energy&fuels

Article

pubs.acs.org/EF

Thermal Cracking and Catalytic Hydrocracking of a Colombian Vacuum Residue and Its Maltenes and Asphaltenes Fractions in Toluene

Adan Y. León,[*,†,‡] Alexander Guzman,[§] Dionisio Laverde,[†,‡] Raghunath V. Chaudhari,[*,∥,⊥] Bala Subramaniam,[*,∥,⊥] and Juan J. Bravo-Suárez[*,∥,⊥]

[†]School of Chemical Engineering and [‡]Corrosion Research Group − GIC, Industrial University of Santander, Bucaramanga 680002, Colombia

[§]Ecopetrol S.A. - Colombian Petroleum Institute, Piedecuesta, Piedecuesta 681011, Colombia

[∥]Center for Environmentally Beneficial Catalysis and [⊥]Chemical & Petroleum Engineering Department, The University of Kansas, Lawrence, Kansas 66045, United States

ABSTRACT: Thermal cracking and catalytic (molybdenum naphthenate) hydrocracking processes in toluene solvent were carried out in a batch reactor for a typical Colombian heavy vacuum residue and its corresponding separated maltenes and asphaltenes fractions. The thermal cracking and catalytic hydrocracking tests were performed at 430 °C and 13.5 MPa for 25 min in the presence of nitrogen and hydrogen, respectively. Additionally, catalytic hydrocracking was also conducted after conditioning the vacuum residue at 380 °C, and 12.2 MPa of H_2 for 60 min with activated carbon. The cracking and catalytic hydrocracking performances of the vacuum residue and its components (maltenes and asphaltenes) were assessed by evaluating the effects on the yield and quality of the products (gas, toluene-insoluble solid, and liquid) utilizing SARA (saturates, aromatics, resins, and asphaltenes) composition and removal of sulfur and heavy (Ni, V) metals analyses. The vacuum residue showed asphaltene conversions of 53.1 and 43.1 wt % (excluding the yield of toluene-insoluble solids) under conditions of thermal cracking and catalytic hydrocracking, respectively. When the vacuum residue was pretreated with activated carbon and then catalytically hydrocracked, the asphaltenes conversion was higher (68.7 wt %, excluding the yield of toluene-insoluble solids) when compared to that during thermal cracking and catalytic hydrocracking in the absence of such pretreatment. Overall, the results showed that the hydrocracking of a vacuum residue in toluene with a molybdenum naphthenate catalyst is effective in forming liquid products that are lighter and with a lower concentration of sulfur and Ni and V heavy metals. These heteroatoms are removed in the toluene-insoluble solid products that concentrate recalcitrant sulfur and nickel complex (i.e., porphyrinic) aromatic compounds to a greater extent. The primary function of the thermally activated carbon pretreatment was to increase the yield of lighter liquid products as a likely result of the conversion of more reactive vanadium-containing complex structures into simpler components that remain in the liquid product and which otherwise would have been rejected in the toluene-insoluble solid fractions.

1. INTRODUCTION

Increasing worldwide fuel demand and rising petroleum prices have motivated an interest in the processing of heavy and extra-heavy crude oil. Additionally, it has been projected that vacuum residues (VRs) will increase between 35 and 50% with respect to processed crude.[1] Due to the decline of conventional crude, numerous studies have been reported for the use of vacuum residues toward gas oils and fuels. Vacuum residues are, however, more difficult to process, since they possess an atmospheric equivalent boiling point (AEBP) higher than 525 °C and contain significant amounts of asphaltenes and resins, which are considered the most polar and complex petroleum fractions.[2,3] These species are also characterized by a high degree of aromaticity and a lower proportion of paraffinic and naphthenic hydrocarbons. Reducing the complexity of these structures would contribute to the utilization and integration of converted VRs in conventional refining processes.

Vacuum residues also contain significant amounts of heteroatoms, such as sulfur (S), oxygen (O), and nitrogen (N), and heavy metals, such as nickel (Ni), vanadium (V), and iron (Fe), which are present in the range of a few parts per million (ppm) to more than 1200 ppm. Metals, such as K, Mg, Na, and Ca, are also present in the form of inorganic salts, such as chlorides and sulfates, while the heavier metals are distributed in higher proportions as metal porphyrins, particularly for vanadium(IV) and nickel(II).[4−7] These heteroatoms and heavy metals are mostly concentrated in the heavier fractions, such as resins and asphaltenes, which can cause serious problems in subsequent refining processes by promoting catalyst deactivation. Therefore, the effective removal of these species in the final products is a significant challenge for refiners worldwide. For this reason, it is important to investigate improved and novel processes to upgrade these crude oil fractions into high quality middle distillates.

Some of the technologies for vacuum residue upgrading include thermal cracking processes and catalytic hydrocracking,

Received: January 8, 2017
Revised: February 16, 2017
Published: February 22, 2017

DOI: 10.1021/acs.energyfuels.7b00078
Energy Fuels 2017, 31, 3868−3877

both of which play an important role in the conversion of low-quality unconventional hydrocarbons.[8,9] Thermal cracking is the process of choice among noncatalytic processes in the refining of vacuum residues. They include delayed coking processes, visbreaking, and flexicoking, among others. Hydrotreating and fluid catalytic cracking are, on the other hand, the most important catalytic processes. Processes in the presence of solid catalysts are, however, vulnerable to deactivation by the deposition of heavy metals. It is worth noting that the quality of the products from these processes will depend primarily on the processing technology, the operating conditions, the nature of the load, and the elements to be removed.[10,11]

In the treatment of vacuum residues, the removal of asphaltenes, complex resins, and heavy metals is essential to improve product quality in the later stages of refining. For this purpose, conventional methods, such as solvent deasphalting,[12−14] have been widely used to obtain high yields of light fractions. Unconventional methods for removal of contaminants in vacuum residues include microwave irradiation and membranes, which have been used for pretreating and removing heavy metals and heteroatoms from heavy crudes. For example, Wang et al.[15] applied microwave irradiation to reduce sulfur and nickel in a vacuum residue by approximately 56 and 82%, respectively. Shang et al.[16] also evaluated the microwave assisted demetallization with methanesulfonic acid, obtaining removal efficiencies of Ni and V of 83 and 85%, respectively. Ashtari et al.[17,18] also demonstrated the application of ceramic membrane monoliths at 75−190 °C for reducing asphaltenes, Ni, and V by 60−87, 42−67, and 19−29%. Similarly, polymeric membranes have also been used.[19]

In the hydroconversion of heavy oil and petroleum residues, carbon-based catalysts have received significant attention. For example, Piskorz et al.[20] performed heavy oil hydroconversion with activated carbon in the presence of dodecane as hydrogen donor, reaching liquid product yields of about 85 wt % and sulfur removal of 42 wt % at 405 °C and 13.7 MPa. Xu et al.[8] also evaluated the effect of an activated carbon supported NiMo catalyst in the hydrotreating of a vacuum residue in the presence of toluene at 380 °C, obtaining an asphaltene conversion efficiency of 68−79 wt % and S and N removal efficiencies of 23 and 31%, respectively. The use of solvents at supercritical conditions is particularly attractive, as they can act as hydrogen donors through a hydrogen-shuttling mechanism in the presence of activated carbon[8,21−23] and increase the solubility of asphaltenes and/or coke precursor species, improving their reactivity.

