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Free radical behavior in thermal cracking reaction using petroleum heavy oil and model compounds

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Abstract

Thermal cracking mechanism of heavy oil, especially an effect of hydrogen partial pressure was investigated in the thermal cracking reaction using model compounds and Kuwait Vacuum Residue (KW-VR). Free radical recombination was not affected by the change of hydrogen partial pressure. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the hydroprocessing of petroleum heavy oil, thermal cracking reactions occur concurrently with the main catalytic reaction. Generally, in case of heavier feedstocks, the influence of thermal cracking reactions is more overwhelming and the considerable amount of sludge also increases. So, the control of thermal cracking reactions becomes more important. It seems that asphaltene thermal cracking relates closely to the sludge formation, but the reaction mechanism is not elucidated sufficiently, due to the complex structure of asphaltene. Ideally, it is necessary to investigate asphaltene on a molecular level. In this study, 1, 2-diphenylethane (DPE) and dibenzylsulfide (DBS), which represent a part of asphaltene structure, were used as model compounds to examine thermal cracking reaction. Our purpose is to elucidate a thermal cracking mechanism of heavy oil, especially to clarify the effect of hydrogen partial pressure on thermal cracking reaction. We conducted the experiments using model compounds and KW-VR.

2. Experimental

The model compounds reactions were conducted in a high-pressure fixed-bed continuous flow reactor system. The reactor had an ID of 6.23 mm, length of 380 mm, volume of 12 ml, material of SS316, and was heated to keep an isothermal temperature by utilization of a sand-bath. The reaction conditions were: the temperature, 673–773 K; the pressure, 1–5 MPa and the flow rate of nitrogen and/or hydrogen of 6 Nl/h. The feedstock was a solution of 5 wt.% model compounds in *n*-dodecane solvent and the liquid flow rate was 6 ml/h. The reaction phase was gaseous under these reaction conditions. Thermal cracking reactions were carried out with 12 ml of quartz beads (20–40 mesh).

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Liquid products were analyzed by GC-FID and identified by GC-MS. GC-FID analysis were performed by a GL Sciences GC-353 chromatograph. The column was a 30 m×0.25 mm i.d. fused silica capillary (OV-1701). Using the same GC conditions, GC-MS analysis were performed on a Hewlett–Packard 5890 chromatograph, directly interfaced to a HP 5972 mass selective detector. Mass spectra were analyzed using a Wiley 138K computer data system.

The experiments of KW-VR were conducted in a 300 ml stirred batch autoclave. The feedstocks were prepared by mixing about 24 g of KW-VR and 80 ml of 1, 2, 4-trimethylbenzene (TMB). The reaction conditions were: 673 K, 6 MPa for 1 h. TMB solvent keeps liquid phase under the condition. Hydrogen partial pressure was changed and controlled by changing the ratio of hydrogen and nitrogen. The other conditions were maintained uniformly. After the reaction, the gases were recovered in a gas sampling bag, and the products was collected with tetrahydrofuran (THF). The gases, C1–C4 hydrocarbons and H_2S, were analyzed by GC-TCD. Light oil, TMB and THF were evaporated at 433 K, 10 mm Hg and then these samples were analyzed by GC-FID. Next, other heavier products were separated into five major fractions with a variety of solvents and alumina column chromatography shown in Fig. 1. The five major fractions are sludge, asphaltene, resin, aromatic and saturate. In this report, sludge is defined as toluene insoluble. Elemental analysis of C, H, N and S, were carried out and the average molecular weight was analyzed with VPO.

3. Results and discussion

3.1. Model compounds experiments

DPE and DBS were chosen as the model compounds. These compounds represent parts of asphaltene structure [1,2] taking part in the thermal cracking reaction. Moreover, *n*-dodecane, which is supposed to represent saturate surrounding asphaltene, is selected as a solvent. DPE was often used in pyrolysis studies concerning coal liquefaction [3–6]. L.W.Vernon [3] investigated the influence of hydrogen partial pressure on the hydrocracking of DPE, and proposed the radical chain mechanism which produced especially benzene (BZ) and ethylbenzene (EB) by an attack of hydrogen radical. B. Fixari [7] investigated the thermal behavior of DBS in hydrogen donor solvents, and reported the role of compounds such as benzylthiol, H_2S and the corresponding thiyl radicals. But the influence of hydrogen partial pressure on the thermal cracking of DBS was not investigated. So it was not elucidated where hydrogen radical attack. Furthermore, the mechanism of combination of free radical is not clarified. In this study, it was investigated whether the ratio of products of stabilization to toluene (TOL) and combination of benzyl radical to DPE were

