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Depolymerization and demetallation treatments of asphaltene in vacuum residue

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Abstract

The asphaltene fraction [hexane insoluble (HI)] of a vacuum residue (VR) was treated under ultrasonic irradiation at 40°C in THF or 150°C in 1-methyl naphthalene (1-MN) in the presence of an adsorbent composed of modified macro-reticular polystyrene resin. Such a treatment was found effective to convert the asphaltene into the hexane soluble (HS: maltene) without any hydrogen consumption. 61 and 72% of the HI was converted by the adsorption treatment at 40°C in THF and 150°C in 1-MN, respectively, to HS materials having lower molecular weights. About 65% of the metal contaminants in the original asphaltene remained with the newly formed maltenes after this treatment. Structural analyses of the asphaltene and maltene fractions before and after the treatment suggests decoagulation and/or depolymerization of the asphaltene into maltene, while the porphyrin moiety becomes soluble, being transformed to the maltene fraction. The roles of polar solvent, ultrasonic irradiation, and adsorbent are discussed based on the above results. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Depolymerization; Asphaltene; Demetallation

1. Introduction

It is desirable to remove metallic compounds in petroleum residues before catalytic hydrocracking and hydrodesulfurization reactions in refineries, because they cause severe catalyst deactivation [1–3]. They are usually concentrated in the asphaltene fraction which is known to be comprised of micellular aggregates [4]. The micellular structure is believed to be formed through intermolecular aromatic plane stacking, hydrogen bonds, and charge transfer interactions. Such a micelle structure of the asphaltene interferes with its conversion into smaller molecules as it promotes the production of sludge and coke precursors over the catalyst through regressive reactions of dealkylation and dehydrogenative condensations, especially under the severe conditions used to achieve high conversions via hydrocracking [5–8]. The metallic compounds in the asphaltene and/or polar fractions are deposited onto the catalyst along with a considerable amount of carbon precursors, and deactivate the hydrogenation activity. These deposits also enhance dehydrogenation reactions and coke formation in the hydrotreating processes [9].

Hence, the decoagulation of the asphaltene fraction is very desirable prior to demetallation so as to allow the demetallation to proceed with minimal carbon deposition. There have been many reports on attempted ways to handle the asphaltene, such as

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removal, solvation, and hydrogenation. Lin and Yen recently reported that the ultrasonic irradiation accelerated the asphaltene conversion to soluble fractions with the aid of surfactant [10].

In the present study, mild demetallation treatment of asphaltene fraction in a petroleum vacuum residue (VR) was examined using adsorbents such as cation exchange resins or sulfur modified macroreticular polystyrene resins in solvents under ultrasonic irradiation, in an attempt to remove the metalloporphyrins from the asphaltene as well as to convert the asphaltene to more soluble maltene. The roles of solvent, ultrasonic irradiation, and the nature of the adsorbent are examined with the objective to achieve the efficient demetallation and depolymerization of asphaltene in petroleum residues under mild conditions.

2. Experimental

2.1. Materials

Two adsorbents were used in this study. The first was Amberlite XAD-1 which had been modified using the procedure described in US Patent 4,136,021 [11]. The modification consisted of treating the resin with elemental sulfur at 220°C to achieve a chemically bound sulfur content of 13 wt.% (SAM-13). The second adsorbent was a conventional sulfonated ion-exchange resin (Amberlyst XN-1010) containing highly acidic sulfonic acid groups.

An Arabian heavy crude vacuum residue (VR) and its heavier fraction fractionated by commercial solvent deasphalting (DAS) were used in the present experiments. Both materials were further fractionated by hexane precipitation. In the present study, the hexane insoluble (HI) and hexane soluble (HS) fractions were defined as asphaltene and maltene, respectively. The elemental analyses of the materials before and after the hexane fractionation are summarized in Table 1. Metal contents in VR-HI fraction were measured by ICP (Inductively Coupled Plasma Atomic Emission Spectrometer, SPS 1500, SEIKO Electronics Co.) after the combustion at 815°C for 1 h followed by extraction with 10N HCl for 3 h. VR and its fractions were also analyzed by ESR (JES-RE, JEOL Co.) for the identification of vanadyl porphyrin derivatives, EPMA (Electron Probe Microanalyzer, EPMA-8705, Shimadzu Co.), NMR (VARIAN VXR-400S spectroscopy; $CDCl_3$ solvent, ca. 10 wt.% of the solute; ca. 5 mg of Cr acetylacetonate was added as a relaxation enhancing reagent for the quantitative ^{13}C-NMR measurement), Gel permeation chromatography (GPC; UV detector (254 nm), Shodex column: KF802.5, eluent solvent: THF, 1 wt.% concentration of the solute; calibrated with polystyrenes of standard molecular weights), and elemental analyses were used for structural and compositional analyses.