This work presents a systematic study of the effect of thermal cracking and catalytic hydrocracking on the quality of liquid products derived from a typical Colombian VR and its constituent fractions, maltenes and asphaltenes. For this purpose, a series of thermal cracking and catalytic hydrocracking investigations were performed with toluene as solvent and using a homogeneous molybdenum naphthenate catalyst. The latter process was performed with and without pretreatment with activated carbon. The vacuum residue and its isolated maltenes and asphaltenes were subject to elemental analysis (C, H, N, S, V, Ni) as well as ^{1}H and ^{13}C NMR to determine the aliphatic and aromatic contents. The toluene soluble and insoluble product fractions obtained from the various runs were characterized by SARA analysis[24−26] and X-ray fluorescence spectroscopy,[27] respectively. In this manner, the effects of adding activated carbon to preferentially concentrate asphaltenes and heavy metals and the resulting effects on product quality were discerned. This is the first report of a Colombian vacuum residue upgrading with combined activated carbon treatment and catalytic hydrocracking using a dispersed molybdenum catalyst. The results of this work are thus aimed at guiding future studies on the selection of solvents, pretreatment strategies, and cracking conditions that maximize the production of light hydrocarbon components from VRs.

2. EXPERIMENTAL SECTION

2.1. Materials. In this work, a model Colombian vacuum residue was used, which will be called VR, along with its corresponding isolated maltenes (MVR, containing saturates, aromatics, and resins), and asphaltenes (ASVR). The vacuum residue VR was obtained from a crude oil processed in a distillation unit of Ecopetrol S.A. − Colombian Petroleum Institute (ICP). The vacuum residue was selected for its high content of Ni (360 ppm) and V (95 ppm) metals and asphaltenes (29 wt %). The asphaltenes (ASVR) were precipitated with *n*-heptane from the VR in a volume ratio of 40:1 followed by reflux for 1 h. Then, asphaltenes were separated by filtration (Whatman filter paper #42). The soluble fraction was then rotovaporated to separate the *n*-heptane and the maltenes (MVR) fraction. The separation of asphaltenes and maltenes was carried out following the ASTM D6560 and ASTM D2007 standards. The reactions were carried out in the presence of toluene (98.9%, Sigma-Aldrich) with and without pretreatment with activated carbon (Darco G-60, Sigma-Aldrich). The analyses were carried out in the presence of different solvents, such as *n*-heptane (99%, Sigma-Aldrich), dichloromethane (99.5%, Fisher Scientific), and methanol (99.8%, Fisher Scientific). The following adsorbents were used: silica gel (28−200 mesh, Sigma-Aldrich, P/N 214396), alumina (150 mesh, Sigma-Aldrich, P/N 199443), and Florisil (30−60 mesh, Sigma-Aldrich, P/N 46384). The molybdenum naphthenate catalyst was synthesized using previously reported methodologies.[28−31] Briefly, the catalyst was prepared by reaction between naphthenic acid (Technical grade, Sigma-Aldrich, P/N 70340) and bis(acetylacetonate) dioxomolybdenum(VI) (Sigma-Aldrich, P/N 227749) mixed in a mass ratio of 3.74:1 and followed by reflux at 190−196 °C for 5 h.

2.2. Thermal cracking and catalytic hydrocracking reactivity. Reactivity testing by thermal cracking and catalytic hydrocracking was conducted in the presence of nitrogen and hydrogen, respectively. The tests were carried out in a Parr reactor with a capacity of 100 cm^3 equipped with mechanical stirring, temperature control, and a gas (e.g., H_2, N_2) delivery unit to maintain constant pressure throughout the reaction. Figure 1 shows a schematic representation of the reaction setup.

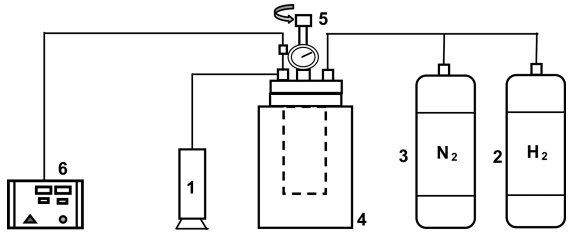

Figure 1. Schematics of the Parr reactor used during thermal cracking and catalytic hydrocracking: (1) high pressure syringe pump; (2) hydrogen gas cylinder; (3) nitrogen gas cylinder; (4) reactor and heater; (5) mechanical stirrer; (6) temperature control.

In a typical run, the homogeneous toluene-VR (30:70 wt/wt) load mixture was initially added to a high-pressure syringe pump (ISCO, LC-5000) reservoir (1, 2), which was preheated to 90 °C by means of a heating tape. After purging with nitrogen or hydrogen, 30 cm^3 of toluene was added to the reactor followed by pressurization to 5.6 MPa (at ambient temperature) for thermal cracking and catalytic hydrocracking tests. For catalytic hydrocracking, approximately 0.70 g

DOI: 10.1021/acs.energyfuels.7b00078
Energy Fuels 2017, 31, 3868−3877

of molybdenum naphthenate was dissolved in the toluene present in the reactor, which corresponded to ~1000 ppm of Mo catalyst based on the overall final volume of load + solvent ~45 cm^3. Subsequently, the reactor temperature was ramped up to 430 °C in two steps: (1) the reactor temperature was brought to 380 °C, after which 15 g of toluene-VR load was pumped to the reactor at a mass flow rate of 7.5 g/min and (2) once addition was complete, the temperature was set to 430 °C, and held for 22 min at a constant stirring speed of ~1200 rpm (the total time since the start of the addition of the toluene-VR load was ~25 min). This procedure was found to minimize the initial formation of toluene-insoluble materials as the toluene-VR load was added to the reactor. At the end of the reaction, the heating oven surrounding the reactor was lowered and the reactor cooled rapidly in a water bath.