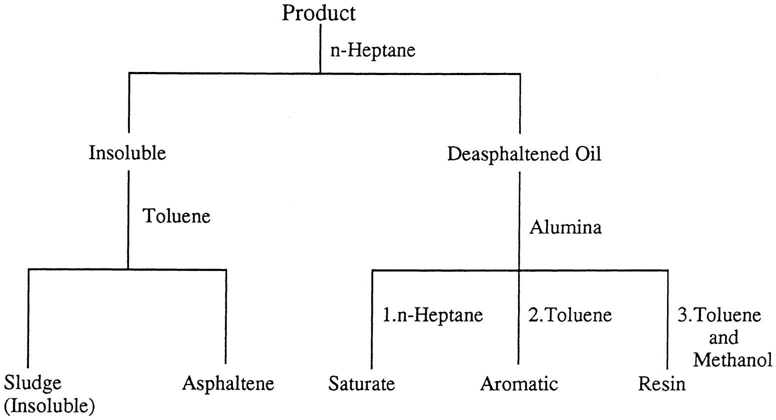

Fig. 1. Simplified representation of the separation into five major fractions.

influenced by the hydrogen partial pressure. In order to keep a constant resident time, a gas flow rate and total pressure were maintained uniformly. The hydrogen partial pressure was controlled by changing the ratio of hydrogen and nitrogen. The results of using DPE and DBS are shown in Tables 1 and 2.

The cleavage of C–C bond of DPE hardly occurred under the industrial hydroprocessing conditions at 673 K. Accordingly, the DPE thermal cracking reaction was conducted at 773 K. However, C–C bond in actual heavy oils bridges not only between monoaromatics, but also polyaromatic ring sheets. For this reason, it is likely that the C–C bond energy of actual asphaltene decreases and C–C bond cleavage can occur at lower temperature. From the results of DPE thermal cracking shown in Table 1, combination of benzyl radical cannot be evaluated. The conversion of DPE is going up slightly with an increase of

Table 1
Effect of hydrogen partial pressure on thermal cracking of DPE (5 wt.%)

Serial No.	Run1	Run2	Run3
Reaction conditions			
Temperature, K	773	773	773
Pressure, MPa	3	3	3
Liquid flow rate, ml/h	6	6	6
H_2 flow rate, Nl/h	1	3	6
N_2 flow rate, Nl/h	5	3	0
Solvent (95 wt.%)	*n*-dodecane	*n*-dodecane	*n*-dodecane
Conversion of DPE, wt.%	36.6	39.9	41.4
Selectivity of products, wt%			
Benzene	8.8	10.7	12.0
Toluene	69.1	67.6	66.2
Ethylbenzene	5.6	8.5	10.8
Styrene	4.5	4.0	2.8
1, 1-Diphenylethane	0	0	1.4
9, 10-Dihydrophenanthrene	2.1	1.8	1.6
Stilbene	7.9	5.5	3.5
Phenanthrene	2.1	1.8	1.6
Decomposition of solvent, wt.%	23.2	28.3	32.6

Table 2
Effect of Hydrogen partial pressure on thermal cracking of DBS (5 wt.%)

Serial No.	Run4	Run5	Run6
Reaction conditions			
Temperature, K	673	673	673
Presssure, MPa	1	1	1
Liquid flow rate, ml/h	6	6	6
H_2 flow rate, Nl/h	1	3	6
N_2 flow rate, Nl/h	5	3	0
Solvent (95 wt.%)	*n*-dodecane	*n*-dodecane	*n*-dodecane
Conversion of DBS, wt.%	41.9	82.8	91.0
Selectivity of products, wt.%			
Toluene	80.2	87.0	87.8
Benzyl mercaptan	11.5	4.7	2.5
1, 2-Diphenylethane	0.0	2.9	6.5
Stilbene	8.3	5.4	3.2
TOL/(TOL+DPE+STB)×100	90.6	91.3	90.1
Decomposition of solvent, wt.%	0.6	1.3	1.8

