

ISOLATION AND CHARACTERIZATION OF ASPHALTENES IN THE PRODUCTS OBTAINED BY HYDROCRACKING PROCESS OF PETROCHEMICAL INDUSTRY WASTES

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Abstract

In this study, the isolation and characterization of asphaltenes in the liquid products obtained by hydrocracking of heavy hydrocarbons were investigated. Hydrocracking experiments were carried out with aromatic-rich cracker fuel oil (ARCFO) which is one of the “off-spec” products of petrochemical industry and its blends with the heavy vacuum gas oil (HVGO) which is feedstock of hydrocracking unit in refinery. In case of ARCF, hydrocracking reactions with or without catalysts were carried out at a 6.0 MPa initial hydrogen gas pressure at different temperatures of 400, 425 and 450°C for a reaction time of 120 min. The catalyst employed was commercial DHC-8 catalyst. The effects of catalyst and the temperature on the properties of the asphaltenes in liquid product from hydrocracking were investigated by elemental analysis and FT-IR. In case of blends, the effects of blend ratio and catalyst on the properties of the asphaltenes were investigated.

Key words: asphaltenes, hydrocracking, non-standard fuel oil

1. INTRODUCTION

For both economic and environmental reasons, utilization of the wastes from petroleum and petrochemical industry as energy raw material has become important. The one of the ways for the assessment of these wastes could be their processing by conventional refinery process, such as cracking, hydrocracking, to convert liquid and gas fuels. Hydrocracking is a highly flexible petroleum refining process that can use different type of heavy petroleum fractions (Sahu et al. 2015; Özkan et al. 1999). But, these wastes are rich in asphaltenes which are not very amenable to refinery processes because asphaltenes are known to increase the viscosity of the oils (Chacon-Patino 2015; Davarpanah, Vahabzadeh & Dermanaki 2015; Özkan et al. 1999; Sharma et al. 2007; Sheu 2002; Sun et al. 2015; Wu & Kessler 2015).

Presenting complex molecular structures asphaltenes are disposed to create agglomerates that flocculate and precipitate according to the physiochemical conditions of the environment in which they are present (Coelho et al. 2007; Davarpanah, Vahabzadeh & Dermanaki 2015; Sharma et al. 2007; Sheu 2002; Wang et al. 2013; Wu & Kessler 2015). They can cause serious problems in the petroleum/petrochemical industry like absorbing on different surfaces, changing surface wettability, plugging pipeline, blockading the extraction well, deposition in the storage tanks, as well as deactivating catalysts, which can result in damages, economical losses and contamination of the ecosystems (Chacon-Patino 2015; Coelho et al. 2007; Davarpanah, Vahabzadeh & Dermanaki 2015; Sharma et al. 2007; Sheu 2002; Wang et al. 2013; Wu & Kessler 2015). Asphaltenes are known to be consisted of condensed polynuclear aromatics carrying alkyl, heteroatoms (nitrogen, oxygen, sulphur) and trace amount of nickel and vanadium (Chacon-Patino 2015; Sahu et al. 2015; Sun et al. 2015; Wang et al. 2013; Wu & Kessler 2015). These compounds contain a stack or cluster of naphthenic and aromatic molecules, fused ring aromatic molecules, small aliphatic side chains and polar functional groups (Sahu et al. 2015). The heteroatoms of N, O and S in asphaltenes are present in the form of functional groups such as thiophene, sulphide, sulfoxide, hydroxyl, carbonyl, carboxyl, pyrrole and pyridine (Chacon-Patino 2015). The asphaltenic fractions heavy metals such as V and Ni are generally in the form of metal complexes as petro-porphyrins (Chacon-Patino 2015). It is reported in the literature that the results obtained from Furiil crude oil revealed average asphaltenes molecular

