

Elemental sulfur as an effective promoter for the catalytic hydrocracking of Arabian vacuum residue

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Abstract

The effect of elemental sulfur on the conversion of residue for catalytic hydrocracking of Arabian heavy vacuum residue was tested using an autoclave reactor. The reaction condition was 703 K and 5.0 MPa of hydrogen partial pressure. Adding only a small amount of sulfur increased the conversion of residue from 64 to 80 wt%, as well as the yield of middle distillate from 23 to 31 wt%. This should be attributed to the free-radical initiation effect of sulfur. Sulfur promoted the decomposition of residue at the catalytic hydrocracking condition. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

With growing demand for high quality transportation fuels and middle distillate products, obtaining high conversion from heavy oil and bitumen is becoming the predominant research target of residue upgrading processes. Catalytic hydrocracking, which was named hydrothermal cracking before, has been developed to obtain maximum middle distillate yield (kerosene + gas oil) from residual oil [1–3]. In order to compare conveniently, the relevant terminologies are introduced as follows. Catalytic hydrocracking is referred to as hydrocracking in the presence of catalyst; non-catalytic hydrocracking is referred to as hydrocracking in the absence of catalyst; thermal cracking referred to as cracking in the absence of hydrogen and catalyst. Catalytic hydrocracking involves free-radical chain reactions and catalytic hydrogenation reactions: (1) C–C and C–X (heteroatom) bonds rupture to produce free radicals; (2) free-radical dissociation to produce low-boiling products; (3) radical's catalytic hydrogenation, resulting in chain reaction termination, heteroelements removal and C=C bond saturation of olefin and aromatic, etc. [4,5].

The cracking of residual oil is thermodynamically favored at a high reaction temperature. With the increase of temperature, selectivities to by-products, coke and gaseous hydrocarbon, will increase, and the selectivity of

middle distillate will become lower. How to obtain high conversion at low reaction temperature is the key to solve this contradiction. According to the mechanism of free-radical chain reactions, some effective initiators may enhance the conversion of residue by increasing the concentration of free radicals. The present authors have reported [6] that the addition of di-*tert*-butyl-peroxide remarkably enhanced the conversion of bitumen and its model compound during catalytic and non-catalytic hydrocracking. From economical point of view, it is not practical to utilize this additive in a commercial process. A cheaper substance, elemental sulfur was tried to add into feedstock to obtain high conversion, as well as high yield of the middle distillate at low temperature. Some literatures reported the effect of sulfur or sulfur compounds on the production of coke and the thermal cracking of straight-run diesel fraction [7–9]. It was reported that during the production of coke from asphaltene, the reaction of asphaltene with sulfur showed interesting results during the treatment of asphaltene at 423–523 K [7]. The condensation between aromatic and aliphatic moieties of asphaltene was obviously promoted by elemental sulfur, which in turn converted to H₂S, producing coke with good grade. Kawamura et al. [8] showed that during the thermal cracking (in the absence of hydrogen and catalyst) of straight-run diesel oil, the addition of organic sulfur compound 3-pentaerithritol tetrakis-3-mercaptopropionate (PTMP) reduced the formation of coke in the reactor. They supposed that the sulfur compound reacted with the hydrocarbon radicals formed by thermal decomposition and

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Table 1
Properties of AVR

API gravity	5.9
CCR (wt%)	22.4
C (wt%)	83.40
H (wt%)	9.90
S (wt%)	4.92
N (wt%)	0.43
V (wt ppm)	120
Ni (wt ppm)	53
Fe (wt ppm)	19
Asphaltenes, HI (wt%)	25.8
Residue, 798 K (wt%)	95.0

generated alkylthio radical ($RS\cdot$), which tend to react with unsaturated hydrocarbons to prevent the recombination of hydrocarbon radicals, thereby suppressing the formation of coke. Few researchers examined the effect of the addition of elemental sulfur on the conversion of heavy oil in catalytic hydrocracking or non-catalytic hydrocracking conditions. The present work showed the promotional effect of the addition of a small amount of sulfur on the decomposition of residue, resulting in the increase of conversion and the yield of middle distillate during hydrocracking of residue.

2. Experimental

Arabian heavy vacuum residue (AVR) was employed as feedstock in experiments. Its properties are listed in Table 1. This feed has high metal impurities content ($V + Ni + Fe = 193$ wt ppm) and high Conradson carbon residue content (22.4 wt%). Its asphaltene content is 25.8 wt% (HI). Hydrocracking reactions (catalytic or non-catalytic) were carried out in a 75 cm^3 autoclave reactor. Bimetallic catalyst $NiMo/\gamma-Al_2O_3$, prepared by co-impregnation method was employed. The precursors of active metals were $Ni(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. After impregnation, catalyst was degassed in vacuum, and then dried at 393 K for 12 h in air and calcinated in air at 773 K for 4 h. Before use, the catalyst was reduced in a $120\text{ cm}^3\text{ min}^{-1}$ hydrogen flow at 723 K for 4 h and then was sulfided in 20% H_2S/H_2 mixture at the same conditions.