An average structure model of the asphaltene fraction was calculated by the CAChe calculation based on the above analytical data.

2.2. Demetallation treatments

VR-HI or DAS-HI (0.1 g) dissolved in 25 cc of THF or 1-methylnaphthalene (1-MN) was mixed with adsorbent (0.2 g) and treated under ultrasonic irradiation conditions at 40 or 150°C for 1 h. After the adsorption treatment, the solution was filtered and

Table 1
Elemental analyses of VR, DAS, and their fractions[a]

Sample	Content (wt.%)	C (wt.%)	H (wt.%)	N (wt.%)	(S+O)diff. (wt.%)	Ash (wt.%)	Metal contents (ppm)[b]	
							V	Ni
VR	—	84.6	10.4	0.36	4.6	0.16	95	27
HS	90.3	84.2	14.7	0.26	0.9	—	—	—
HI	9.7	82.5	7.3	0.71	8.9	0.54	920	240
DAS		82.9	9.2	0.45	7.2	0.21	115	38
HI	18.3	83.7	7.3	0.58	7.8	0.66	1120	290

[a] HS: hexane soluble, HI: hexane insoluble.

[b] Measured by ICP after the combustion at 815°C for 1 h and acid extraction.

the solid adsorbent was washed with THF or 1-MN and the washings were combined with the original filtrates. The washed adsorbents were dried at 50°C under vacuum overnight. In all cases the adsorbents gained weight by only about 1% which indicated that very little of the maltene or asphaltene was lost to the adsorbent. The average deviation by this procedure in three-time repeated runs was estimated to less than 3% in the material balance. The recovered adsorbents were analyzed by elemental analysis and EPMA measurement to characterize the nature of the materials that were irreversibly adsorbed during the ultrasonic treatment. The filtrates were fractionated by hexane precipitation into HS and HI materials and isolated by solvent evaporation. The HI and HS fractions were analyzed by NMR, elemental analyses, GPC, and ESR before and after the ultrasonic/adsorption treatments.

3. Results

3.1. Structural analyses of the original VR asphaltene

The elemental analyses of VR fractions are summarized in Table 1. The VR (95 ppm V) was fractionated by hexane precipitation to yield 90% maltene (HS) and 9.7% asphaltene (HI). As expected, the metal-containing compounds were concentrated in the asphaltene (HI) fraction with higher contents of nitrogen and sulfur. The contents of V and Ni measured by ICP were about ten times larger in HI than those in HS. A much lower H/C atomic ratio of ca. 1.05 was also noted for the HI fraction. DAS prepared from the other VR by commercial solvent deasphalting contained 18% HI, containing 1120 ppm of V.

3.2. Adsorption treatments of VR-HI

Table 2
Adsorptive treatment of asphaltenes with ion exchange resin under ultrasonic irradiation[a]

Asphaltene	Adsorbent	Solvent	Temp. (°C)	Conv. to HS (%)
VR-HI	No	THF	40	27
VR-HI	SAM-13	THF	40	61
VR-HI	Amberlyst	THF	40	55
VR-HI	No	1-MN	40	23
VR-HI	No	1-MN	150	46
VR-HI	SAM-13	1-MN	150	72
DAS-HI	No	THF	40	21
DAS-HI	SAM-13	THF	40	45
DAS-HI	SAM-13	1-MN	150	63

[a] Asphaltene 0.1 g, solvent 25 cc, resin 0.2 g, 1 h treated.

Table 2 summarizes the conversion of HI to HS by the ultrasonic treatment in THF or 1-MN with the adsorbents. It was observed that 61% of HI was converted to HS by this treatment in THF at 40°C for 1 h in the presence of SAM-13 (sulfided Amberlite). Only 27% of HI was converted to HS by the treatment without the adsorbent under the same conditions. The other adsorbent, Amberlyst 1010, gave 55% conversion to HS under the same conditions.