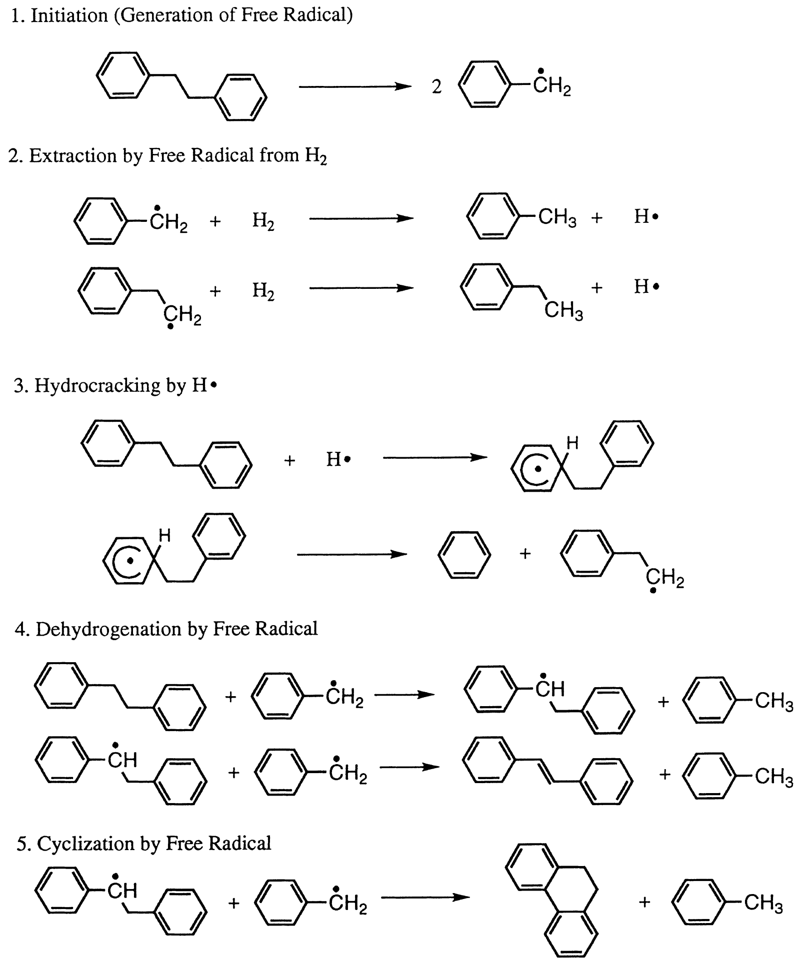

Fig. 2. Thermal cracking reaction scheme of 1, 2-diphenylethane.

hydrogen partial pressure, due to the increasing yield of BZ and EB. These results suggest a reaction mechanism as shown in Fig. 2. This is similar to the reaction mechanism proposed by L.W. Vernon [3]. From scheme 2 of Fig. 2, hydrogen radical is generated more frequently in higher hydrogen partial pressure. This hydrogen radical promotes hydrocracking of DPE (scheme 3), so it produces more BZ and EB. Free radical is stabilized to TOL and EB (scheme 2) by hydrogen molecule. Moreover, the amount of stilbene (STB), phenanthrene (PHE) and styrene (ST) decreases with the increase of hydrogen partial pressure.

Thermal cracking of *n*-dodecane, which represent saturate, occurred under the same conditions. This results are shown in Table 3. The comparison between Tables 1 and 3 suggests that DPE thermal cracking affects *n*-dodecane decomposition. *n*-Dodecane decomposition products are from C_5 to C_{10} unsaturated compounds such as *n*-decene, *n*-nonene and so on. These results indicate that free radicals, such as benzyl radical, extracts hydrogen atom from *n*-dodecane, and beta scission occurs consecutively.