After being pressurized with hydrogen to set the initial pressure at a room temperature, the reactor was heated and shaken down and up during the whole reaction period to ensure efficient contact between gas, liquid, and solid. The shaking frequency was 70 min^{-1} . It took about 10 min to raise the temperature from room temperature to the target temperature. The reaction time was calculated from the time when the desired reaction temperature was reached. The reaction conditions were: temperature, 703 K; initial pressure, 5.0 MPa; reaction time, 0–60 min; catalyst/oil ratio, 0.2 (catalyst 2.0 g and oil 10.0 g). In the case of sulfur-added experiment, 3 wt% of elemental sulfur (0.3 g) was added into oil.

After the reaction, the reactor was cooled down quickly to room temperature. The gaseous product was released to a collecting bag and then was analyzed by gas chromatography (Shimadzu GC-8A). The liquid product was separated from solid by filtration using an aspirator. The weight of obtained liquid was W_1 . During the filtration, a small amount of light oil, which was in naphtha distillate range, was effluent with air and condensed by ice water. Its weight (less than 0.1 g) was W_2 . Although a small amount of oil (about 0.3–0.6 g, which varied with catalyst and reaction conditions) absorbed in solid could not be obtained, its weight W_3 was available. The weight of absorbed oil calculated into the weight of liquid product supposing that its composition was the same with the other product. Because the amount of absorbed oil was small, this almost could not affect the experimental accuracy. The total amount of liquid product was $W_1 + W_2 + W_3$. Liquid product W_1 was separated by a distillation gas chromatography (Shimadzu GC-14A) with a silicone OV-1 glass column into five components: naphtha (IBP–443 K), kerosene (443–503 K), gas oil (503–616 K), vacuum gas oil (616–798 K) and residue (>798 K). $W_1 + W_3$ was calculated according to the composition of W_1 . W_2 was added to the amount of naphtha. Any coke formed on the catalyst, the reactor wall (very few) and in the oil were collected for calculation. The amount of coke was determined as follows: after separation from oil by filtration, solid was subject to Soxhlet extraction by toluene for 3 h to remove oil absorbed in the solid, then dried at 393 K in vacuum (<10 mmHg) for 2 h to remove toluene in the solid; the weight of this solid was W_4 ; the amount of coke was $W_4 - W_5$ (W_5 was the weight of fresh catalyst). The yield percentage of products, gas, liquid and coke were determined on the feed oil basis. X-ray fluorescence was used to determine the sulfur content of the liquid product. The mass balances were $100 \pm 2\%$. The relative deviations in coke yields were less than 4%. The relative deviations in distillate yields were within 2%.

3. Results and discussion

A small amount of elemental sulfur (3 wt%) was added into AVR to test the effect of the addition of initiator on catalytic and non-catalytic hydrocracking of the residue. All experiments were conducted at hydrogen initial pressure of 5.0 MPa. The results are compared in Table 2.

The reactions conducted in the presence of catalyst (runs 3 and 4) were catalytic hydrocracking reactions. Whereas reactions conducted in the absence of catalyst (runs 1, 2, 5 and 6) were non-catalytic hydrocracking reactions.

During hydrocracking process, the thermal decomposition process was prevailing. Catalytic hydrocracking is the combination of thermal cracking and catalytic hydrogenation [10]. Comparing non-catalytic hydrocracking (run 1, absence of catalyst) and catalytic hydrocracking (run 3,

Table 2

The effect of sulfur on conversion of AVR (reaction conditions: temperature, 703 K; hydrogen initial pressure, 5.0 MPa; catalyst, 2.0 g; oil, 10.0 g; added S, 0.3 g)

Run number	Feed	1	2	3	4	5	6
Catalyst ^a (wt%)		No	No	20	20	No	No
Sulfur (wt%)		No	3	No	3	No	3
Time ^b (min)		60	60	60	60	0	0
Conversion ^c (%)		79	89	64	80	11	29
Product composition (wt%)							
H ₂ S	–	1	3	2	4	0	2
C ₁ –C ₄	–	5	5	3	5	0	0
Naphtha	–	6	12	5	9	0	1
Kerosene	–	10	11	6	10	1	1
Gas oil	–	22	21	17	22	2	6
VGO	5.0	25	24	29	28	13	24
Residue	95.0	20	10	34	19	84	68
Coke	–	12	16	3	6	N/A	N/A
Middle distillate ^d (wt%)	–	31	32	23	31	3	8
S in liquid product (g)	0.49	0.40	0.46	0.25	0.34	N/A	N/A
H ₂ consumption (Nm ³ /m ³)	–	29	34	117	139	13	26

^a NiMo/Al₂O₃.