For the activated carbon pretreatment of the vacuum residue, 30 cm^3 of toluene was added to the reactor together with 5 g of activated carbon (Darco G-60; S, V, Ni elemental analysis is shown in Table 2). Then, the reactor was pressurized with hydrogen (as previously reported)[8,21−23] to 5.6 MPa (at ambient temperature) and heated up to 380 °C. After reaching 380 °C, 15 g of toluene−VR mixture was pumped to the reactor. The reactor was maintained at a constant temperature of 380 °C for 60 min at a constant stirring speed of ~1200 rpm, after which the reactor was cooled following the procedure described above. Finally, the activated carbon treated vacuum residue was subjected to catalytic hydrocracking with molybdenum naphthenate as described before using 1000 ppm of Mo (based on the final volume of the load + solvent mixture), at 430 °C and at 13.5 MPa of hydrogen for 25 min. The reaction products were diluted with toluene and allowed to stand for 24 h to solubilize and separate the liquid products fraction from formed solids (toluene-insoluble fraction). Here, the toluene-insoluble fraction is constituted largely by coke and possible traces of organic material.[32] Vacuum filtration of the toluene-containing product solution (Whatman cellulose filter paper #42) was performed to remove the solid fraction. Finally, the solvent was separated from the liquid product in a rotary evaporator (Model R215, Buchi). The solid residues from the rotary evaporator were subjected to Soxhlet extraction with toluene for 48 h and dried at 70 °C for 12 h. The gas content was calculated as the mass difference of the weights of the reactor before and after release of the reaction gases.

2.3. Characterization. *2.3.1. SARA analysis.* The separation of asphaltenes from the vacuum residue and products obtained from reactivity tests was performed according to the ASTM D6560 standard. The separation of saturates, aromatics, and resins (SAR) fractions followed the ASTM D2007 standard.[33] Briefly, the separation of asphaltenes was performed by addition of *n*-heptane to the VR or its reaction products in a volume ratio of 40:1 followed by reflux for 1 h. After refluxing, asphaltenes were separated by filtration (Whatman filter paper #42). Heptane in the filtrate was recovered by rotovaporation, and the remaining maltene fraction was separated into its SAR components by elution with solvents of different polarity by open column chromatography, as illustrated in Figure 2. In these tests, we used two chromatographic columns stacked on top of each other (46 cm long × 1.25 cm inside diameter per column). Small amounts of glass wool (each 1 cm in height) were placed at the bottom of the columns (to retain the absorbents) and between different absorbents. The lower column (column #1) contained two adsorbents: silica gel (~20 cm height, bottom of column) and alumina (~20 cm height, top of column), whereas the upper column (column #2) contained the last adsorbent: Florisil (~20 cm height).

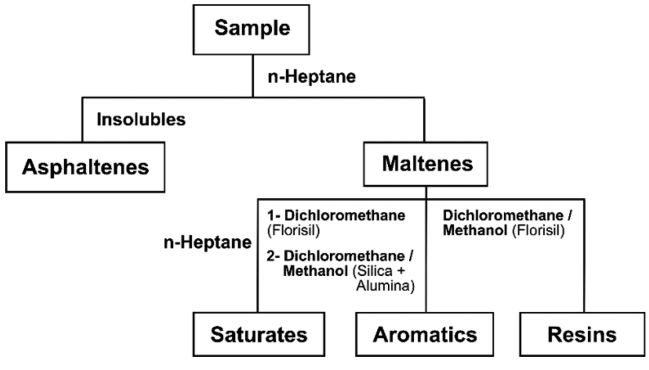

Figure 2. Schematic of SARA fractionation.

In the separation scheme shown in Figure 2, Florisil was used for the separation of aromatics because of its high affinity for aromatic compounds and substances with nitrogen and because of the facile desorption of the retained compounds by solvents such as dichloromethane, acetone, and methanol, among others.[34,35] The saturates fraction was eluted with 150 cm^3 of *n*-heptane (from both columns). Then the two columns were separated. The aromatics fraction was recovered by elution in each packed column separately in two steps. First, 10 cm^3 of dichloromethane and 10 cm^3 of a dichloromethane:-methanol solution (70:30 vol/vol) were used to recover the aromatic fraction absorbed on the column packed with Florisil (column #2). Then, a second aromatic fraction was recovered with 100 cm^3 of dichloromethane:methanol solution (70:30 vol/vol) from the column packed with alumina and silica gel (column #1). Finally, the resins fraction was eluted with 100 cm^3 dichloromethane:methanol solution (70:30 vol/vol) from the column packed with Florisil (column #2). The individual SAR (saturates, aromatics, and resins) fractions were obtained solvent- free by rotovaporation at 40 °C.

2.3.2. ^1H, ^{13}C NMR analysis. ^1H and ^{13}C NMR spectra were measured and analyzed on a Bruker AVIII spectrometer (9.4 T) at a resonance frequency of 400 Hz. All samples were dissolved in $CDCl_3$. For ^1H NMR analysis, the sample was doped with TMS (tetramethylsilane) at a concentration of approximately 4 wt % in $CDCl_3$. ^{13}C NMR spectra were acquired using 0.05 M $Cr(acac)_3$ (chromium(III) acetylacetonate) as a paramagnetic relaxation reagent at a dilution of 15 wt % in $CDCl_3$.

2.3.3. Elemental analysis (C, H, N). A CHNS/O Elemental Analyzer (2400 Series II, PerkinElmer) was used to quantify the amount of C, H, and N in the vacuum residue, maltenes, and asphaltenes. The samples are combusted in a pure oxygen environment, and the resultant combustion gases (CO_2, H_2O, NO_x, and SO_2) are measured with a thermal conductivity detector, from which the weight percents of C, H, N, S, and O are determined. The tests were performed using an acetanilide standard (C = 71.09, H = 6.71, N = 10.36, and O = 11.84 wt %).

2.3.4. Metal analysis by X-ray fluorescence (XRF) spectroscopy. Sulfur and heavy metals (Ni and V) contained in the vacuum residue, asphaltenes, and toluene-insoluble components obtained from reactivity tests were determined by X-ray fluorescence (XRF) spectrometry (Zetium, PANalytical).