weight in the range of approximately 600-1000 Dalton (Sheu 2002). Asphaltenes as the multi-component petroleum fraction are soluble in aromatic solvents such as benzene and toluene and insoluble in low-boiling point n-alkane solvents like n-pentane and n-heptane (Chacon-Patino 2015; Davarpanah, Vahabzadeh & Dermanaki 2015; Sahu et al. 2015; Sheu 2002; Sun et al. 2015). In the mixtures of the solvents with less aromaticity the asphaltenes form larger aggregates due to the lower compatibility of solvent-solute in comparison to the interactions between aromatic solvents and the solutes. The increase in aromaticity of solvent mixtures decreases the π -bond and polarity feature of the solvent and as a result the asphaltene aggregation is affected in a positive way. The inclination of the colloidal particles toward aggregation or separation, as a property of colloidal solution stability/instability, is determined by the overall interactions between these particles, and different types of attractive and repulsive interactions are in fact concerned with stabilization mechanisms in colloidal dispersions. Van de Waals, depletion, steric, hydration and hydrophobic interactions as well as hydrogen bonding, acid-base interactions, metal coordination, and π - π stacking may all play a role in describing the colloidal solution behaviour or production of highly stable aggregates (Chacon-Patino 2015). The aromatic solvents increase the relevance between the aromatic core of asphaltene and the solvent as a result of hydrophobic interactions between them, which in the end ease asphaltene aggregation.

The determination of chemical structure of asphaltenes or even the characterization of its functional groups is one of the challenges in the study of asphaltenes (Chacon-Patino 2015; Coelho et al. 2007; Davarpanah, Vahabzadeh & Dermanaki 2015; Sharma et al. 2007; Wang et al. 2013). The general analytical chemical methods used in asphaltene characterization are ^1H nuclear magnetic resonance (NMR), ^{13}C NMR, Fourier-transform infrared (FTIR) spectroscopy and elemental analysis (Chacon-Patino 2015; Coelho et al. 2007; Davarpanah, Vahabzadeh & Dermanaki 2015; Sharma et al. 2007; Sun et al. 2015; Wang et al. 2013). Being simple, rapid, low cost, facile to sample preparation and feasible widely, the IR analysis is one of the most useful technique choices in the characterization of the functional groups in asphaltenes (Coelho et al. 2007; Sun et al. 2015). In the IR regions of 1,460 and 1380 cm^{-1} for the aliphatic chains $-\text{CH}_2$ and $-\text{CH}_3$ groups of the alkyl substituted asphaltene structures and also the frequency regions of 2,920-2,950 cm^{-1} and 2,927-2,957 cm^{-1} are informative. The 700-900 cm^{-1} region is reported to correspond to the out-of-plane absorption area for the hydrogens in the aromatic ring.

In petrochemical industry, the “off-spec” products are produced from the some process as by-products (Sahu et al. 2015; Özkan et al. 1999). One of them is the aromatic-rich cracker fuel oil (ARCFO) (Özkan et al. 1999). In an ethylene plant, about 4% of feedstock is converted into the “off-spec” product (ARCFO) during naphtha steam cracking process. ARCFO can be only used as a feedstock for the production of carbon black. However, more interesting approach for utilization of ARCFO is mixing it with a heavy petroleum fraction then treating them conventionally in a refinery unit, such as hydrocracking unit. The hydrocracking process, which basically converts high boiling molecules into more desirable lower molecular weight products with low olefin and high iso/n-parafin yields, is an important process in modern oil refineries. The operating conditions and catalysts for hydrocracking may vary, depending upon the end product.

In this contribution, we subjected the asphaltene fraction from the aromatic-rich cracker fuel oil (ARCFO), heavy vacuum gas oil (HVGO) and their blends in different percentages to hydrocracking and thermal cracking processes and used FT-IR and elemental analysis to track compositional changes in the asphaltenes after upgrading. The overall definition of asphaltene conversion after the cracking processes can act as a guide regarding effective upgrading methods which could improve the economical valuation of the petrochemical industry wastes in a positive way.

2. EXPERIMENTAL

2.1. Materials

Raw material of ARCFO (aromatic-rich cracker fuel oil) is a by-product of NSC (naphtha steam cracking) plants of PETKIM Petrochemical Holding Co. located in Izmir, Turkey. Heavy vacuum gas oil (HVGO) is provided by TÜPRAŞ Petrochemical Holding Co. located in Izmir, Turkey. DHC-8 catalyst (commercial hydrocracking catalyst) was provided by TÜPRAŞ. It has dual functions consisting of hydrogenation metals on an acidic support (silica-alumina). The solvents used for purification and deasphalting were of technical grade and were purified by distillation before use.

