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Catalytic Coprocessing of Low-Density Polyethylene with VGO Using Metal Supported on Activated Carbon

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The main objective of this study was to explore nonacidic catalysts for recycling of low-density polyethylene (LDPE) by coprocessing with vacuum gas oil (VGO). The focus of this study is to investigate processability of coprocessing LDPE with VGO, and to obtain environmentally friendly liquid fuels from such coprocessing. LDPE and VGO were cracked over activated carbon-supported metal catalysts (M–Ac) and acidic catalysts (HZSM-5, DHC-8) using a batch autoclave at 425, 435, and 450 °C under hydrogen atmosphere. In hydrocracking of LDPE in VGO, the most suitable temperature was found to be 435 °C. The amount of sulfur in liquid products obtained from hydrocracking over activated carbon-supported metal catalysts was lower than that over HZSM-5. Activated carbon-supported metal catalysts acted as an absorbent for sulfur compounds and H_2S and also facilitated hydrodesulfurization (HDS). The hydrocarbon types in liquids were determined by nuclear magnetic resonance (NMR) analysis. In the cases of activated carbon-supported metal catalysts, aromatic species were found between 4% and 8.9%, whereas the liquid product obtained over HZSM-5 has 28% aromatic species. In the presence of activated carbon-supported metal catalysts, the isoparaffin index was found to be between 0.32 and 0.66. However, the isoparaffin index was 0.01 in the liquid obtained over HZSM-5. The presence of lower aromatics and higher isoparaffin index in liquid products obtained over the activated carbon-supported metal catalysts suggest an improved hydrocarbon fuel from an environmental viewpoint.

Introduction

Plastic materials are present in almost every area of daily life. However, the significant growth of plastic consumption also led to increasing amounts of waste plastics. The disposal of plastic wastes is an important environmental problem all over the world. Europe is generating about 15 million tons of post consumer plastic waste[1] while the United States alone generates more than 20 million tons of plastic wastes each year.[2] Recently, the degradation of polymers into liquid hydrocarbons has attracted much attention from the viewpoint of the utilization of waste plastics as an energy resource. There have been many reports on the conversion of plastics to fuels using solid acid catalysts, especially on polyethylene (PE) and polypropylene (PP).[3,8] Solid acid catalysts generally have been pre-

ferred for polymer degradation because of their high cracking abilities.[9]

On the other hand, it was reported that in the use of nonacidic mesoporous silica catalyst (FSM) which possesses no acid sites the degradation rates of PE and PP were as fast as that over an acid catalyst (SA-1), and the liquid yields were higher.[10] Recently carbon-supported metal catalysts have become popular for hydrodesulfurization (HDS),[11–13] hydrogenation,[14,15] and hydrodenitrogenation (HDN)[16] reactions because of their high surface area and because they can function as an absorbent for sulfur and nitrogen compounds. In addition, in the fine chemical industry, precious metals loaded on activated carbon supports are frequently used, because such systems exhibit interesting features with

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regard to their application. Activated carbons are stable in both acidic and basic media.[17] Apart from their use as an absorbent, activated carbons can be used as catalysts in some reactions such as conversion of SO_2 and NO_x, desulfurization reactions, and oxidative dehydrogenations of hydrocarbons and alcohols.[18][20] Activated carbon-supported metal catalysts, especially Ni–Mo loaded on activated carbon, have been used in oxidative dehydrogenation of ethylbenzene[21] and hydrogenation of heavy oil.[22] Uemichi et al. used activated carbon-supported metal catalysts to obtain aromatic hydrocarbons from the pyrolysis of PE[23] and PP[24] They reported that activated carbon-supported Pt, Fe, and Mo catalysts were found to be effective catalysts for the pyrolysis of PE[23] and PP.[24] These two studies have shown that activated carbon-supported metal catalysts are active for cleavage of C–C bonds. Coprocessing of polymers with heavy oils such as VGO or with coal is also an interesting approach. Ng[25] studied the coprocessing of high-density polyethylene (HDPE) with VGO in the absence and presence of catalysts in a fixed bed reactor. In this study, it was reported that higher gasoline yield was obtained in the presence of catalysts and also a synergetic effect was observed.[25] In another study, coprocessing reactions were carried out with the mixture of PE/poly(vinyl chloride) (PVC) in heavy vacuum gas oil (HVGO) by two-step processing. In the first step, the blend was pyrolyzed at 350 °C. In the second step, the dechlorinated mixture was hydrocracked with or without catalysts. What is interesting about this work is that the dechlorination step led to both predegradation of PE and dechlorination of PVC and that PE could be completely cracked in the hydrocracking step with or without a catalyst even though the temperature was only 400 °C.[26] PE/VGO and PP/VGO blends were also coprocessed in the presence of the different types of catalysts (neutral and acidic) under H_2 atmosphere. The product distribution varied with the kind of polymer in the blend and the type of catalysts.[27]

In case of coprocessing of waste plastics with VGO, catalysts used must be resistant to the impurities, such as chlorine and nitrogen compounds from waste plastics. For this purpose, activated carbon-supported metal catalysts were chosen in the present study. The focus of this study is to investigate processability of coprocessing of LDPE with VGO in the presence of activated carbon catalysts for obtaining environmentally friendly liquid fuels.