The HI conversion increased to 72% at a higher temperature of 150°C in 1-MN solvent by the same treatment with SAM-13 adsorbent. THF solvent was more effective at 40°C than 1-MN in the absence of the adsorbent for the dissolution the asphaltene.

The same treatment converted 45 and 63% of the particular DAS-HI using SAM-13 in THF and 1-MN, respectively. Thus, the conversions were lower than those of VR-HI.

3.3. Structural changes of asphaltene by the treatment

Table 3 summarizes the H/C atomic ratio and the structural parameters of VR-HS and VR-HI calculated

Table 3
Average structural parameters[a] of VR fractions before and after the treatment

Sample[b]	H/C (−)	fa	σ	Haus/caus
VR-HI-Or.	1.05	0.56	0.59	0.78
VR-HS-Or.	2.08	0.34	0.45	0.84
HI-Tr.No	0.98	0.60	0.58	0.75
HS-Tr.No	1.09	0.52	0.61	0.79
HI-Tr.SA.	0.90	0.62	0.56	0.73
HS-Tr.SA.	1.12	0.49	0.60	0.81

[a] fa: aromatic carbon degree; σ: substituent degree; Haus/caus: aromatic condensed-ring degree.

[b] Or.: original; Tr.No: no adsorption treatment; Tr.SA.: treated with SAM-13(THF solvent).

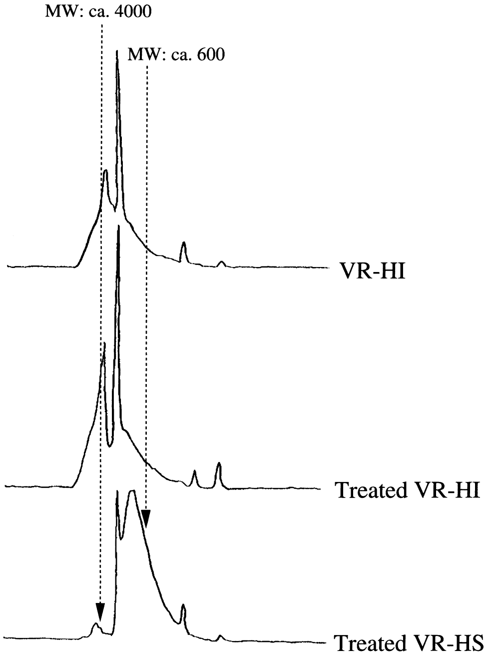

Fig. 1. GPC spectra of VR-HI before and after the adsorption treatment.

by quantitative ^{13}C-NMR measurements before and after ultrasonic treatment in the presence of SAM-13 in THF. The HS produced by the adsorption treatment had a lower fa (carbon aromaticity) value, a higher σ value (degree of substitution) and Haus/Caus (extent of aromatic ring condensation), indicating that the produced HS from the HI fraction contained relatively more alkyl chains and a smaller aromatic ring size than the remaining HI.

Fig. 1 illustrates the GPC chromatograms of HI before and after the adsorption treatment with SAM-13 in THF. These chromatograms show that the original HI consists mainly of the two components which have maxima in their molecular weight distributions at about 1000 and 4000, respectively. The content of the heavier component was decreased substantially by the treatment. A lower molecular weight fraction of around 1000 appeared in the HS fraction after the treatment and the GPC chromatogram of the product HS was almost identical to that of the original HS in the vacuum residue. These results indicate that the relatively larger molecular weight components with the more aliphatic groups in the HI are converted by the treatment to a HS material through the dissociation of the asphaltene aggregate structure. The added adsorbent appears to prevent reassociation of the dissociated species.

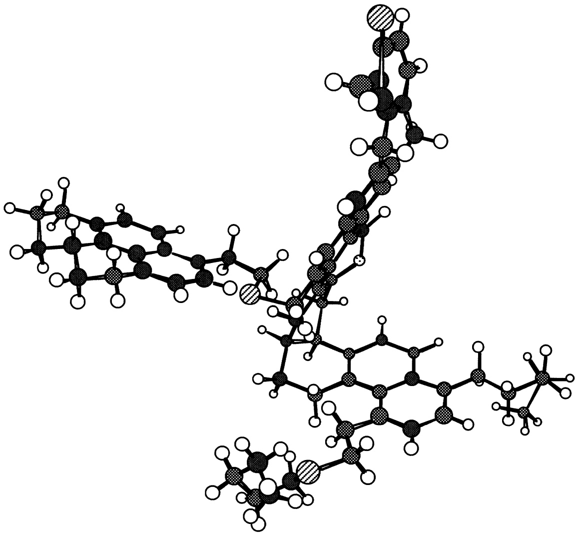

Fig. 2. Unit structure model of asphaltene.