^b Reaction time was calculated after temperature reached 703 K.

^c Conversion = (1 – residue in product/residue in feed) × 100%.

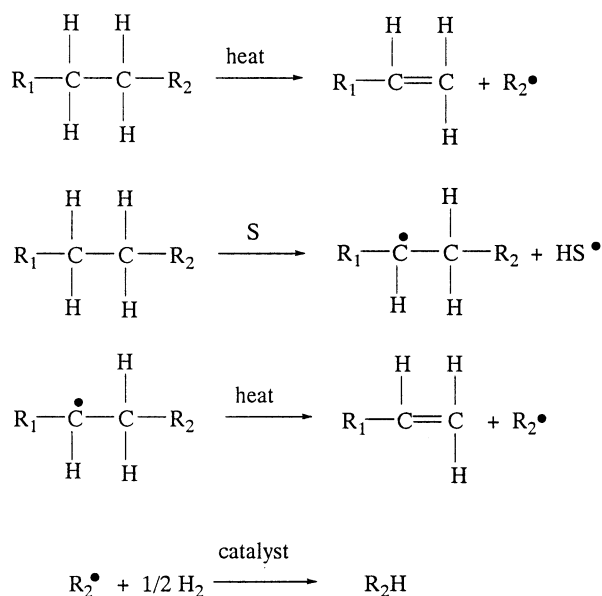
^d Kerosene + gas oil.

presence of catalyst) at the same temperature and hydrogen pressure, it was found that catalyst greatly suppressed coke from 12 to 3 wt% and C₁–C₄ gas from 5 to 3 wt%, and that catalyst lowered the residue conversion from 79 to 64 wt%. This resulted from the catalytic hydrogenation of free radicals (hydro-quench). The pyrolysis of large hydrocarbon molecules produces free radicals, which may react with other hydrocarbon molecules by abstracting a hydrogen atom to produce stable distillates and new radicals during hydrocracking process. Therefore, the chain reactions are readily propagated. The present authors have already demonstrated that the concentration of free radicals in catalytic hydrocracking of Kuwait atmospheric residue was controlled at a lower level in the presence of hydrogenation catalyst and pressurized hydrogen atmosphere than in their absence [1], with the conclusion that catalyst can hydrogenate free radicals to stable molecules. Therefore, catalyst may lower the concentration of free radicals during catalytic hydrocracking process. This reasonably resulted in the decrease of residue conversion of catalytic hydrocracking comparing to non-catalytic hydrocracking. Simultaneously, the secondary cracking was suppressed by catalyst. Therefore, more valuable middle distillates and fewer by-products, gas and coke, were produced in catalytic hydrocracking than in non-catalytic hydrocracking [3]. One of the important advantages of catalytic hydrocracking was higher yield of middle distillates. However, the conversion of catalytic hydrocracking still needs to be increased.

It is clear from Table 2 that when only 3 wt% of sulfur was added in both non-catalytic and catalytic hydrocracking of AVR, the conversions were obviously promoted. In case

of non-catalytic hydrocracking, the addition of sulfur increased the conversion from 79 to 89%, but the yield of middle distillates just increased 1%, the yield of coke increased from 12 to 16 wt% (runs 1 and 2). In case of catalytic hydrocracking, the addition of sulfur remarkably increased the conversion from 64 to 80 wt%, and increased middle distillate selectivity in the product from 23 to 31 wt% (runs 3 and 4). Simultaneously, the formation of coke increased from 3 to 6 wt%. Although run 2 got the highest conversion and the highest middle distillate selectivity, its coke yield was greatly higher than the other runs. When catalyst was present, the formation of coke was remarkably suppressed from 12 to 3 wt% (runs 1 and 3) or from 16 to 6 wt% (runs 2 and 4). Comparing runs 2 and 4, when small amount sulfur was added, catalytic hydrocracking could obtain almost the same middle distillate yield with non-catalytic hydrocracking even though its residue conversion was 9% lower than the latter, but the formation of coke was about half of that in the latter. This showed one of the advantages of catalytic hydrocracking. The above results supposed that on one hand, sulfur promoted the condensation of asphaltene as mentioned by Speight [7] in the thermal treatment of asphaltene, which resulted in the formation of coke; on the other hand, sulfur promoted the decomposition of residue, which resulted in the yield increase of middle distillate. Similarly, the conversion of residue was promoted by sulfur from 11 to 29 wt% (runs 5 and 6) in non-catalytic hydrocracking, even if the reaction time was 0 min. Therefore, sulfur was an effective promoter to both non-catalytic and catalytic hydrocracking of AVR.