2.3.5. Molecular parameters. There are many molecules present in the vacuum residue, and their structures vary according to their nature and SARA compositional distribution. Therefore, in this work, we studied the average molecular parameters of the vacuum residue and its respective isolated maltenes and asphaltenes to relate their relationship with the products obtained in the reactivity tests by thermal cracking and catalytic hydrocracking. In general, these parameters can be used to classify the possible groups or structural fragments present in hypothetical structures as determined from correlations available in the literature. The parameters were estimated from elemental analysis and normalized data areas acquired by ^1H and ^{13}C NMR spectroscopy. For the analysis of the samples we used the most commonly reported parameters such as f_a, n, % C_a, % C_{al}, CAr^{AA}, CAr^{AAA}, R_A, and φ (see Table 1 for definitions).[36−38] ^{13}C NMR and ^1H NMR spectra were integrated using the Mestre 3.0 program to obtain band areas necessary to calculate the average molecular parameters. Table 1 shows a summary of the structural assignments in ^1H and ^{13}C NMR which describe the general features of a petroleum fraction.

DOI: 10.1021/acs.energyfuels.7b00078
Energy Fuels 2017, 31, 3868−3877

Table 1. Structural Assignments in ^{1}H and ^{13}C NMR[a]

Chemical shift (ppm)	Structural assignment	Average molecular parameter
H_1 1.00−0.50	Hγ to aromatic ring/terminal CH_3	$H_\gamma = H_1.H/100$
H_2 1.85−1.00	Hβ to aromatic/in paraffinic CH and CH_2	$H_\beta = H_2.H/100$
H_3 4.50−1.85	Hα to aromatic ring	$H_\alpha = H_3.H/100$
H_4 9.30−6.30	Aromatic proton	$H_{ar} = C_{Ar-H} = H_4.H/100$
C_1 20.0−18.0	Substituted aromatic carbon	$C_{Ar-CH3} = C_1.C/100$
C_2 130.5−118	Protonated aromatic carbon + Pericondensed aromatic carbons	$C_{Ar-H+p} = C_2.C/100$
C_3 136.0−128.0	Catacondensed aromatic carbons	$C_{Ar}^{AA} = C_3.C/100$
C_4 137.0−132.0	Naphthenic carbon in aromatic carbon	$C_{Ar-N} = C_4.C/100$
C_5 160.0−133.0	Alkyl substituted aromatic carbon	
	Aromatic carbon	$C_{Ar} = (C_1+C_2+C_3+C_4+C_5)$
	Pericondensed aromatic carbons	$C_{Ar}^{AAA} = (C_{Ar-H+p} - C_{Ar-H})/100$
	Atomic ratio,	$C/H = (C/12)/H$
	Number of aromatic rings	$R_A = (C_{Ar}^{AA} + C_{Ar}^{AAA} + 2)/2$
	Aromaticity factor	$f_a = C_{Ar}/C$
	Average length of paraffinic chain	$n = (H\alpha+H\beta+H\gamma)/H\alpha)$

[a] C_{Ar}^{AA} = aromatic carbons shared by at most two rings; C_{Ar}^{AAA} = single bridgehead carbons attached to three rings; fa = ratio of aromatic/total carbon; C/H = ratio atomic; n = average length of paraffinic chain; φ = parameter that defines the size of the macrostructure; H = total hydrogen % H; C = total carbon %C.

3. RESULTS AND DISCUSSION

3.1. Thermal and Catalytic Hydrocracking. Table 2 shows the characterization of the vacuum residue (VR), its corresponding maltenes (MVR) and asphaltenes (ASVR), and the activated carbon.

To gain a better understanding of the reactivity of the vacuum residue (VR) and its corresponding isolated maltenes (MVR) and asphaltenes (ASVR), the effects of the chemical structure of the components on obtained products must be assessed. Therefore, to follow the formation of products from these feeds during thermal cracking and catalytic hydrocracking, we use average molecular parameters derived from ^{1}H and ^{13}C NMR characterization using procedures previously reported in the literature and summarized in Table 1.[37,39,40] These results from high-resolution NMR spectroscopy provide valuable information on the quantitative distribution of carbon and hydrogen among various chemical structures.

Table 2. Characterization of Vacuum Residue, Maltenes, Asphaltenes, and Activated Carbon[a]

Property	VR	MVR	ASVR	Activated Carbon (Darco G-60)
Saturates, wt %	13.4	18.8		
Aromatics, wt %	32.2	45.3		
Resins, wt %	25.5	35.9		
Asphaltenes, wt %	29.0		100	
S, wt %	1.7		2.7	0.14
V, ppm	360		950	ND
Ni, ppm	95		250	ND
C, wt %	87.2	86.0	86.9	
H, wt %	9.0	9.5	7.1	
N, wt %	0.47	0.33	1.2	
H/C	1.24	1.32	0.98	
Aromaticity factor, fa	0.52	0.33	0.79	
Average alkyl chain length, n	10.0	5.0	15.5	
Aromatic carbon, % C_a	51.8	32.7	78.9	
Aliphatic carbon, % C_{al}	48.2	67.3	21.1	
Catacondensed aromatic carbons, C_{Ar}^{AA}, % carbon content/ Total C	6.6	2.5	17.1	
Pericondensed aromatic carbons, C_{Ar}^{AAA}, % carbon content/ Total C	16.8	9.3	31.0	
Number of aromatic rings, RA	12.7	6.9	25.0	
Condensation index, φ	0.81	0.80	0.90	

[a] ND: not detected. The MVR and ASVR fractions were obtained by methods described in Section 2.1.

The results in Table 2 show that the H/C ratio obtained from elemental analysis is a parameter that allows an approximate knowledge of the aromatic character of the samples under study. For example, asphaltenes have lower aromatic character because, compared to maltenes, they are composed of a higher content of polycondensed aromatic rings, as evidenced by the low atomic ratio H/C, high condensation index, and high aromaticity factor. Asphaltenes also show a larger number of pericondensed (peripheral) and catacondensed aromatic carbons and lower content of alkyl substituents in the aromatic rings, in agreement with previous characterization results of model asphaltenes and maltenes showing similar trends in average molecular parameters.[26,39,41,42]

Figure 3 presents the yields of liquid, gas, and toluene-insoluble products obtained from thermal cracking and catalytic hydrocracking of VR and the corresponding maltenes (MVR) and asphaltenes (ASVR). The mass balance was obtained by gravimetry. The samples were evaluated at the same reaction conditions of 430 °C, 13.5 MPa of N_2 (thermal cracking) or H_2 (hydrocracking), and 25 min of total reaction time.