2.2. Hydrocracking experiments

Experiments were carried out in a shaking-type autoclave (100 cm³). After loading of ARCFO or its blends with HVGO into the autoclave, the autoclave was sealed and purged with hydrogen. Thereafter, it was pressurized to 6 MPa with hydrogen. In catalytic experiments, catalyst (10 %) was mixed with feedstock before loading. All of the hydrocracking reactions were performed at temperatures of 400, 425 and 450 °C and for a reaction time of 120 min. At the end of the reaction time, the reactor was cooled to room temperature by blowing cold air. After the gaseous products were vented, the reactor contents were filtered to separate solid and liquid parts.

2.3. Precipitation of asphaltenes

The extraction of asphaltenes from hydrocracking liquid was carried out according to ASTM D6560 method (ASTM International (American Society for Testing and Materials) 2012). In a typical run, the mixture of 1 g of the liquid and 30 ml n-hexane was heated under reflux for 1 h. And then the insoluble asphaltenes were filtrated by Whatman filter paper and washed with 200 ml of freshly distilled and hot n-hexane until the solvent was colorless. Finally, the residue was dried in an oven at 105°C and stored in a vacuum desiccator. Deasphalting experiments were repeated at least twice and the data obtained were accurate $\pm 1-2\%$.

2.4. Analysis

Elemental analysis of the asphaltenes was carried out by a LECO CHNS 932 elemental analyzer according to ASTM D5291-96 (ASTM International (American Society for Testing and Materials) 1996). Infrared spectroscopy spectra were recorded on pressed pellets of a 2 wt % mixture of asphaltenes in spectroscopy-grade KBr which was dried before use at 100°C for overnight in an oven. FTIR was performed on a Fourier transform infrared spectra were measured on a Perkin Elmer FTIR spectrophotometer (spectrum BX-II).

3. RESULTS AND DISCUSSION

3.1. Asphaltene yield

It is well-known that yields of asphaltenes in upgrading processes are a direct consequence of the feedstock composition and reaction environment (Chacon-Patino 2015). The asphaltene yield of raw materials and the asphaltenes obtained in the liquid products from hydrocracking processes are given in Fig 1. For ARCFO at higher temperatures of 425°C and 450°C, the catalyst decreased the asphaltene yield with respect to thermal run. High temperatures led to an increase in the asphaltene yield in thermal run while temperature had no considerable effect in catalytic run. A synergetic effect was observed for the blends processed of ARCFO with HVGO, i.e. asphaltene amount was less than the theoretical amount. In contrast to ARCFO case, catalyst led to decrease in the asphaltene yield. The effect of catalyst might be explained as follows: during the hydrocracking processes besides the fragmentation reactions also recombination reaction occurs. Here, the catalyst prevented the recombination reactions.