The hypothetical mechanism for the effect of sulfur



Scheme 1. Hypothetical mechanism for effect on hydrocracking of AVR.

on hydrocracking of AVR is depicted in Scheme 1. (Hypothetical mechanism for effect of sulfur on hydrocracking of AVR.) When adding a small amount of elemental sulfur into heavy oil, sulfur can abstract H from hydrocarbon molecule to form free radicals even at a lower temperature. Besides C–C bond breakage, this was an additional way to initiate the chain reaction. The concentration of free radicals was readily raised by the addition of sulfur; therefore, the reaction rate was enhanced. After abstracting H from hydrocarbon, sulfur was converted to hydrogen sulfide. It was proved by the concentration change of H_2S in product. Comparing run 2 with run 4 (sulfur was added in both runs), H_2S yield in run 4 was greater than that in run 2. Therefore, catalyst improved the quench of $\text{HS}^\bullet$ radical and increased the yield of H_2S . During the period of temperature rising up to reaction temperature, no H_2S was detected in the gaseous product (run 5), indicating that during the temperature-elevating stage, no S in the oil was converted into H_2S . However, when 3 wt% of S (0.3 g) was added into feed, 0.24 g ($2.4\% \times 10.0$ g) of H_2S was measured in the gaseous product, and the conversion of residue was increased from 11 to 29% (run 6). This should be attributed to the hydrogen abstracting from hydrocarbon by the added S. Eighty percent of the added S was converted into H_2S even at the temperature-elevating stage. The sulfur contents in liquid products at long reaction time (runs 1–4) were measured by X-ray fluorescence and shown in Table 2. In the case of catalytic hydrocracking, with adding sulfur, H_2S content in gaseous product increased from 2 to 4 wt% (runs 3 and 4), and the sulfur amount in liquid increased from 0.25 to 0.34 g. The mass balances of sulfur were between 83 and 93% in runs 1–4. Maybe some sulfur was included in coke and not detected. Considering the result of runs 6 and 2, it was referred that most of the H_2S in the gas was from

the added S, and S in the liquid products was the original sulfur compound in the feed. The changes of sulfur concentration in the product of both gas and liquid provided evidence to the hypothetical mechanism proposed above.

The results above suggested that catalytic hydrocracking of AVR involved free-radical chain reactions and catalytic hydrogenation reactions. It was considered that in the chain reactions, the initial step of hydrocarbon molecule rupture to form free radicals was the slowest one, and the overall reaction rate was readily controlled by this step. When sulfur was added into AVR, it easily abstracted H from oil molecule and produced free radicals in the condition of hydrocracking, finally enhancing the conversion of residue. Savage and Klein [11] investigated the thermal reactions of alkylnaphthenic and alkylhydroaromatic moieties, which are likely present in petroleum asphaltenes, via the model compounds such as tridecylcyclohexane (TDC) and 2-ethyltetralin (2ET). The pyrolyses of both compounds were consistent with free-radical reaction mechanisms. Abstraction of the hydrogen attached to tertiary carbon atom bonded to the cyclohexyl carbon, bearing the tridecyl substituent in TDC or ethyl substituent in 2ET, was the most rapid hydrogen abstraction step because relatively stable tertiary radicals were produced. All other abstraction steps were slower because they led to less stable secondary or primary radicals. Insofar as, the hydrogen attached to tertiary carbon atom in heavy oil should be preferably abstracted by sulfur and tertiary free radical is readily formed; therefore, the concentration of free radicals in the reactants was increased and the chain reactions were promoted.

Run 1 is the so called non-catalytic hydrocracking; its residue conversion is almost equal to that of run 4. However, the formation of coke in run 1 was 12 wt%, which was almost twice higher than that in run 4. A more important point is that with the reuse of used catalyst, the coke formation decreased. This is especially useful for upgrading of heavy oil in long-term run [10]. When using catalyst (catalytic hydrocracking), the quality of product oil is obviously improved by hydrogenation reaction comparing to non-catalytic hydrocracking [1]. For non-catalytic hydrocracking, the addition of sulfur promoted the conversion of residue from 79 to 89%, but the yield of middle distillate slightly increased 1% (runs 1 and 2). This resulted from the promotional effect of sulfur on the condensation reactions which might form coke; in fact, the coke yield increased from 12 to 16 wt%. However, for catalytic hydrocracking, the addition of sulfur not only promoted the conversion of residue from 64 to 80%, but also increased the yield of middle distillate from 23 to 31 wt% (runs 3 and 4). Less coke was formed comparing to runs 1 and 2. Catalyst played the important role to suppress the condensation reaction and promote the yield of middle distillate. As a promoter, sulfur was more effective in catalytic hydrocracking than in non-catalytic hydrocracking.

4. Conclusion

Elemental sulfur was an effective free-radical initiator to enhance the conversion of Arabian vacuum residue and increased the yield of middle distillate during catalytic and non-catalytic hydrocracking.

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