The results show that the yield of toluene insolubles increases in the following ascending order: maltenes < vacuum residue < asphaltenes for both thermal and catalytic hydrocracking. Moreover, the results also indicate a significantly lower formation of toluene insolubles and gaseous products in all cases during catalytic hydrocracking. Table 2 shows that asphaltenes have larger values of molecular parameters, such as percentage of aromatic carbon, number of aromatic rings, condensation index, and content of catacondensed and pericondensed aromatic carbons. This indicates that the asphaltenes fraction is more complex in its aromatic structure in comparison with that of maltenes, that is more recalcitrant,

DOI: 10.1021/acs.energyfuels.7b00078
Energy Fuels 2017, 31, 3868−3877

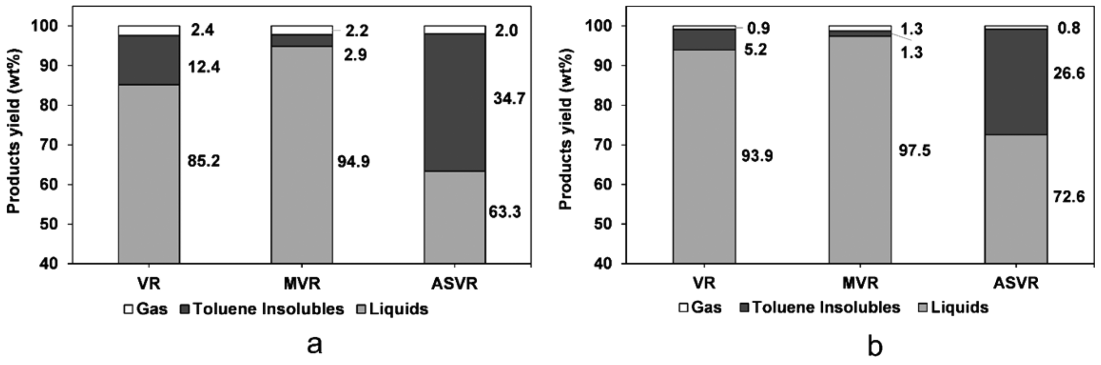

Figure 3. Distribution of product yields obtained from (a) thermal cracking (TC) and (b) catalytic hydrocracking (CH). MVR and ASVR were obtained from VR following the procedure described in Section 2.1.

and will tend to promote formation of the toluene-insoluble fraction likely from free radical condensation reactions.[26,43]

It is worth noting that the product distribution obtained from the VR treatment is dependent on the content of its constituting maltenes and asphaltenes. Therefore, the complexity of these components will play an important role in the reactivity and performance of individual maltenes (MVR), asphaltenes (ASVR), and ultimately the vacuum residue (VR). The results in Table 2 and Figure 3 suggest that aromatics, resins, and asphaltenes could have a significant effect as promoters or precursors in the formation of toluene-insoluble compounds. It is clear, for example, from the reactivity of maltenes (MVR) and asphaltenes (ASVR) fractions that asphaltenes are a major precursor to toluene-insoluble compounds. These results are consistent with the results reported by Guo et al.[44] and Alvarez et al.,[45] who reported that the content of toluene insolubles obtained by thermogravimetry in an atmospheric residue varies according to their SARA composition. For example, they reported a yield of toluene insolubles of 16.3% for the atmospheric residue, 3.8% for aromatics, 4.6% for resins, and 43.1% for asphaltenes. Additionally, it can be seen from Figure 3 that catalytic hydrocracking results in a measurable reduction in the yield of gases and toluene-insoluble products, for example, for the MVR from 2.2 to 1.3 wt % and 2.9 to 1.3 wt %, respectively. We hypothesize that, under reaction conditions, molybdenum naphthenate forms MoS_2 nanoparticles which can catalyze hydrogenation, ring opening, and hydrogenolysis reactions of naphthenic rings to form lighter species while preventing the polycondensation of aromatic structures. Because of the relatively small molybdenum amounts (in the parts per million level) and the high complexity of the reaction mixture, its characterization by diffraction and spectroscopic techniques is challenging. Nevertheless, the likely presence of dispersed MoS_2 would be consistent with favorable activity for reactions that utilize hydrogen, as MoS_2 is a well-known catalyst for hydrogenation, hydrodenitrogenation, and hydrodesulfurization reactions.[11,46−50] This is in agreement, for example, with similar hydrocracking liquid yields and coke suppression for a Canadian bitumen in the presence of either exfoliated MoS_2 nanoparticles or molybdenum naphthenate as a precursor for in situ formation of MoS_2.[50] Other dispersed MoS_2 precursors, such as Mo micelle emulsions, have been used for hydroconversion of vacuum residue.[51] Since hydrocarbon radical species (likely coke precursors) are expected to form at the thermal reaction conditions of this work, it is reasonable to assume that the formed MoS_2 nanoparticles, which are dispersed in the reaction medium, not only would catalyze hydrogenation and hydrogenolysis reactions but also stabilize radical species which otherwise would form coke.

Figure 4 shows the effect of catalyst presence on the inhibition or reduction in the formation of toluene insolubles

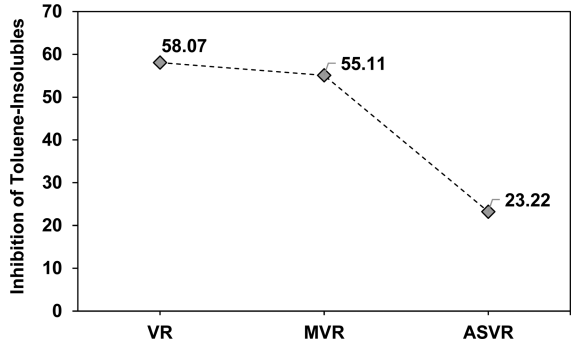

Figure 4. Effect of molybdenum catalyst in inhibiting the formation of toluene insolubles in the vacuum residue (VR) and its corresponding maltenes (MVR) and asphaltenes (ASVR) fractions.