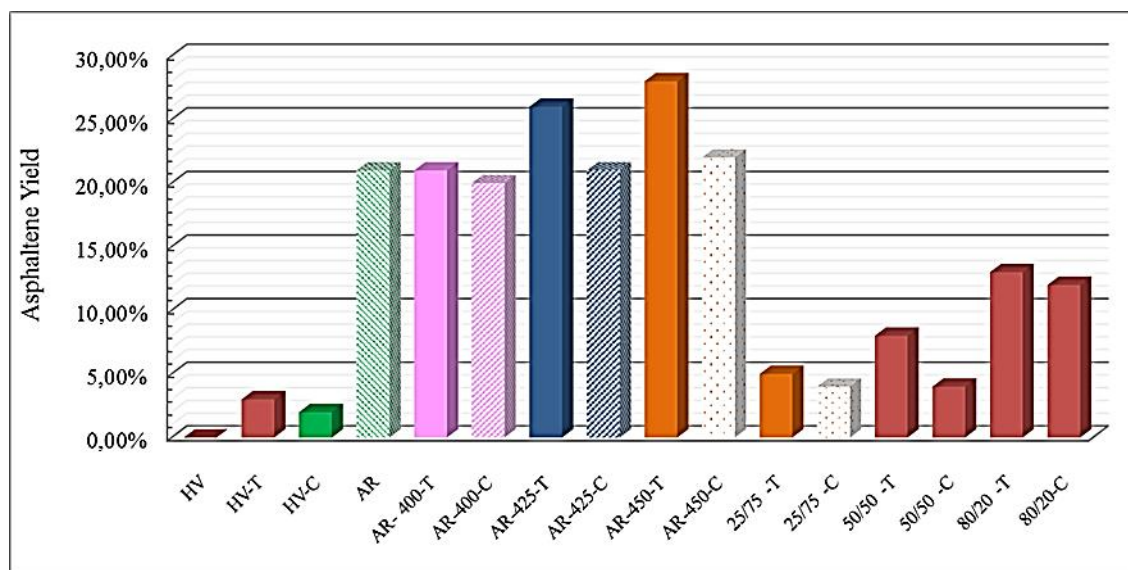


Fig. 1. Asphaltene yield of raw materials and the asphaltenes obtained in the liquid products from hydrocracking processes (HV:HVGO; AR: ARCFO, T:thermal, C:catalyst, 400,425,450 are the temperatures in °C; AB/CD refers to ARCFO%/HVGO% blends (for all blends the temperature is 450°C), hydrocracking conditions: 60 bar H₂, 120 min).

3.2. Elemental analysis results

Elemental composition of carbon, hydrogen, sulphur and nitrogen of the asphaltenes from crude ARCFO and the asphaltenes in the liquid products obtained from hydrocracking process of ARCFO are given in Table 1. From the elemental analysis, it can be concluded that the asphaltenes obtained after hydrocracking process contains lower H/C ratio, which confers to a higher aromatic degree in comparison to crude ARFO. The higher the temperature is the higher aromatic content of asphaltenes is. At 400°C, the catalyst increased the aromatic content of the asphaltene, while at 425°C and 450 °C it had no considerable effect on the formation of aromatic compounds. Moreover, the analysis confirms that contents of heteroatoms in asphaltenes significantly differ depending on hydrocracking in comparison to crude ARCFO asphaltenes. It is interesting that the asphaltenes of the hydrocracked ARCFO contained higher amount of heteroatoms (especially nitrogen and sulfur) than that of crude ARCFO. However, it is well known that hydrocracking process provides the removal of the heteroatoms from petroleum fractions. This shows that heteroatoms in ARCFO might be present in condensed rings. As temperature increased, in general, the heteroatom content increased.

Elemental analysis of the asphaltenes from hydrocracked HVGO and ARCFO/HVGO blends are given in Table 2. In case of HVGO alone, the catalyst increased the aromatic content of the asphaltene. In comparison to the asphaltenes from hydrocracked HVGO, as the ARCFO content increased in the blends, the aromatic content of the asphaltenes increased. The effect of the catalyst on the aromatic content of the asphaltenes in 25% ARCFO / 75% HVGO and 50% ARCFO / 50% HVGO blends is negligible, while in 80 % ARCFO / 20 % HVGO blend the catalyst increases the aromatic degree slightly. HVGO asphaltene contains higher N/C ration with respect to the blends with ARCFO. By using ARFO, the heteroatom ratio of the asphaltenes in the blends decreases in comparison to HVGO itself which is a desired property. Furthermore, the use of catalyst decreases the heteroatom content of the asphaltenes obtained from the hydrocracked blends.

	AR	AR-400-T	AR-400-C	AR-25-T	AR-425-C	AR-450-T	AR-450-C
C	91.46	91.43	92.13	90.49	92.84	93.12	91.20
H	6.33	5.27	4.70	4.90	5.10	4.84	4.62
N	0.08	0.10	0.12	0.13	0.09	0.15	0.16
S	0.14	0.27	0.28	0.30	0.31	0.36	0.54
O*	1.99	2.93	2.77	4.18	1.66	1.53	3.48
H/C	0.83	0.69	0.61	0.65	0.66	0.62	0.61
O/C	0.02	0.02	0.02	0.03	0.01	0.01	0.03

Table 1. Elemental analysis results of the asphaltenes from crude ARCFO and the asphaltenes obtained in the liquid products from hydrocracking process of ARCFO (AR: ARCFO, T:thermal, C:catalyst, 400,425,450 are the temperatures in °C; hydrocracking conditions: 60 bar H₂, 120 min).