Experimental Section

Materials. Activated carbon was purchased from Carla Erba Reagent (Code number: 332658). The activated carbon was manufactured from biomass powder. The vacuum gas oil (VGO) used in this work was a broad vacuum distillate with a boiling range 242–578 °C, and which is a base feed for the hydrocracking unit in a refinery in Izmir, Turkey. The vacuum gas oil sample contains 2.55% total sulfur and 766 ppm nitrogen. Low-density polyethylene (LDPE) (as 3.2-mm extruded pellets, MW: 68500, % crystals: 26.3, $d = 0.918–0.922$ g cm^{-3}) sample was supplied by ALPET-Izmir, Turkey. It did not contain filling, stabilizers, etc. The DHC-8 catalyst used is a commercial catalyst, which is being used in the hydrocracking unit in the refinery. DHC-8 (BET surface area: 102 m^2 g^{-1}) powder in sulfided form is an amorphous hydrocracking catalyst consisting of nonprecious metals on a silica–alumina support. It is a bifunctional catalyst incorporating both hydrogenating and hydrocracking functions. HZSM-5 [BET surface area: 300 m^2 g^{-1}, (SiO_2/Al_2O_3 = 216 (molar ratio)] was supplied by Toso Chem. Ind., Japan. Metal salts including Co-$(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $(NH_4)_6Mo_7 \cdot 4H_2O$ were purchased from Aldrich and used as received. The solvent including tetrahydrofuran, hexane, and xylenes (mixed) were purchased from Aldrich.

Catalyst Preparation. The commercial activated carbon was purified (for elimination of inorganic impurities) by treatment with a solution of HCl (10 wt %) at room temperature for 24 h. After HCl treatments, the carbon was repeatedly washed with deionized water up to pH = 7, and then it was dried at 105 °C for 24 h. All catalysts were prepared by a wet impregnation method using excess water. Metal salts were dissolved in deionized water to a nominal metal concentration of 5 wt %, and then loaded onto activated carbon by wet impregnation under continuous agitation. This slurry was dried at 105 °C for 24 h and then was thermally treated at 300 °C under a nitrogen atmosphere to remove the nitrate or ammonium groups. For bimetallic catalysts, metal salts were impregnated from their solutions at a nominal metal concentration of 5 wt % for each metal. Activated carbon-supported Co, Ni, Mo, Co–Ni, and Co–Mo are denoted as Co–Ac, Ni–Ac, Mo–Ac, Co–Ni/Ac, and Co–Mo/Ac, respectively.

Hydrocracking Reactions. Reactions were conducted in a 100 mL 316 stainless steel shaking type batch autoclave at, respectively, 425, 435, and 450 °C for 2 h. The reaction time of 2 h does not include the reactor heat-up time of about 45 min. In a typical catalytic hydrocracking experiment, the reactor was loaded with 20 g of vacuum gas oil (VGO), 5 g of polymer, and 2.5 g of catalyst. The reactor was purged three times with hydrogen and then pressurized with hydrogen to 6.5 MPa. The reactor was agitated horizontally at ≈200 cycles/min. After the reaction, the reactor was quenched to room temperature by fan. The gases were released. Reactor content was centrifuged to separate the liquid products. The remaining product in the form of a slurry was solvent-extracted with THF to remove wax compounds. The THF-insoluble materials consisted of coke, catalyst, and undegraded PE. The THF-insoluble was extracted with xylene at 130 °C to separate the undegraded PE. The xylene-insoluble consisted of coke formed during the reaction. Details of the product analysis procedure are available in the literature.[26,27]

Analysis of Liquid Products. The liquid products were analyzed by gas chromatography with a flame ionization detector using a Hewlett-Packard model 6890GC. The column was a HP z-530300 column (30 m long × 0.32 mm diameter) coated with phenylmethylsiloxane cross-linked at a thickness of 0.50 μm. GC-FID was temperature-programmed from 40 to 280 °C at 5 °C/min with a final holding time of 30 min. The data obtained from GC-FID was used to evaluate the simulated distillation curves.[28] The amounts of sulfur in liquid

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Table 1. Metal Contents and Surface Areas of Metal-Loaded Active Carbon Catalyst

catalyst	Co−Ac	Mo−Ac	Ni−Ac	Co−Mo/Ac	Co−Ni/Ac
metal content, wt %					
Co	4.13			4.31	4.32
Mo		3.55		3.76	
Ni			5.00		5.00
surface area, m² g⁻¹	200.33	152.03	233.13	204.26	223.65

products were determined using a Sulfur Determinator SC-132 instrument, which was calibrated by using a standard containing 3% sulfur. Analyses were repeated 2 times for each sample. ^{1}H NMR spectra of liquid products were recorded with a Brocker GMBH DPX-400 using CDCl$_3$ as solvent.

Catalyst Characterization. The BET surface area of the activated carbon-supported metal catalysts was measured using a Micromeritics ASAP 2000 instrument. The metal contents of the catalysts were determined by chemical analysis using an inductively coupled plasma emission spectrometer. Metal supported on activated carbon catalysts were acid-washed and metal concentration in activated carbon determined in the wash using a Leeman Labs PS-3000UV. X-ray photoelectron spectrometry (XPS) spectra were recorded with a Kratos Analytical XSAM 800 pci. XPS quantification was performed by applying the appropriate relative sensitivity factors (RSFS) for the Kratos instrument to the integrated peak areas. These RSFS take into consideration the X-ray cross-section and the transmission function of the spectrometer.

Table 1 gives the properties of the laboratory-prepared mono-metallic (Co, Ni, Mo) and bimetallic (Co−Ni, Co−Mo) catalysts supported on activated carbon.