from thermal and catalytic cracking of the VR and its corresponding maltenes (MVR) and asphaltenes (ASVR) (obtained from the VR by the procedure described in Section 2.1). The percent inhibition of toluene insolubles is defined by

$$\mathrm{TI_{Inh}},\ \mathrm{wt\ \%} = \frac{(\mathrm{TI_{TC}} - \mathrm{TI_{CH}}) \times 100}{\mathrm{TI_{TC}}} \quad (1)$$

where

TI_{Inh}, wt % = percent of inhibition (or reduction) of toluene insolubles

TI_{TC} = percent of toluene insolubles after thermal cracking

TI_{CH} = percent of toluene insolubles after catalytic hydrocracking

The effectiveness of the molybdenum catalyst in reducing the formation of toluene-insoluble products shows a more marked inhibition on MVR than on ASVR, indicating that less toluene insolubles were formed from maltenes than from asphaltenes. The results suggest that the catalyst efficiency is associated with the chemical nature of the samples under study. Figure 4 also shows a percent inhibition of toluene insolubles on VR higher than that of MVR and ASVR, suggesting a synergism when both maltenes and asphaltenes are hydrocracked together. This synergism is likely due to increased asphaltenes solubility in the products from MVR conversion and/or decreased asphaltenes condensation reaction probability toward polycondensed

DOI: 10.1021/acs.energyfuels.7b00078
Energy Fuels 2017, 31, 3868−3877

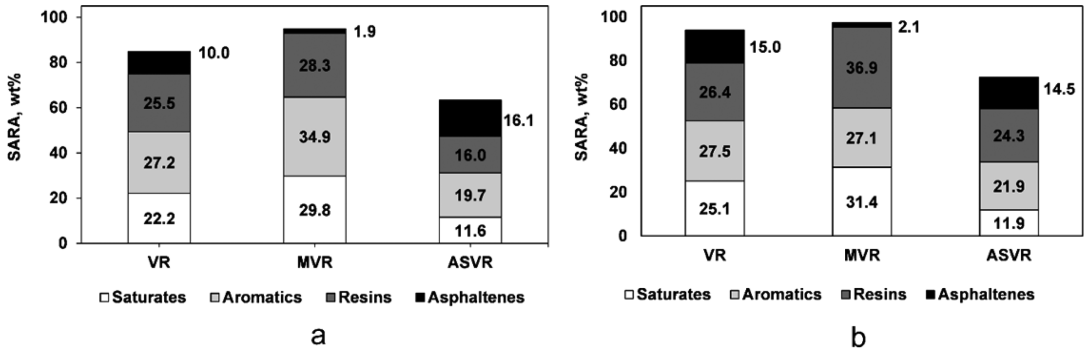

Figure 5. Distribution of yields of SARA components in liquid product fractions obtained from (a) thermal cracking and (b) catalytic hydrocracking.

aromatic structures, resulting ultimately in reduced coke formation.[52] Figure 5 shows the results of SARA analysis for the liquid product fractions obtained from the reactivity tests in Figure 3. The results shown in Figure 5 were obtained from the multiplication of the relative SARA fractions (results not shown) and the product yield given in Figure 3. They further support our hypothesis that the chemical nature of the feedstock (vacuum residue or its corresponding maltenes and asphaltenes) has a significant effect on the variation in chemical composition of products from the thermally or catalytically cracked samples.

The liquids obtained from the thermal cracking process of maltenes (MVR, Figure 5) show that formation of saturates increases, while that of aromatics and resins decreases with respect to the original maltenes fraction shown in Table 2. Moreover, the liquids obtained from the catalytic hydrocracking of maltenes show higher yields of saturates and resins, and a decreased yield of aromatics in comparison with the yields obtained by thermal cracking. The small conversion of maltenes to asphaltenes in both the thermal and catalytic cracking reactions can be attributed to a small contribution from the fusion of aromatic rings with alkyl chains by a free radical mechanism.[26,53,54] From Figure 3, it is clear that the presence of small amounts of catalytic Mo complexes favors the production of liquid products from heavy asphaltenes under hydrocracking conditions. In addition to these results, Figure 5 provides more insights into this catalytic conversion, indicating that a higher content of lighter SAR compounds (maltenes) is obtained from the asphaltenes fraction (ASVR), as more hydrogen is efficiently utilized at reaction conditions favorable for hydrogenation, ring opening, and hydrogenolysis of aromatic structures.

Asphaltenes conversion toward gas, toluene insoluble fraction, and liquids in thermal cracking and catalytic hydrocracking was 83.9 and 85.5 wt %, respectively. Excluding the yield of toluene insolubles, the conversion of asphaltenes toward gas and liquids in thermal cracking and catalytic hydrocracking processes was 49.3 and 58.9 wt %, respectively. The results show that the presence of a catalyst increases the yield of liquid and gas products by approximately 20 wt %. Additionally, the catalyst reduces the formation of gases and toluene insoluble products (Figure 3). The results in Figure 5 also show that, in thermal cracking and catalytic hydrocracking processes, the asphaltenes can be converted to maltenes by further hydrocracking reactions and to toluene insolubles by condensation reactions, likely through a free radical mechanism. These results are in agreement with those previously reported by Ortiz et al.[25] and Du et al.[55]

The XRF technique has been used in this work to determine the content of sulfur, vanadium, and nickel in the untreated (Table 2), thermally cracked, and catalytically hydrocracked (Table 3) fractions (VR, MVR, ASVR). The removal of sulfur and heavy metals during reaction conditions is likely to occur after multiple condensation reactions and solid precipitation (of toluene-insoluble compounds). Based on the results of characterization of the vacuum residue and its asphaltene fraction (Table 1), it is estimated that approximately 45.7, 75.5, and 75.7% of the sulfur, nickel, and vanadium contents are asphaltenic in nature, whereas the rest of the heteroatom species are nonasphaltenic. Table 3 shows the results of sulfur and heavy metal content in toluene insolubles obtained from thermal cracking and catalytic hydrocracking of the vacuum residue (VR) and its corresponding maltenes (MVR) and asphaltenes (ASVR).

Table 3. Sulphur and Heavy Metal (V and Ni) Content in the Toluene-Insoluble Fraction

	Thermal cracking			Catalytic hydrocracking		
Species	VR	MVR	ASVR	VR	MVR	ASVR
S, wt %	2.9	1.5	2.9	2.9	1.3	1.9
V, ppm	1210	270	1350	1710	145	1020
Ni, ppm	660	680	740	1070	865	650

If we define the removal efficiency (R_i) of sulfur and heavy metals in the vacuum residue and asphaltenes as the ratio of the amount of these species in the toluene insolubles fraction to that in the original vacuum residue, then:

$$R_i = \frac{(Y_i W_{i,TI})(X_j F_{feed})}{(W_{i,feed})(F_{feed})} \quad (2)$$

where Y_i is the yield of toluene insoluble species i (e.g., S, V, Ni) from VR or ASVR (Figure 3) in wt %, X_j is equal to 1 for VR or the weight fraction of asphaltenes in the VR for ASVR (Table 2), $W_{i,TI}$ and $W_{i,feed}$ are the weight fractions (or ppm) of species i in the toluene insolubles (Table 3) and feed stream (Table 2), respectively, and F_{feed} is the weight of the feedstock.