A unit structure model of asphaltene molecule is illustrated in Fig. 2 based on the structural parameters in Table 3 and the molecular weight ($C_{70}H_{73}S_3N=1024.6$, selected for the model), where a three dimensional molecular configuration is described based on the CAChe calculation. It is suggested that petroleum asphaltenes contain associated components that can be transformed to soluble maltene fractions by dissociation of the asphaltene aggregate. The reason that this dissociation is more effective in presence of the specific adsorbent is discussed below.

3.4. *Fate of metal-containing compounds in asphaltene by the treatment*

The contents of Ni and V of the adsorbent and asphaltene fractions before and after the adsorption treatment at 40°C were analyzed by ICP and EPMA measurements. The metal contents are summarized in Table 4. A very small amount of metals was detected on the surface of the starting SAM-13 adsorbent. The contents of V and Ni on the adsorbent were increased by the treatment. Though substantial quantities of metals were incorporated into the adsorbent, the

Table 4
EPMA[a] and ICP[b] analyses of metal contents of adsorbent and asphaltene before and after the treatment

Sample name	Metal contents (ppm)	
	Ni	V
SAM-13[b]	15	5
Used SAM-13[b]	80	60
VR-HI[b]	240	920
Tr.-VR-HI[a]	650	360

[a] EPMA semi-quantitative analysis using standard sample.
[b] Measured by ICP after the combustion at 815°C and acid extraction.

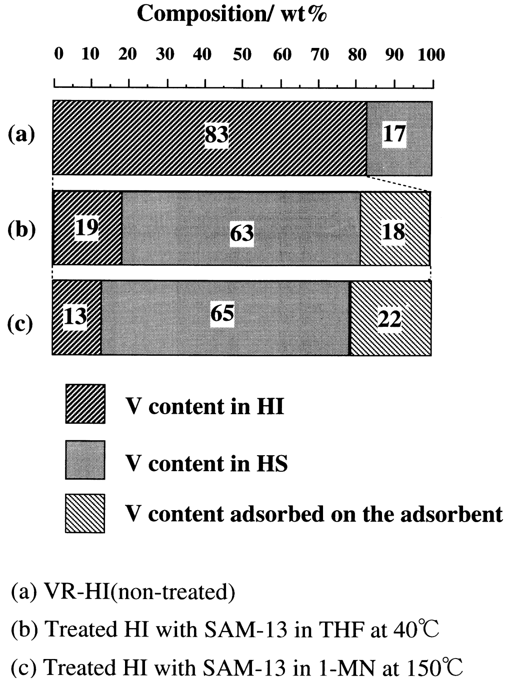

Fig. 3. Balance of vanadium in VR-HI before and after the adsorption treatment.

weight of the adsorbent did not increase by more than 1–2%, so only a small amounts of hydrocarbons were adsorbed by the adsorbent. Fig. 3 illustrates the V balance in the asphaltene calculated based on the material balance and metal contents in the adsorbent and the asphaltene fractions. The vanadyl porphyrin derivatives were also identified by ESR spectroscopy. About 60–70% of metal-containing compounds in the asphaltene were converted to the soluble maltene fraction by the treatment, and about 20% of the metal-containing compounds were adsorbed on the adsorbent, the rest remained in the asphaltene. Slightly larger amounts of V-containing compounds in the asphaltene were adsorbed by the treatment in 1-MN at 150°C, as shown in Fig. 3.