Results and Discussion

Hydrocracking of a LDPE/VGO Blend. A LDPE/VGO mixture was hydrocracked at temperatures of 425, 435, and 450 °C in the presence of H$_2$ and with or without catalysts. Table 2 shows the product distribution which was obtained from the hydrocracking of a LDPE/VGO blend at temperatures of 425, 435, and 450 °C. In hydrocracking experiments, both temperature and catalyst type affected the product distribution and degradation ratio. In terms of both liquid yield and the amount of undegraded polymer, the temperature of 435 °C seems to be the most suitable temperature. Although, the degradation at 425 °C was not enough for good yield, the Co−Ac catalyst gave the highest liquid yield (46.16 wt %) and the lowest amount of waxy compounds. Except for Co−Ac, at this temperature, the other activated carbon-supported catalysts gave lower liquid yield than that of thermal treatment. With increasing temperature from 425 to 435 °C, a dramatic increase in liquid yields and the degradation of waxy compounds were observed. Co, Mo, and Ni catalysts gave similar product distributions. At this temperature, it is interesting that a negative effect was observed in the case of loading dual metals when compared to the mono-metallic case. This may be due to the formation of alloys at 435 °C. Further increase in the temperature led to the formation of more gaseous products, as expected. In the catalytic treatment, the use of catalyst led to more increase in gas formation. At 450 °C, the metal type on activated carbon had no effect on product distribution. At the lowest temperature, the type of catalyst was very important in the degradation of PE.

At 425 °C, Co−Ac gave better results than other activated carbon-supported metal catalysts and thermal treatment. When the temperature was increased to 435 °C, PE was completely degradated in all the catalytic experiments. In the previous studies, it has been observed that the temperature of 435 °C was a critical temperature for the liquefaction of PE.[29,30] The simulated distillation curves of liquids are shown in Figure 1. At the hydrocracking temperature of 425 °C, the liquids from thermal run contained 18% naphtha (boiling point < 172 °C) and 7% middle distillate (172 °C < boiling point < 232 °C). In the case of Co−Ac the fractions of naphtha and middle distillate were 35% and 20%, respectively. However the liquids obtained from M−Ac (except Co−Ac) catalysts were more viscous so we did not need to analyze them with GC. With an increase of hydrocracking temperature to 435 °C, lighter liquids were obtained. Co−Ac and Mo−Ac catalysts gave more lighter liquids than did the other M-Ac catalysts. The liquid from Co−Ac contained 48% naphtha and 15% middle distillate. In the case of Mo−Ac, the fraction of naphtha and middle distillate were found to be 43% and 19%, respectively. Unexpectedly, with increasing cracking temperature to 450 °C, the percentage of the naphtha fraction decreased while the middle distillate increased. At 450 °C, in contrast to catalytic hydrocracking, we obtained the liquid containing lighter compounds in the thermal (noncatalytic) run. 60% of naphtha and 17% of middle distillate were determined in the liquid.

This result (heavier liquid at 450 °C) gave the conclusion that the free radicals in high concentration in hydrocracking over Co−Ac at 450 °C led to formation of gas products and also formation of middle distillates by a hydrogen-quenching reaction.

Comparison of Co−Ac and Acidic Catalysts for Hydrocracking of a LDPE/VGO Blend. To compare the cracking ability of M−Ac catalysts with acidic catalysts, the hydrocracking of a PE/VGO blend was carried out with a commercial catalyst, DHC-8, and an acidic cracking catalyst, HZSM-5. Figure 2 shows the product distribution from the hydrocracking at three different temperatures of 425, 435, and 450 °C in the presence of nonacidic (Co−Ac) and acidic catalysts. As Co−Ac gave better results than the other metals, the product distribution over Co−Ac was used for comparison in Figure 2. In the presence of acidic catalysts both the temperature and the type of catalysts affected the product distribution and the degradation ratio of PE as is the case with M−Ac catalysts. At 425 °C, the degradation ratio of LDPE in the presence of Co−Ac, DHC-8, and HZSM-5 was 83.6 wt %, 73 wt %, and 100 wt %, respectively. When the temperature was increased to 435 °C, the degradation ratio was more than 96 wt % in hydrocracking over Co−Ac and DHC-8. The variation in product distribution depends on the temperature and the type of catalysts. Hydrocracking runs over HZSM-5 gave the highest gas yield at all temperatures. The maximum liquid yield (53.56 wt %) at 425 °C was obtained over HZSM-5, whereas HZSM-5 gave the lowest liquid yield at 435−450 °C. In the case of HZSM-5, the increases in temperature above 425 °C led to more

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Table 2. Product Distribution from Hydrocracking of PE/VGO Blend over M−Ac Catalyst[c]

reaction temp. °C	425						435						450					
catalyst (M−Ac)	−	Co	Mo	Ni	Co−Ni	Co−Mo	−	Co	Mo	Ni	Co−Ni	Co−Mo	−	Co	Mo	Ni	Co−Ni	Co−Mo
reaction products, wt %																		
gas[a]	20.3	22.2	20.2	28.0	30.2	17.8	21.7	28.8	26.8	24.3	25.3	29.7	40.5	49.0	51.6	52.0	51.8	55.8
liquid	31.2	46.1	25.8	23.6	22.9	14.0	68.5	54.9	53.6	55.2	39.1	57.0	56.0	33.7	32.6	34.8	30.8	30.5
wax	44.4	28.3	46.7	45.5	41.7	56.4	9.3	15.8	19.2	20.3	34.2	9.4	3.3	17.0	14.7	12.1	16.2	13.6
asphaltene	3.5	0.9	1.7	2.0	1.0	1.4	0.4	0.9	0.8	1.4	0.8	0.5	-	0.9	0.9	0.6	0.6	0.7
coke	-	trace	1.1	0.3	1.2	3.2	0.1	0.3	trace	trace	trace	3.8	trace	0.1	0.9	1.0	1.0	trace
undegraded polymer[b]	21.4	16.4	30.6	12.4	19.4	2.4	2.0		1.2				trace					