Figure 6 presents the results of the removal efficiency of S, V, and Ni in toluene insolubles obtained from the thermal and catalytic hydrocracking processes. The results show that the removal efficiency increases in the following order: S < V < Ni, and it appears more significant when the samples are subjected to thermal cracking conditions and in the absence of a catalyst. These differences in removal efficiency appear to be related to the carbon rejection and high conversions toward toluene insolubles during thermal cracking and in the absence of a

DOI: 10.1021/acs.energyfuels.7b00078
Energy Fuels 2017, 31, 3868−3877

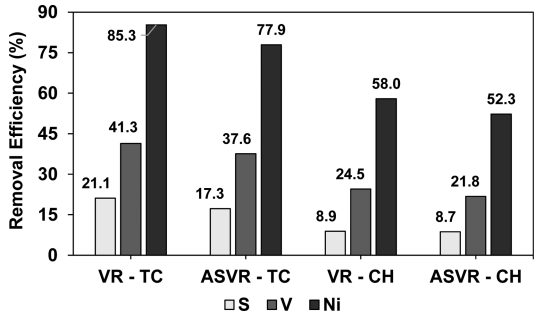

Figure 6. Removal efficiency of S, V, and Ni from VR and ASVR fractions by thermal (TC) and catalytic hydrocracking (CH).

catalyst. All these results cumulatively suggest that, during the cracking and hydrocracking of vacuum residues, asphaltenes are a major precursor of toluene insoluble products which act as a sink for the efficient removal of heavy metals and sulfur components.

To gain insights into the reactivity of heavy metal containing compounds, the selectivity of the removal of heavy metals such as Ni and V is defined as the ratio of the efficiency of removal of Ni and V:

$$\text{Selectivity} = \frac{R_{\text{Ni}}}{R_{\text{V}}} \tag{3}$$

A high value of this selectivity indicates that Ni participates preferentially in carbon rejection reactions. Figure 7, for

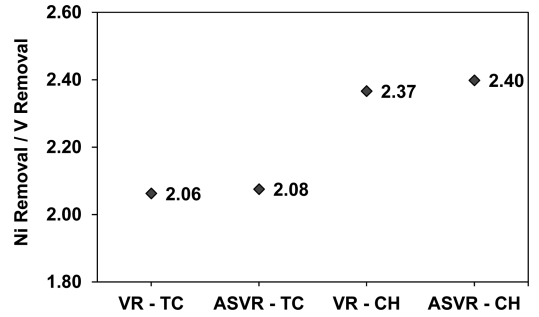

Figure 7. Selectivity of metal removal of Ni/V in VR and ASVR as a function of treatment by thermal cracking (TC) and catalytic hydrocracking (CH).

example, shows that the catalytic hydrocracking process has a more significant effect on this selectivity for the removal of Ni. These results strongly suggest that Ni is likely present as nickel porphyrinic compounds in heavily polycondensed aromatic structures in asphaltenes and maltenes of the vacuum residue, which appear to be stable toward hydrogenation, hydrogenolysis, and ring opening, but not to condensation reactions to form toluene-insoluble compounds.[16]

3.2. Effect of activated carbon pretreatment on catalytic hydrocracking. In the past, activated carbon has been investigated for cracking and removal of heavy metals and sulfur in petroleum products such as vacuum residues and bio-oil, among others.[8,21−23,56] Although the role of activated carbon is not well understood, it has been hypothesized that it can facilitate the transfer of hydrogen from reacting species including toluene solvent and the vacuum residue via hydrogen free radicals.[8,21−23] In this work, we carried out an activated carbon pretreatment of the vacuum residue VR at 380 °C to further investigate its effect on the yield and quality of the products obtained in the subsequent catalytic hydrocracking process at 430 °C. When the vacuum residue was subjected to a pretreatment at 380 °C with an activated carbon (VR-P380), the obtained yields of gases, toluene-insolubles, and liquids products were 0.84, 2.2, and 97.0 wt %, respectively (Figure 8).

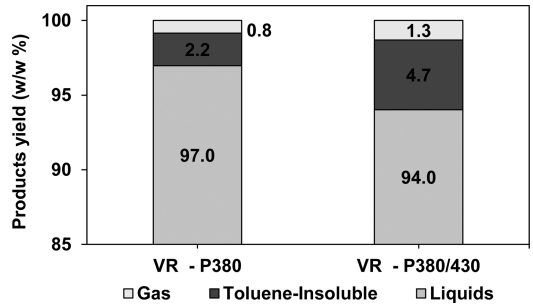

Figure 8. Distribution of product yields obtained from pretreatment with activated carbon at 380 °C (VR-P380) and subsequent catalytic hydrocracking at 430 °C (VR-P380/430).

After this pretreatment at 380 °C, the catalytic hydrocracking of the liquid fraction at 430 °C resulted in product yields similar to those of the untreated VR (Figure 3b, VR), that is, gas, toluene insoluble, and liquid yields of 0.9, 5.2, and 93.9 wt %, respectively.

To explore the possible effect of the activated carbon pretreatment on the resulting chemical structures of the liquid components, further SARA analyses were carried out for the VR after the carbon pretreatment (VP-P380) and after subsequent catalytic hydrocracking (VR-P380/430). The results are summarized in Figure 9, determined in a manner

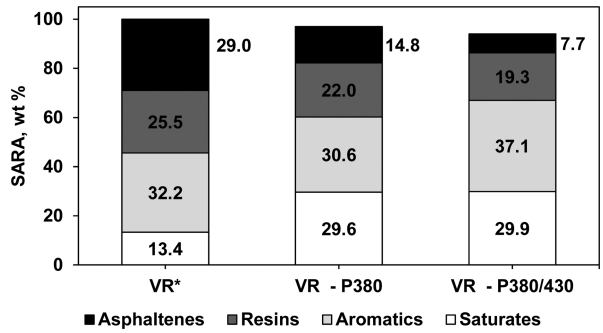

Figure 9. SARA analysis of original vacuum residue (VR*), its liquid products after pretreatment with activated carbon (VR-P380) and after subsequent catalytic hydrocracking (VR-P380/430).