I. Nakamura, K. Fujimoto et al. [8] reported the hydrothermal cracking of *n*-dodecylbenzene. In thermal cracking, 673 K, 7.5 MPa in hydrogen atmosphere, the selectivity of TOL in products is higher than that of BZ. It is well known that acid-catalyzed cracking of alkylbenzene is often assumed to occur by complete cleavage of the side chain from the aromatic

Table 3
Thermal cracking of *n*-dodecane

Serial No.	Run7	Run8	Run9
Reaction conditions			
Temperature, K	773	773	773
Pressure, MPa	1	3	5
Liquid flow rate, ml/h	6	6	6
H_2 flow rate, Nl/h	6	6	6
Solvent (100 wt.%)	*n*-dodecane	*n*-dodecane	*n*-dodecane
Decomposition of solvent, wt.%	3.8	19.1	32.3
Selectivity of products, wt.%			
1-Decene	16.2	9.5	7.5
1-Nonene	16.5	11.4	10.6
1-Octene	17.4	12.5	12.2
1-Heptene	17.0	13.5	13.9
1-Hexene	16.7	14.0	15.0
1-Pentene	7.4	12.1	13.4
Unknown	8.8	27.0	27.4

ring, whereas in thermal cracking, alkylbenzene is often cracked at the bond between alpha and beta carbon counting from the aromatic ring.

Amano [9] reported the thermal demethylation reaction of TOL. Hydrogen radical attacks carbon (SP^2) of aromatic ring which possesses methyl group, and generate methylcyclohexadienyl radical, which is a sigma complex as intermediate. Afterwards, BZ and methyl radical are generated by cracking of methylcyclohexadienyl radical due to the excessive energy. If this mechanism is applied to the aliphatic bonding of heavy oil, since hydrogen radical causes dealkylation reaction of alpha-carbon, it results in an increase of aromatization.

In the thermal cracking of DBS, dimerization of benzyl radical producing DPE and STB can be justified postulated from the results presented in Table 2. The main product is TOL from benzyl radical. In other words, benzyl radical is stabilized by hydrogen molecule, as a result, TOL and hydrogen radical are generated. BZ was not identified, therefore, generated hydrogen radical attacked sulfur atom rather than the aromatic ring. Furthermore, the conversion of DBS markedly increases with the increase of hydrogen partial pressure compared to that of DPE. This result could be attributed to the following three reasons. The first reason is that electrophilic hydrogen radical attacks more electronegative sulfur atom than aromatic carbon. The second reason is that the dissociation energy of C–S bond is fairly small in comparison with that of Ph–C bond of DPE. The third reason is that generated H_2S and mercapto radical affects radical chain reactions. Stenberg and Hei [10] reported that the presence of sulfur in the thermolysis of DPE considerably reduces the severity of the conditions required to cleave the aliphatic C–C bond.

Moreover, TOL (hydrogenated product of benzyl radical) and DPE+STB (dimerized product of benzyl radical) are formed in the ratio of about 9:1. The reason is speculated that the hydrogen radical generated in proportion to hydrogen partial pressure rapidly hydrocracks DBS, and the benzyl radical concentration increases in proportion to hydrogen radical. Hence, finally, the concentrations of hydrogen molecule, hydrogen radical and benzyl radical have the same proportional relation. These results confirm the reaction mechanism shown in Fig. 3.

Accordingly, hydrogen radical attacks sulfur atom in DBS, and then the C–S bond is cleaved at the same position as in thermal cracking, so the conversion of DBS is significantly increased. It should be noted that the ratio of stabilization to TOL and dimerization of free radical is independent of hydrogen partial pressure.

3.2. *Kuwait vacuum residue experiment*

The reaction of model compounds was performed under gaseous phase. The effect of free radical and hydrogen partial pressure are possibly different