[a] Calculated from mass balance. [b] Based on PE charge. [c] Standard deviations on conversion products: ±1.0%.
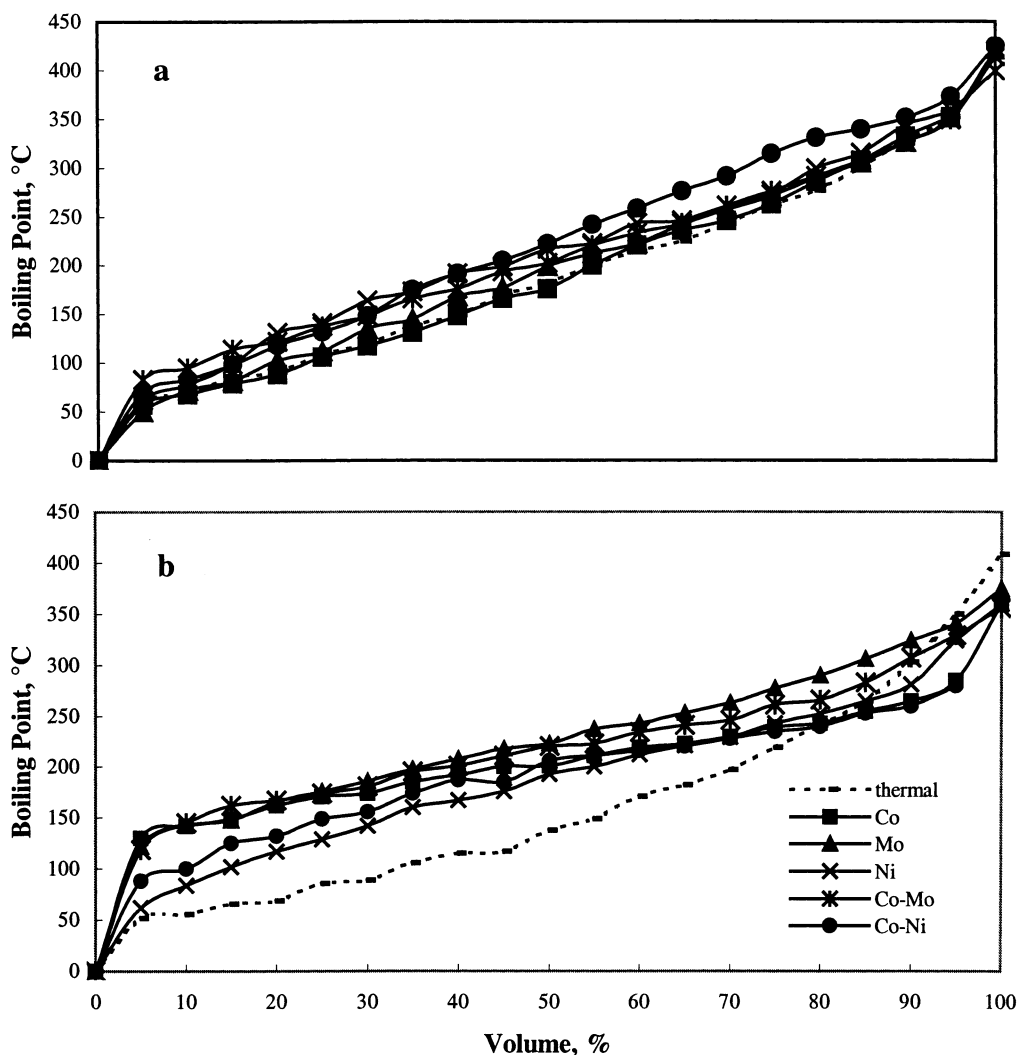

Figure 1. Simulated distillation curves of liquids obtained from hydrocracking of PE/VGO blend over different M−Ac catalysts: (a) at 435 °C, (b) at 450 °C.

gas formation. However, over Co−Ac the increase of the temperature from 425 to 435 °C led to more degradation of waxy compounds to liquids. Further increase in the temperature (from 435 °C to 450 °C) led to degradation of liquids and formation of more gas products. This is due to differences in degradation mechanisms.