	25/75-T	25/75-K	50/50-T	50/50-K	80/20-T	80/20-K	HV-50-T	HV-50-K
C	88.28	91.10	91.71	93.83	91.20	90.90	83.68	77.12
H	4.85	4.89	4.86	4.96	4.61	4.71	5.10	4.23
N	0.46	0.46	0.27	0.18	0.16	0.12	0.98	1.04
S	1.38	1.04	0.79	0.32	0.54	0.40	1.97	1.10
O*	5.03	2.51	2.37	0.71	3.49	3.87	8.27	16.51
H/C	0.66	0.64	0.64	0.63	0.61	0.62	0.73	0.66
O/C	0.04	0.02	0.02	0.01	0.03	0.03	0.07	0.16

Table 2. Elemental analysis of the asphaltenes from hydrocracked HVGO and ARCFO/HVGO blends in different ratios (AB/CD refers to ARCFO%/HVGO%, T:thermal, C:catalyst, HV:HVGO; hydrocracking conditions: 450°C, 60 bar H₂, 120 min).

3.3. FTIR analysis results

FTIR results of the asphaltenes from crude ARCFO and the asphaltenes obtained in the liquid products from hydrocracking process of ARCFO are given in Table 3 which reveals similar characteristic peaks. Due to their complicated molecular structure, the peaks can be investigated in three parts of aromaticity, aliphaticity and polar functionality. Especially the aromatic moiety stretching bands for =C-H are in the range of 3047-3019 cm⁻¹ and out-of-plane =C-H bending are in the range of 956-713 cm⁻¹. Moreover the peaks observed between 1654-1490 represents -C=C stretching vibrations. For the aliphatic characteristics, the absorption bands observed between 2927-2851 cm⁻¹ corresponds to -C-H stretching vibrations while the peaks in the range of 1457-1437 cm⁻¹ and 1381-1376 cm⁻¹ refers to -C-H bending vibrations of CH₂ and CH₃, respectively. The absence of significant peaks between 725-720 cm⁻¹ indicates that long aliphatic chains (bigger than four carbon atom) are not present in the asphaltenes. In comparison to crude ARCFO asphaltenes, hydrocracked ARCFO asphaltenes intensity signals between 3000-2800 cm⁻¹ and 1500-1300 cm⁻¹ related to saturated -C-H are lower, indicating a lower amount of aliphatic groups, which is also in agreement with the elemental analysis results. For polar functionalities, stretching vibrations of -OH and/or -NH were assigned between 3676-3232 cm⁻¹; -SH stretch between 2500-2610 cm⁻¹ and C=O stretch between 1914-1723 cm⁻¹. The C=O and -SH stretching vibrations are weak. The absorption peaks in the range of 1300-1020 cm⁻¹ may correspond to the -C-N, C-O and S=O and the absorptions between 674-568 cm⁻¹ may refer to -C-S stretch. The identification of nitrogen containing functional groups is hard due to the overlaps.

FTIR results of the asphaltenes from hydrocracked HVGO and ARCFO/HVGO blends in different ratios are presented in Table 4. In comparison to ARCFO, the FTIR spectra of HVGO and its blends with ARCFO are more complex presumably due to HVGO. Similar functional groups as the ones obtained for ARCFO were observed. In general the intensities of the polar functional groups are increased presumably due to the higher heteroatom content in comparison to ARCFO. This is also consistent with the elemental analysis results. While the C=O stretching was very weak for ARCFO, for HVGO and its blends with ARCFO its intensity is increased considerably. Moreover while the –SH stretching was negligible for ARCFO, it is more significant in HVGO and the mixtures.

The FTIR results obtained in this study are in agreement with the relevant findings reported in the literature.