4. Discussion

The present study demonstrated that a mild ultrasonic/adsorption treatment of petroleum asphaltenes with a sulfur modified polystyrene resin in THF or 1-MN was effective for the dissociation of soluble metalloporphyrin compounds which are concentrated in petroleum asphaltene fractions as micelle-like aggregate structures in combination with more polar components which contain considerable quantities of polar functional groups. It is believed that much of this association in the asphaltene aggregate is through van der Waals interactions between long-chain alkyl groups substituted on polyaromatic rings of both maltene and polar asphaltene structures. This weak interaction can be disrupted by the ultrasonic/adsorption treatment. Such effects of ultrasound on the cavitation and solubilization of asphaltenes have been recognized by a combination use of surfactant [10]. Other non-covalent interactions such as aromatic plane stacking, hydrogen bonding, and/or charge transfer may also be disrupted by the ultrasonic/adsorption treatment. These interactions can be more effectively weakened or disrupted by conducting the treatment in a dispersing solvent such as THF or 1-MN. The adsorbent may also selectively interact with the metal-containing compounds, accelerating the release of metallic compounds from the asphaltene as well as aiding the decoagulation of asphaltene micelle-like aggregate structure which may be cross-linked by metals. Such a decoagulation and depolymerization scheme is schematically illustrated in Fig. 4 based on the model unit structure of asphaltene described in Fig. 2 and the asphaltene aggregate model proposed by Yen [4].

Based on the change of molecular weight of asphaltene by the ultrasonic/adsorption treatment, it can be assumed that four molecules of the asphaltene unit structure are associated through the non-covalent interactions to form the aggregate structure, whereas

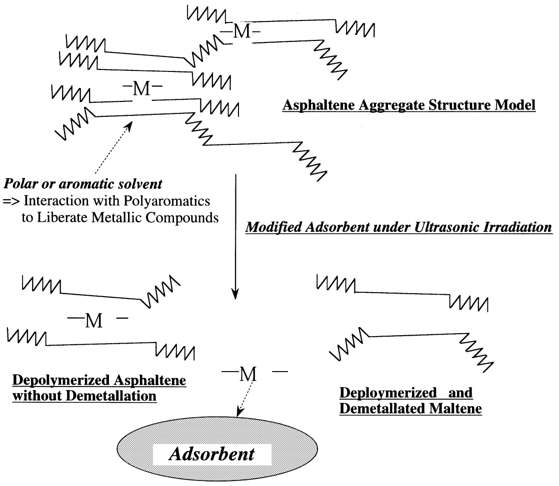

Fig. 4. Depolymerization and demetallation scheme of asphaltene aggregate by adsorption treatment.

much of the metal-containing compounds may be occluded by these non-covalent interactions. The aggregate is dissociated by solvation with THF or 1-MN assisted by the ultrasonic irradiation. It should be noted that a portion of the unit structure of a petroleum asphaltene may indeed be soluble in hexane and may have a similar structure and molecular size to a conventional maltene fraction. The adsorbent interacts rather selectively with the metallic compounds, accelerating the depolymerization of the asphaltene to soluble maltene having a lower molecular weight.

Hydrotreatment under severe conditions, especially at higher temperatures (above 400°C) converts the asphaltene to smaller molecules through dealkylation and dehydrogenative condensation reactions. Side reactions include production of coke-precursors and deactivation of catalysts by the deposition of metallic compounds and coke on the catalyst surface [9]. We reported [12] that a NiMo sulfide catalyst supported on ultrafine carbon particles of hollow spheres were more effective than conventional NiMo/Al_2O_3 catalysts, in enhancing the liberation of metalloporphyrins from the aspthaltene aggregate during their conversion into the hexane soluble materials under mild hydrogenation conditions (340°C). We believe that this enhancement was due to higher hydrogenation activity for the polyaromatics as a result of higher dispersions of the active metal species on the catalyst surface as well as in the reactant medium in the slurry phase with the carbon support [12–14].

Thus, it may be possible to design a sequential resid upgrading process which consists of mild depolymerization of asphaltenes using an adsorbent followed by the demetallation by hydrotreating with NiMo sulfides supported on carbon nanoparticles. The materials produced through these mild pretreatments can be more extensively hydrocracked and more deeply hydrodesulfurized using conventional technology to produce light clean distillates without severe catalyst deactivation.

The supercritical propane extraction is conventionally applied to the deasphaltening treatment of vacuum residues, however, this process tends to produce more amount of asphaltene because of its limited solubility. The present study revealed that the most of asphaltene can be converted into the maltene fraction soluble in hexane without any chemical reactions, indicating that the asphaltene fraction can be fed to the following catalytic processes with least catalyst deactivation.

Based on the above discussion, the benefits of the present procedure are pointed out as follows;

1. Simple procedure for the solubilization of asphaltene without any chemical reaction under ultrasonic irradiation.
2. Enhanced decoagulation and demetallation pretreatment of asphaltene fraction by polar or aromatic solvent with the aid of adsorbent.
3. Elucidation of depolymerization and demetallation mechanism of asphaltene.

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