In contrast to cracking over HZSM-5 and Co−Ac, the product distribution was not significantly changed with an increase in the temperature in the case of DHC-8. This shows that the catalytic activity of DHC-8 was almost stable at the temperatures between 425 and 450 °C. HZSM-5 is well-known as an acidic catalyst. It has many Brønsted acid sites. Cracking pathways on acidic HZSM-5 may involve the formation of carbenium ion

(cation) by proton transfer from the surface acid site followed by β-scission. A β-scission leads to an olefin and regenerates the Brønsted acid site. Olefins are saturated by H_2 in hydrocracking reactions. Since DHC-8 is a hydrocracking catalyst, it has dual functions: hydrogenation (dehydrogenation) and cracking. A simplified reaction scheme for hydrocracking is available in the literature.[31] Mechanistically, the first step in the hydroconversion of (normal) alkanes is dehydrogenation to produce olefinic intermediates, which then form carbenium ions on the acid sites. These carbenium ions

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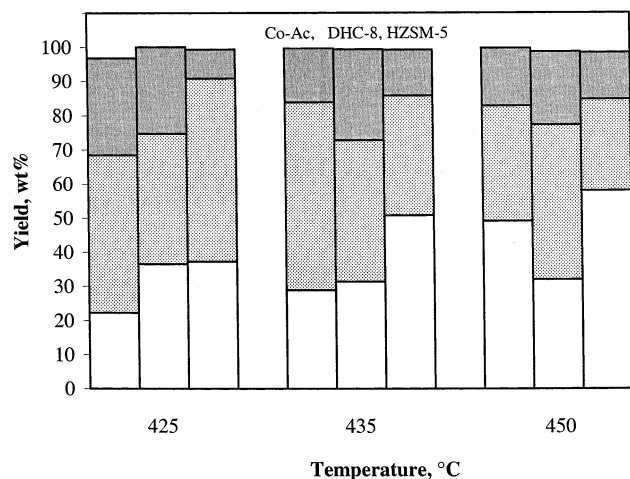
Figure 2. Product distribution from hydrocracking of PE/VGO blend over different catalysts: ☐ gas, ◪ liquid, ■ wax.

can then undergo the usual acid-catalyzed reactions, namely β-scission and subsequent isomerization, which may be followed by further β-scission. The isomerized and/or cracked species can then be desorbed from the acid site and hydrogenated to the corresponding alkane. The products of cracked alkenes can undergo further cracking reactions (secondary cracking) to yield further lighter products. In addition, alkenes can react in bimolecular hydrogen transfer reactions with naphthenes in a process that may ultimately lead to coke.

On the other hand, in the cracking over an activated carbon-supported metal catalyst, hydrocarbons are cracked via a radical mechanism. The secondary free radical is formed by hydrogen abstraction by a primary radical formed by an initiation reaction, which is usually homolytic C−C bond cleavage. As also suggested by

$$R-CH_2-CH_2-CH_2-R + \cdot Ac \rightarrow$$
$$R-CH_2-\dot{C}H-CH_2-R + H{:}Ac$$
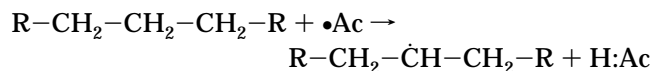
Nakamura et al.,[32,33] the concentration of free radicals is controlled at a lower level in pressurized hydrogen; the activated carbon-supported metals activate the hydrogen molecule to from hydrogen atoms which can hydrogenate free radicals and olefins to suppress over-cracking. Because of this effect, in this study, hydrocracking over M−Ac gave a different product distribution from that of the thermal hydrocracking, although in both cases the reaction mechanisms are based on radicals. The reason for less gas formation over M−Ac than that over acidic catalyst at 425 and 435 °C is suppression of the over cracking of the hydrocarbon radical. It should be noted that, in addition to H_2, H_2S was also present in our experiments, because sulfur compounds in VGO convert to H_2S under hydrocracking conditions. Nakamura et al.[34] also studied the effect of H_2S on the degradation of PP over an activated carbon-supported metal catalyst.[34] They suggested that hydrogen in H_2S can be abstracted by the hydrocarbon radical to form a stable hydrocarbon and HS·, which either abstracts a hydrogen from PP or becomes stabilized on

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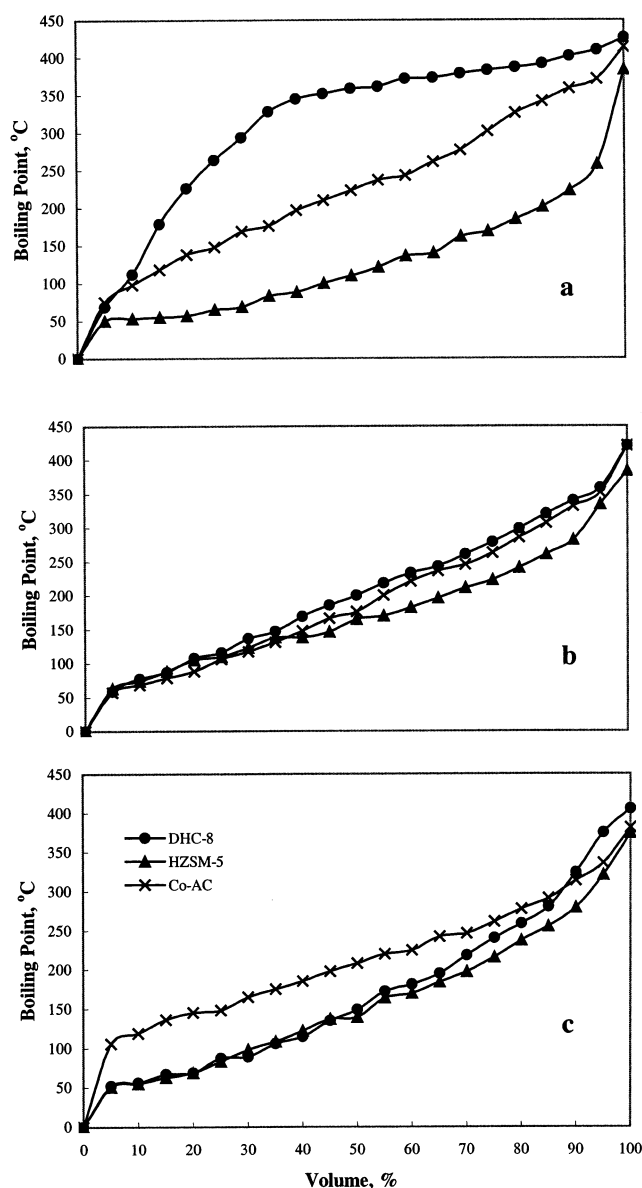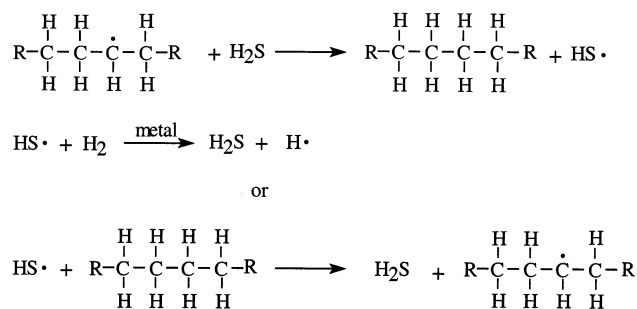(34) Nakamura, I.; Fujimoto, K. *Catal. Today* **1996**, *27*, 175−179.