ν (cm ⁻¹)	AR	AR-400-T	AR-400-C	AR-425-T	AR-425-C	AR-450-T	AR-450-C
-OH stretch (3700-3100) -NH stretch (3500-3100)	3436	3425	3422	3434 3232	3434 3277	3676 3340	3435 3271
=CH stretch 3150-3000	3044	3042	3030	3047	3036	3019	3036
-CH stretch 3000-2800	2922 2868	2923 2862	2924 2868	2920 2868	2920 2862	2927	2920 2851
-SH stretch 2600-2550		2556	2500	2625	2610	2571	2598
C=O stretch 1900-1680	1914	1907	1899	1907	1901 1723	1871	1910 1735
-C=C stretch 1660-1600 (aromatic) 1600-1480 (alkenes) -NH-NH ₂ band 1640-1520	1600 1490	1616	1619	1602	1605	1654	1602
-CH ₂ band 1480-1430	1451	1438	1450	1440	1437	1457	1454
-CH ₃ band 1390-1375	1376				1376	1381	
-C-N stretch 1360-1030 -C-O stretch 1250-1050 S=O stretch 1070-1030	1267 1158 1032	1261 1177 1074	1225 1020	1261 1174 1069	1152 1072	1300 1298 1121 1034	1267 1172 1067
=CH out-of-plane bend alkene 1000-650 aromatic 900-690	813 780 750	872 816 760	844 763 752	872 819 760 752	811 754 713	956 875 758	869 819 755
-C-S stretch 705-550	604	660	682	654	674	671 568	651

Table 3. Infrared spectroscopic results of the asphaltenes from crude ARCFO and the asphaltenes obtained in the liquid products from hydrocracking process of ARCFO (AR: ARCFO, T:thermal, C:catalyst, 400, 425, 450 are the temperatures in °C; hydrocracking conditions: 60 bar H₂, 60 min).

ν (cm ⁻¹)	25/75-T	25/75-C	50/50-T	50/50-C	80/20-T	80/20-C	HV-T	HV-C
-OH stretch (3700-3100)	3676 3575	3680 3596	3737 3669	3549 3358	3676 3520	3677 3407	3719 3602	3719 3585
-NH stretch (3500-3100)	3407	3382	3575 3389 3221	3204	3506 3379 3282	3372	3487	3467
=CH stretch 3150-3000	3019	3042	3148 3025	3040	3025	3137 3030	3070	3042
-CH stretch 3000-2800	2927	2910	2918 2862	2847	2922	2927	2957	2918 2857
-SH stretch 2600-2550	2573	2569	2526	2620	2587	2565		2521
C=O stretch 1900-1680	1901 1736	1878 1745	1907 1767	1878 1798 1683	1742	1734	1703	1731 1706
-C=C stretch 1660-1600 (aromatic) 1600-1480 (alkenes) -NH -NH ₂ bend 1640-1520	1653	1600	1622 1541	1508	1624	1599	1616 1538	1613 1535
-CH ₂ bend 1480-1430	1454	1454	1454	1440	1454	1438	1429	
-CH ₃ bend 1390-1375	1372	1365				1381		1393
-C-N stretch 1360-1030 -C-O stretch 1250-1050 S=O stretch 1070-1030	1218 1121 1037	1306 1225 1118 1018	1314 1216 1197 1037	1302 1249	1181 1110 1051	1219 1121 1037	1269 1177	1362 1261 1113 1043
=CH out-of-plane bend alkene 1000-650 aromatic 900-690	959 900 792	956 834	931 844 749	919 783 725	956 874 808 760	959 861 760	923 883 811	819
-C-S stretch 705-550	673 569	676 569	674 566	602	643 567	671 568	665	668

Table 4. Infrared spectroscopic results the asphaltenes from hydrocracked HVGO and ARCFO/HVGO blends in different ratios (AB/CD refers to ARCFO%/HVGO%, T:thermal, C:catalyst, HV:HVGO; hydrocracking conditions: 450°C, 60 bar H₂, 60 min)

4. CONCLUSION

It can be concluded that hydrocracking process affects the amount of the asphaltenes as well as aromatic and heteroatom contents of the asphaltenes. At higher hydrocracking temperatures, the asphaltene amount was higher. On the other hand, the use of catalyst decreased the asphaltene amount. For the mixture of ARCFO with HVGO, the asphaltene amount was less than the theoretical amount supposed to be. After hydrocracking process, the aromaticity degree and the heteroatom content of the asphaltenes from ARCFO increased with respect to the asphaltenes obtained from crude ARCFO. The heteroatom content of the asphaltenes obtained from the ARCFO/HVGO blends was lower in comparison to HVGO alone which is a desired property. The FTIR results indicate that the heteroatoms in the asphaltenes were in the form of functional groups such as -OH, -NH, -SH, C=O, C-O, C-N, C=S and C-S. The FTIR results are in agreement with the elemental analysis.

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