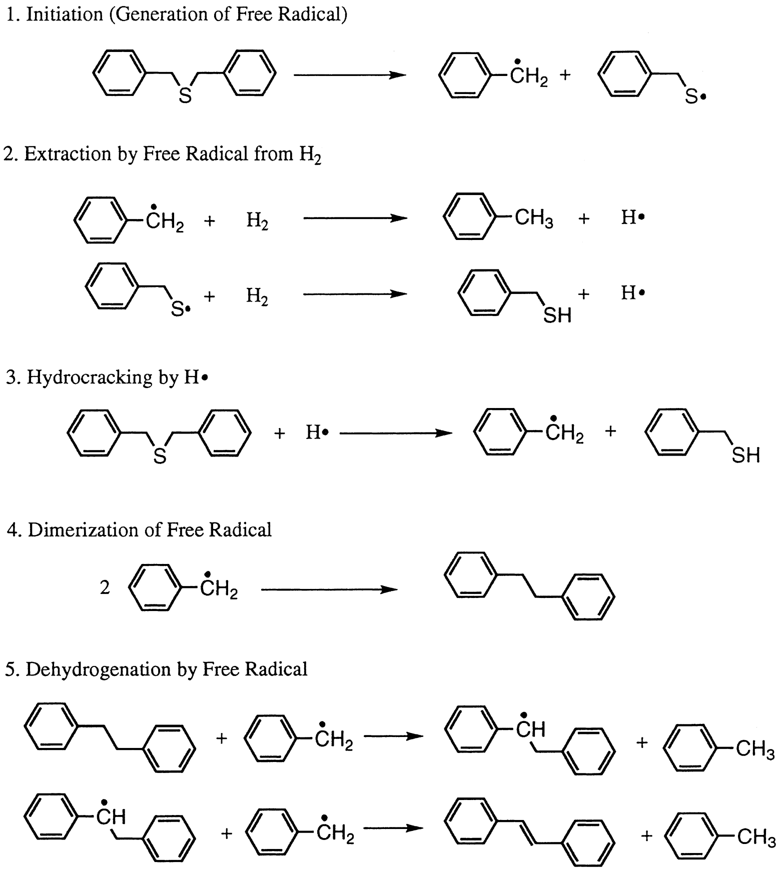

Fig. 3. Thermal cracking reaction scheme of dibenzylsulfide.

between gaseous and liquid phase. It is not clarified quantitatively and qualitatively how many bonds are represented by model compounds and what type of bonds are there in heavy oils. In the next experiment, actual feedstocks were used to obtain the relation between the results of model compounds and actual heavy oils. The mixture of KW-VR and TMB was used to make it easy to collect heavy liquid product after the reaction. We confirmed experimentally that TMB solvent was liquid phase. The results of thermal cracking reactions were shown in Table 4.

In comparison between feed and products of Table 4, the selectivity of asphaltene and resin increase, and those of aromatic and saturate decrease after the reaction at all conditions. It seems that aromatic and saturate changed into asphaltene and resin. Selectivity of products do not change so clearly with the change of hydrogen partial pressure. But sludge decreases with the increase of hydrogen partial pressure. This results correlate with the suppression of dehydrogenation or condensation.

The amount of H_2S increased with the increase of hydrogen partial pressure. This result shows the same trend as the results of the model compounds. The origin of H_2S is presumably sulfide bond, and sulfide bond cleave to make thio radical, then thio radical change consecutively to thiol, mercapto radical, and finally to H_2S. As mentioned before, it is known that mercapto radical and H_2S enhance thermally radical chain reactions. The increase of H_2S with the increase of hydrogen partial pressure implies that the generated hydrogen radical attacks sulfur atom as well as DBS reaction. But the amount of H_2S is less than 1/500 of the total sulfur. Accordingly, mercapto radical and H_2S slightly affects under this condition.

Table 4
Thermal cracking of KW-VR

Serial No.	Feed	Run10	Run11	Run12
Reaction conditions				
Temperature, K	—	673	673	673
H_2 pressure, MPa	—	1	3	6
N_2 pressure, MPa	—	5	3	0
Time, h	—	1	1	1
Rotation, rpm	—	500	500	500
KW-VR, g	—	34.44	36.25	33.60
1, 2, 4-TMB, ml	—	80	80	80
Recovery, wt.%	—	97.6	100.2	100.0
Selectivity of products, wt.%				
Sludge	—	1.0	0.7	0.2
Asphaltene	7.7	10.4	14.6	13.0
Resin	19.6	26.1	26.2	27.8
Aromatic	47.2	42.3	39.8	40.7
Saturate	25.5	15.8	14.6	14.7
Light oil	—	4.0	3.5	3.0
Gas	—	0.5	0.6	0.6
H_2S gas, mg	—	9.0	12.0	14.0
Sulfur content, wt%				
Asphaltene	8.2	7.8	7.7	7.3
Resin	6.2	5.9	5.7	5.6
Aromatic	6.4	6.4	6.6	6.6
Saturate	1.1	0.9	0.9	1.0
Mass balance to whole	5.2	5.2	5.4	5.3

Four major fractions of asphaltene, resin, aromatic and saturate were analyzed for sulfur content shown in Table 4. The sulfur contents of aromatic and saturate stay almost the same as in the feedstock under all conditions, whereas those of asphaltene and resin decrease with the increase of hydrogen partial pressure. Products have the same total sulfur contents as in the feed. Therefore, the reason is considered as that the sulfur contents of asphaltene and resin were diluted by aromatic and saturate.