Figure 3. Simulated distillation curves of liquids obtained from hydrocracking of PE/VGO blend over different catalysts (a) at 425 °C, (b) at 435 °C, and (c) at 450 °C.

the supported metal catalyst by hydrogen. On the basis of Nakamura's comment, for this study the role of H_2S may be shown as follows, where HS· is formed from reaction of a radical:

ASTM-simulated distillation curves of liquids are shown in Figure 3. The composition of the liquid products varied with the type of catalysts and the temperature. At all temperatures, by using HZSM-5, the

Table 3. Product Distribution from Hydrocracking of VGO Alone, PE Alone, and PE/VGO Blend at 435 °C over Different Catalysts[c]

feed, 25 g	VGO				PE				PE/VGO			
catalyst, 2.5 gr	−	DHC-8	HZSM-5	Co−Ac	−	DHC-8	HZSM-5	Co−Ac	−	DHC-8	HZSM-5	Co−Ac
reaction products, wt %												
gas[a]	33.7	27.0	44.9	22.6	24.1	59.6	78.5	28.7	21.6	31.3	50.7	28.8
liquid	60.8	60.0	40.4	60.8	60.6	31.0	12.2	42.0	68.5	41.3	34.9	54.9
wax	5.4	12.5	14.2	14.2	14.9	7.5	6.9	27.6	9.2	26.6	13.4	15.8
asphaltene	0.2	0.3	0.7	0.5	0.6	0.2	0.0	1.8	0.4	0.5	0.8	0.9
coke		0.3	0.3	2.2	0.3	1.6		1.6	0.1		0.6	0.3
undegraded polymer[b]						0.2	0.2		2.0	3.6	1.0	-

[a] Calculated from mass balance. [b] Based on PE charge. [c] Standard deviations on conversion products: ±1.0%.

naphtha fraction was always higher than that over Co−Ac and DHC-8. The increase in temperature generally increased the lighter fractions. At 425 °C, hydrocracking over Co−Ac produced 33 wt % naphtha fractions and 19 wt % middle distillate. In the cases of DHC-8 and HZSM-5, the yields of the naphtha fraction and middle distillate were found to be 12 wt % and 7 wt %, 60 wt % and 20 wt %, respectively. As expected, when the temperature was increased from 425 to 435 °C, the lighter compounds in liquid products increased significantly. At 435 °C, by using Co−Ac and DHC-8, the naphtha fractions were found to be 45% and 50%, respectively. The middle distillate fraction was found to be about 23% with both Co−Ac and DHC-8 catalysts. When the temperature was increased from 435 to 450 °C, the naphtha fraction increased for HZSM-5, DHC-8, whereas the naphtha fraction decreased from 50% to 35%, and the middle distillate fraction increased from 15% to 27% for Co−Ac. This result can be rationalized by the considerations discussed before (the effect of hydrogen quenching reactions).

The Investigation of Cracking Ability of VGO in the Presence of LDPE. One of the goals of this study was to investigate the processability of PE using a refinery stream. To observe the effect of PE on the hydrocracking process, hydrocracking of VGO and PE by itself was performed. The product distribution from hydrocracking experiments at 435 °C is shown in Table 3. The presence of PE affected the cracking properties of VGO in the cases of thermal and catalytic hydrocracking with DHC-8. In thermal hydrocracking the amount of gas products obtained from VGO/PE blend was less than that from VGO alone, whereas liquid yield was more. Considering the weight fractions of blend and assuming that VGO in the blend gave the same product distribution as that in VGO alone, the gas yield would be at least about 55 wt % and the liquid yield would be around 35 wt %. However, the obtained gas and liquid yield were 21.7 wt % and 68.5 wt %, respectively. The differences in gas and liquid yields between obtained and calculated (based on VGO) values may be due to interaction between radicals formatted during the degradation of VGO and PE. These interactions hindered the formation of gaseous and favored liquids. In hydrocracking over DHC-8, the liquid yield obtained from VGO/PE was less than that from VGO alone, whereas waxy compound yield was more. In contrast to thermal hydrocracking, the presence of PE decreased the liquid yield of VGO. The differences in the effects of PE on the VGO cracking may be due to their degradation behaviors, which are different from each other. It is interesting that in the hydrocracking over Co−Ac and

HZSM-5, the yields between obtained and calculated values were similar. HZSM-5 has a very high cracking activity. The feed content did not affect the product distribution. Although in hydrocracking over Co−Ac, the degradation mechanism is radical, hydrogen quenching (with H·) was perhaps more pronounced than hydrocarbon quenching (with R·).

