed to H_2S and S in coke. It is theorized that this conversion is attributed mainly to polymerization and condensation reactions of the polycyclic

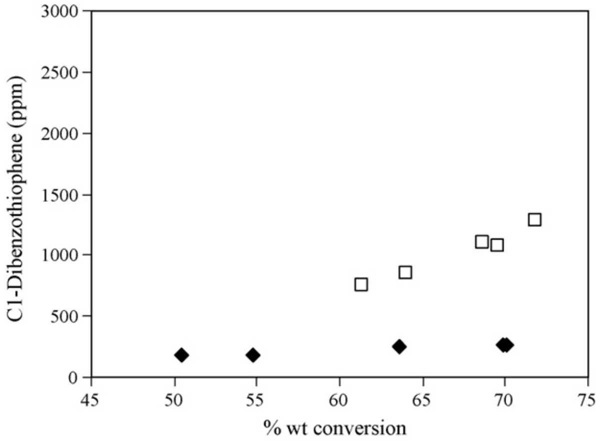


Fig. 7. C_1-dibenzothiophene concentration after cracking of gas oil and gas oil + 4,6-dimethyl-dibenzothiophene mixture: (◆) gas oil, (□) gas oil + 4,6-dimethyl-dibenzothiophene.

sulfur compound to coke, which are favored under the FCC conditions. In Fig. 7 the increased concentration of C_1-dibenzothiophenes is shown, while from Fig. 1 it is shown that minor delta concentrations in gasoline range sulfur compounds were observed.

Summarizing the above results, the main reaction pathways of 4,6-dimethyl-dibenzothiophene are isomerization for the production of other C_2-dibenzothiophenes and polymerization and condensation reactions for the production of S in coke.

4. Conclusions

The reactivity order of the five heavy sulfur compounds during the FCC process, using a steamed deactivated catalyst and excluding the isomerization reactions is: 3-decyl-thiophene > benzothiophene > dibenzothiophene > 4,6-dimethyl-dibenzothiophene > 2-methyl-benzothiophene. The alkylated C_{10}-thiophene was mainly desulfurized. Other main sulfur containing products after C_{10}-thiophene cracking were thiophene and shorter chain alkyl-thiophenes indicating dealkylation and side cracking reactions, respectively. Additionally alkyl-benzothiophenes were observed, indicating the possibility of cyclization reactions. Benzothiophene mainly participated to desulfurization and alkylation reactions for the production of C_1-benzothiophenes, while it is cracking did not influence the sulfur concentration in gasoline. 2-Methyl-benzothiophene cracked in a small extent to benzothiophene, influencing slightly the sulfur concentration in gasoline, while mainly isomerized to other C_1-benzothiophenes. The cracking products of dibenzothiophene and 4,6-dimethyl-dibenzothiophene were accumulated in the LCO fraction. The specific polycyclic sulfur compounds followed mainly alkylation and isomerizations reactions, respectively. Both were especially stable compounds, which did not easily crack and do not affect the sulfur concentration in the gasoline range during their cracking. Scheme 1 summarizes the above results.

Consequently, this study showed that the sulfur compounds in gas oils that are responsible for the sulfur content in the gasoline fraction are the long chain alkylated thiophenic derivatives through dealkylation and side cracking reactions for the production of thiophene and shorter chain alkylated thiophenic compounds accumulated in the gasoline range. On contrary, the heavy polycyclic sulfur compounds in the gas oils are stable molecules, which do not affect the sulfur content in the gasoline product during their cracking and they also difficultly desulfurize. Their main reaction pathways are isomerization and methyl shift.

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