Next, these fractions were analyzed with VPO and CHN coader in detail. Fig. 4 shows a relation between hydrogen partial pressure and average molecular weight of each fraction. Average molecular weight of asphaltene and resin decrease with the increase of hydrogen partial pressure. Those of aromatic and saturate slightly decrease. So, it is recognized that the thermal cracking reaction proceeded with the increase of hydrogen partial pressure.

Fig. 5 shows a relation between hydrogen partial pressure and H/C atomic ratio. In comparison between feed and products, H/C of feed decrease by thermal cracking reaction at all conditions. H/C of saturate increases with the increase of hydrogen partial pressure. The reason is that the higher hydrogen partial pressure prevents the dehydrogenation of saturate.

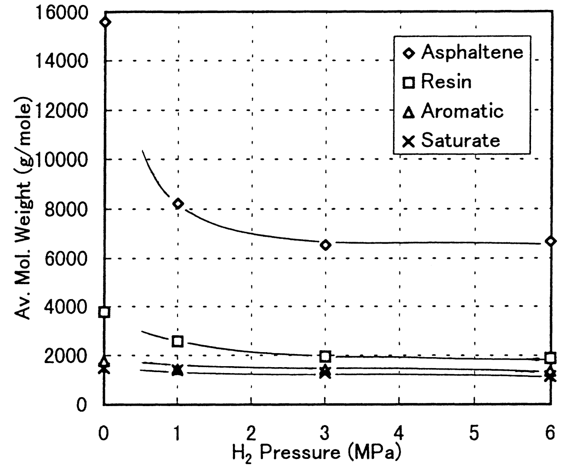

Fig. 4. Average molecular weight of each fraction in KW-VR thermal cracking.

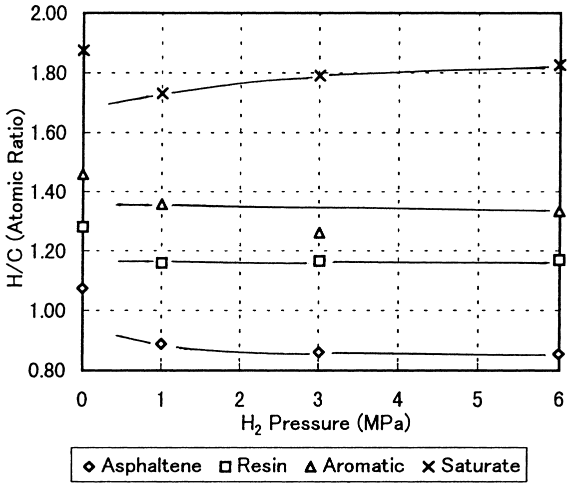

Fig. 5. H/C of each fraction in KW-VR thermal cracking.

But, H/C of asphaltene decreases with the increase of hydrogen partial pressure, so the result is supposed that the hydrocracking and dealkylation occurs predominantly by hydrogen radical under the same mechanism as BZ is generated in DPE thermal cracking.

In Fig. 6, speculated thermal cracking mechanism of heavy oil are proposed to be as follows according to the results of the model compounds. At the beginning, all fractions generate free radicals by decomposition. As the average molecular weight of each fraction becomes smaller, especially asphaltene. Generated free radicals extract hydrogen atom from other hydrocarbon molecule or hydrogen molecule to be stabilized to small molecules or combine with other radicals to form hard asphaltene. Then generated hydrogen radical attacks sulfur bridges and aromatic