Hydrocarbon Types in Liquid Products. Nuclear magnetic resonance analysis was used to determine the percentage of aromatic, paraffinic, and aliphatic species in hydrocarbon fuels, which were obtained from hydrocracking of LDPE/VGO blend at 435 °C. From the integrated areas of the NMR spectral regions given in Table 4, the hydrocarbon types including aromatics, paraffins, and olefins as well as H/C atomic ratios were estimated using literature correlations devolved by Myers et al.[35] from data on 36 gasoline samples. In these equations, A, B, C, D, E, and F represent the integrated area of the spectral regions defined by chemical shifts in parts per million (ppm) from TMS as shown in Table 4. To obtain volume percents, Myers et al. included corrections for the varying densities of the different hydrocarbon types. Myers et al. found that these correlations given below as eqs 1−4 gave an average standard deviation for the three hydrocarbon types compared with FIA (fluorescent indicator adsorption) data of 2.5% and a standard deviation of 0.055 based on the H/C ratio from combustion analysis.

$$\text{Aromatics, vol \%} = \frac{(A + C/3)0.97 \times 10^2}{(A + C/3)0.97 + (D - 2B + E/2 + F/3)1.02 + 3.33B} \quad (1)$$

$$\text{Paraffins, vol \%} = \frac{(D + 3B + E/2 + F/3)1.02 \times 10^2}{(A + C/3)0.97 + (D - 2B + E/2 + F/3)1.02 + 3.33B} \quad (2)$$

$$\text{Olefins, vol \%} = \frac{3.33B \times 10^2}{(A + C/3)0.97 + (D - 2B + E/2 + F/3)1.02 + 3.33B} \quad (3)$$

$$\text{H/C} = \frac{A + B + C + D + E + F}{(A + C/3)1.28 + (D - 2B + E/2 + F/3)1.02 + 3.42B} \quad (4)$$

This equation was also used to determine octane number and isoparaffinic and aliphatic species in liquids

(35) Myers, M. E.; Stollsteimer, J., Jr.; Wims, A. M. *Anal. Chem.* **1975**, *47* (13), 2301−2304.

Table 4. NMR Spectral Regions

	proton type	chemical shift region (ppm)
A	ring aromatics	6.6–8.0
B	olefin	4.5–6.0
C	α-methyl	2.0–3.0
D	methine (paraffins)	1.5–2.0
E	methylene (paraffins)	1.0–1.5
F	methyl (paraffins)	0.6–1.0

Table 5. The Amounts of Hydrocarbon Types in the Liquid Products from Hydrocracking over Different Catalysts at 435 °C

feed–catalyst	aromatics	paraffins	olefins	H/C	IPI[a]
VGO/PE	3.45	96.55	0.00	2.05	0.58
VGO/PE–HZSM-5	28.04	71.96	0.00	1.66	0.01
VGO/PE–DHC-8	4.16	95.84	0.00	1.93	0.00
VGO/PE–Ac	6.08	93.92	0.00	2.08	0.47
VGO/PE–Co/Ac	6.14	93.86	0.00	2.04	0.39
VGO/PE–Mo/Ac	7.27	92.73	0.00	2.05	0.66
VGO/PE–Ni/Ac	8.94	91.06	0.00	2.04	0.53
VGO/PE–Co–Ni/Ac	5.64	94.36	0.00	2.04	0.41
VGO/PE–Co–Mo/Ac	4.00	96.00	0.00	2.00	0.32

[a] IPI: iso paraffin index.

which were obtained from upgrading of a plastics pyrolysis.[36] Table 5 shows the content of hydrocarbon types in liquid products from the hydrocracking of a PE/VGO blend at 435 °C. In the presence of M–Ac catalysts, aromatic species were found to be between 4% and 8.94% and paraffinic species were found to be between 91.06% and 96%. In the case of bimetallic catalysts, the aromatic contents decreased very slightly. The use of DHC-8 had no significant effect on the aromatic and paraffinic content. However, surprisingly, the isoparaffin index was found to be zero. Compared to other tested catalysts, HZSM-5 gave the highest amount of aromatic species (28.04%). Park et al.[7] obtained a similar result. The use of HZSM-5 gave the liquid containing more than 75% of aromatics in the catalytic degradation of PE.[7] They concluded that aromatization seems to be favorable on the Brønsted acid sites on HZSM-5. The isoparaffin index of liquids obtained over M–Ac was more than that of acidic catalysts. The presence of lower aromatics and higher isoparaffin index in liquid from the M–Ac catalysts suggest an improved hydrocarbon fuel from an environmental viewpoint.

Sulfur Amounts in Liquid Products. In this study, our concern includes not only converting PE/VGO blend to fuels but also obtaining liquid products having better quality. Sulfur content in liquid fuels is one of the key factors in fuel quality. Because the base feed VGO has 2.55% sulfur, we determined the sulfur contents in liquids. The percentages of sulfur contents in liquid products obtained from PE/VGO blend with different catalysts at 435 °C are given in Table 6. It is well-known that activated carbon is used for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions partly because of their role as an absorbent for sulfur and nitrogen compounds.[11–13,16] It is known from the literature that carbon-supported Co–Mo and Ni–Mo sulfides are more active HDS catalysts.[37] Although there have been several attempts to relate the surface properties of the carbon-supported catalysts to the differences in

Table 6. Concentration of Sulfur in Liquids from Hydrocracking of VGO/PE Blend over Different Catalysts at 435 °C

catalyst	sulfur amount, wt % (± 0.01)
none	1.3197
active carbon	1.2104
Co–Ac	1.1123
Ni–Ac	0.9741
Mo–Ac	0.9311
Co–Ni/Ac	0.9429
Co–Mo/Ac	0.8996
HZSM-5	2.2030
DHC-8	0.6493

Table 7. Concentration of Elements on/near the Surface of Metal-Loaded Active Carbon, Atom %

sample	C	O	N	Co	Mo	Ni
Co–Ac	85.10	10.70	1.40	2.70	0.00	0.00
Mo–Ac	84.80	11.30	3.10	0.00	0.80	0.00
Ni–Ac	79.30	15.10	0.00	0.00	0.00	5.70
Co–Mo/Ac	83.20	12.00	2.90	1.20	0.70	0.00
Co–Ni/Ac	67.70	20.70	0.00	5.20	0.00	6.50

HDS activities, the understanding of the metal precursor/carbon interactions is not yet comprehensive enough.

In this study, it can be seen clearly that metal loading increased the HDS activity of activated carbon. To explain the variation in sulfur amount in liquids with metal type, the M–Ac catalysts were investigated by XPS. The results from XPS are shown in Table 7. By considering the sulfur amounts in liquids, the order of HDS activity of M–Ac can be ranked as follows: Co–Ni/Ac > Ni–Ac > Co–Ac. It may be suggested that HDS activity depend on the concentration of metal and/or oxygen groups on the surface of activated carbon. However, in the case of Mo–Ac, the HDS activity was independent of the concentration of metal and oxygen groups. Although the amounts of both oxygen groups and Mo was lower than that of other M–Ac catalysts, the liquids obtained over Mo–Ac and Co–Mo/Ac had lower sulfur amounts. A similar result has been reported by Calafat et al.[37] They found that the dispersion of Mo did not affect the HDS activity, whereas Ni concentration and oxygen functional groups were responsible for HDS activity.[37] It is noted that using HZSM-5 catalyst produced the liquid having highest sulfur, even higher than that of the thermal case. This may be due to the formation of more aromatics during the hydrocracking of PE/VGO. Farag et al.[11] studied the HDS of diobenzothiophene (DBT) over Co–Mo based carbon and alumina catalyst. The presence of naphthalene in HDS of DBT inhibited the HDS activity. They suggested that aromatic hydrocarbons in great excess compared with sulfur species appear to occupy the active sites for de-sulfurization and hydrogenation.[11] The DHC-8 gave the lowest sulfur concentration among the catalysts used. As we mentioned before, DHC-8 is a commercial hydrocracking catalyst consisting of nonprecious hydrogenation metals on silica alumina.

Conclusion

The conversion of a LDPE/VGO blend to fuels was carried out in the presence of nonacidic catalysts (activated carbon-supported metal catalysts) and the acidic catalysts (HZSM-5 and DHC-8, commercial hydrocracking catalysts). The effects of catalyst type on product distribution and the properties of liquid fuel

(36) Joo, H. S.; Guin, J. A. *Fuel Process. Technol.* **1998**, *57*, 25–40.
(37) Calafat, A.; Laine, J.; Lopez-Agudo, A.; Palacios, J. M. *J. Catal.* **1996**, *162*, 20–30.

obtained from hydrocracking of LDPE/VGO blend were investigated.

• In cracking over the activated carbon-supported metal catalysts, the most suitable temperature was found to be 435 °C. While the type of metal on activated carbon affected the product distribution and liquid fuel composition at lower temperatures (especially at 425 °C), at 450 °C metal type had no considerable effect. Activated carbon-supported cobalt (Co−Ac) catalysts seemed to be better than the other catalysts.

• In hydrocracking over DHC-8 commercial catalyst, the product distribution was not changed considerably with the temperature. At 425 and 435 °C, it gave less liquid than that in the case of the Co−Ac catalyst.

• HZSM-5 showed the highest cracking activity. At the lowest temperature, it produced the highest amount of liquid, whereas above 425 °C, it gave the highest gas yield.

• Activated carbon-supported metal catalysts produced the liquids having lower aromatics and higher isoparaffin index in comparison to the runs with the acidic catalysts.

• The DHC-8 gave the liquid having lowest sulfur concentration, whereas the liquid containing the highest amount of sulfur was obtained over HZSM-5.

• Activated carbon-supported metal catalysts showed good HDS activity. The sulfur contents in liquids varied with the metal type.

Consequently, for successful coprocessing of the plastics with a refinery stream, a catalyst that has a combination of hydrocracking, hydrogenation, HDS, and HDN abilities is needed. Activated carbon-supported metal catalysts seem to possess all of these properties but to different extents. However, further study is needed to optimize activated carbon-supported metal catalysts.

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