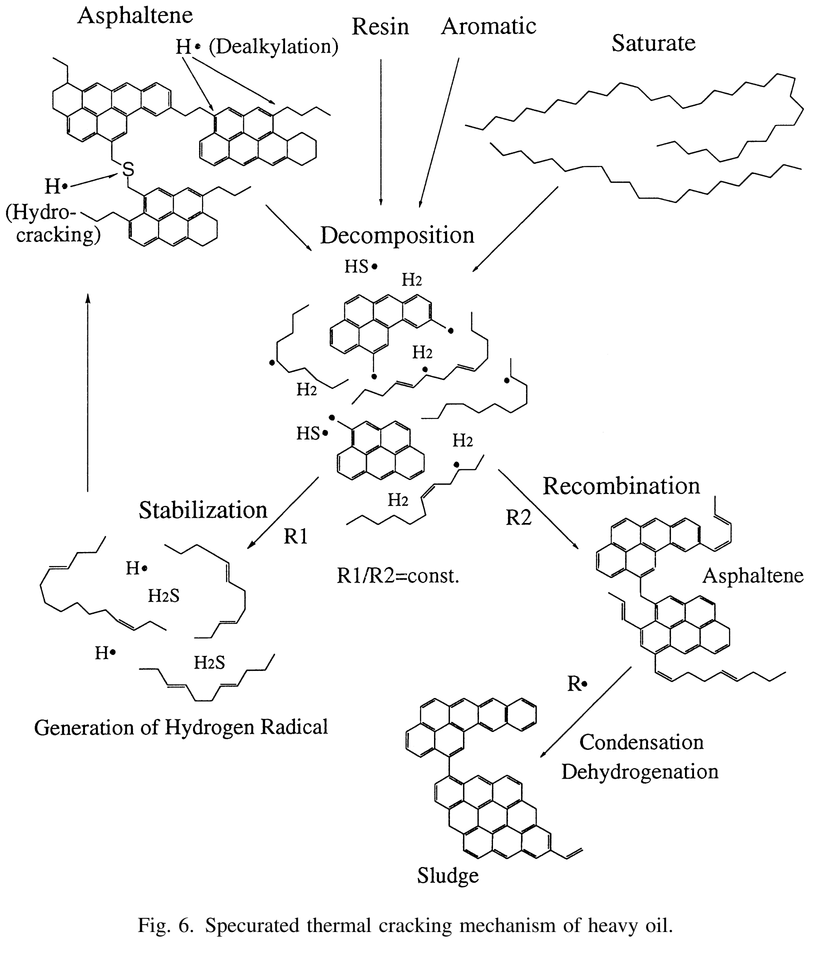

Fig. 6. Specurated thermal cracking mechanism of heavy oil.

sheets in asphaltene structure, so dealkylation and hydrocracking occurred. As a result, the higher hydrogen partial pressure proceeds recombination, dealkylation and hydrocracking. Thus, hard asphaltene was produced. Sludge decreases with the increase of hydrogen partial pressure. So it is recognized that the higher hydrogen partial pressure deters condensation or dehydrogenation as formed styrene from EB of DPE thermal cracking.

As mentioned before, the ratio of stabilization and combination of the free radical is constant, but it varies with reaction conditions and the kind of reactants because of the dependence of the ratio on their reaction rates. In this experiment, reaction is performed under liquid phase in which molecules can collide more frequently than gaseous phase, and heavy molecules in feedstock are described as having naphthenic structures which easily donate hydrogen atom to free radical and heavy counter radicals extracted hydrogen atom should be more stable than benzyl radical of model compounds. Therefore, it is proposed that, in the case of KW-VR, hydrocarbon radical plays main role in radical chain reactions rather than hydrogen radical and the ratio of stabilization and combination of free radical is much lower than 90% of DBS.

4. Conclusions

In order to elucidate the thermal cracking mechanism of petroleum heavy oil, the experiment of using model compounds and KW-VR were conducted by changing the hydrogen partial pressure. The results of model compounds and KW-VR had the following same trends. The thermal cracking conversion of model compounds and the amount of H_2S gas generated from KW-VR enhanced with the increase of hydrogen partial pressure. Moreover, average molecular weight of each fraction of KW-VR decreases with the increase of hydrogen partial pressure. The BZ yield from DPE increased and H/C of asphaltene attributed to dealkylation and hydrocracking decreased with the increase of hydrogen partial pressure. Styrene and stilbene yield from model compounds decreased and H/C of saturate increased with the increase of hydrogen partial pressure.

The recombination mechanism in KW-VR thermal cracking reaction might be more clarified by model compound experiments. The ratio of stabilization and recombination rate is possibly constant as well as DBS thermal cracking mechanism. However, model compounds are too simple and the actual heavy oil is too complex to clarify the thermal cracking mechanism of it. We must investigate further how the results of model compounds can be applied to the actual heavy oil.

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