similar to that outlined in Figure 5 (the product of the relative SARA fractions and the yield of liquid products in Figure 8). The pretreatment of the VR at 380 °C with activated carbon produces a low yield of toluene insolubles (2.2 wt %) and a reduction in the yields of asphaltenes, resins, and aromatics of about 50, 15, and 5%, respectively. This indicates that lower temperatures (as done in the activated carbon pretreatment) minimize the formation of toluene-insoluble solids (e.g., coke), whereas at higher temperatures (as done during catalytic hydrocracking) its formation increases. Despite this, asphaltenes conversion is lower at low temperature, so there is a trade-off to maximize, for example, lighter liquid (maltene) products content by increasing asphaltenes conversion (at

DOI: 10.1021/acs.energyfuels.7b00078
Energy Fuels 2017, 31, 3868−3877

higher temperatures) while minimizing coke formation (at lower temperatures). The results of Figure 9 clearly show that the activated carbon pretreatment of the vacuum residue does indeed result in a higher content of lighter saturates, aromatics, and resins (maltenes) of 86.3 wt % in comparison with 79.0 wt % for the unpretreated VR (Figure 5b) after catalytic hydrocraking. A similar behavior has been observed by other authors.[16,25]

The liquid product obtained from the catalytic hydrocracking at 430 °C of the pretreated vacuum residue at 380 °C (VR-P380/430) mainly consists of saturates and aromatics (Figure 9) which constitute the maltenes fraction. This maltenes fraction is expected to contain a higher aliphatic carbon fraction and shorter average aliphatic chain length (Table 2). When comparing the SARA analysis results for the catalytic hydrocracking of the VR that was not treated (Figure 3b) and pretreated at 380 °C (Figure 9), it can be noted that the activated carbon pretreatment favors the conversion of resins and asphaltenes in the original VR toward lighter saturates and aromatic compounds. This suggests the participation of complex aromatic species (retained in the activated carbon or converted to less complex liquid fractions during pretreatment) as precursors in condensation reactions toward toluene-insoluble compounds. As seen from Figures 5 and 9, asphaltenes are the main precursors in the formation of toluene-insoluble compounds; however, they can also be converted efficiently to maltenes in the presence of a homogeneous molybdenum catalyst[43,57] and when pretreated with activated carbon.

We have also performed sulfur and heavy Ni and V metals content analysis on the toluene-insoluble compounds derived from the pretreated VR-P380 and subsequently catalytically hydrocracked VR-P380/430 samples (Figure 6), and the results are presented in Table 4. The combination of lower

Table 4. Sulfur and Vanadium and Nickel Heavy Metals Content in Toluene-Insoluble Products Derived from Thermal-Activated Carbon Treatment of Vacuum Residue and Its Subsequent Catalytic Hydrocracking

	Catalytic hydrocracking		
Species	VR-P380	VR-P380/430	VR (fromTable2)
S, wt %	1.3	2.9	2.9
V, ppm	480	745	1710
Ni, ppm	345	1090	1070

temperature pretreatment with an activated carbon resulted in a measurable amount of toluene insolubles (2.2 wt %) which likely retained some sulfur and vanadium and nickel heavy metals at 1.3 wt % and 480 and 345 ppm, respectively. To better visualize the removal of these species from the VR, Figure 10 shows the species removal efficiency (defined by eq 3) when the vacuum residue is subjected to pretreatment at 380 °C with activated carbon (VR-P380) and when catalytically hydrocracked at 430 °C with (VR-P380/430) or without (VR-CH) such pretreatment.

Comparison of the removal efficiency between the untreated (VR-CH in Figure 6) and the activated carbon pretreated VR (VR-P380/430 in Figure 10) reveals little effect of this pretreatment in the removal of sulfur and nickel. Removal of vanadium, on the other hand, was significantly (55%) lower. This suggests that pretreatment with activated carbon favors preferentially the conversion of reactive vanadium-containing

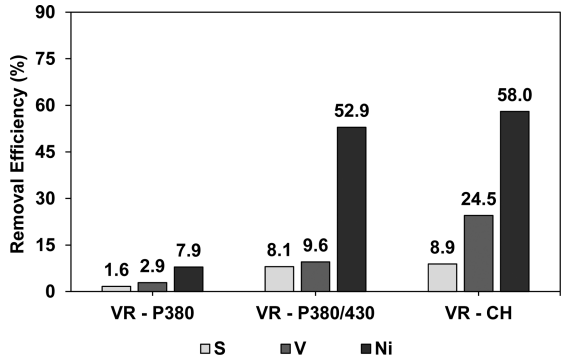

Figure 10. Removal efficiencies of VR pretreatment at 380 °C (1) with activated carbon (VR-P380) or (2 and 3) with catalytic hydrocracking at 430 °C (2) with (VR-P380/430) or (3) without (VR-CH) such pretreatment.

complex aromatic molecules into simpler ones that are likely retained in the liquid product. Sulfur and nickel complexes are present in more recalcitrant aromatic species which are mainly rejected in the toluene-insoluble compound as a result of condensation reactions at higher temperature treatments.

One aspect that is not fully understood in the present study is the role of the toluene solvent. Some authors have hypothesized that toluene itself can also act as a hydrogen-donating agent through a hydrogen-shuttling mechanism.[8,58−60] Proving that such a mechanism exists at our reaction conditions, however, will require additional reactivity studies, advanced characterization techniques, and/or the use of isotopically labeled probes which are beyond the scope of the present work. An alternative hypothesis is that toluene increases hydrogen solubility at reaction conditions of high temperature and pressures. Preliminary thermodynamic calculations at 380 °C and 13.5 MPa suggest that at our reaction conditions a significant fraction of toluene is in the supercritical state (toluene critical point = 318 °C and 4.1 MPa).[8,61] At this state, it is known that supercritical fluids can increase the solubility of gases such as hydrogen in the reaction medium, increase its local concentration,[8,20,62,63] and ultimately favor hydrogen-based reactions such as those required in the conversion of asphaltenes to maltenes. Further systematic experiments with different solvents are needed to study the effect of the solvent nature and their effect in the solubility of hydrogen, the vacuum residue, and its components, and ultimately their effect in their conversion toward lighter hydrocarbon fractions.

4. CONCLUSIONS

In this work, we found that the reactivity behavior of isolated maltenes (saturates, aromatics, and resins) and asphaltenes toward cracking and hydrocracking reactions was very different and offered insights into the reactivity of a more complex typical Colombian vacuum residue. Formation of liquid products from the vacuum residue was significantly higher at catalytic hydrocracking than at thermal cracking conditions. This is the result of the increased reactivity of the corresponding maltenes and asphaltenes fractions toward lighter compounds during hydrocracking and in the presence of a dispersed molybdenum naphthenate catalyst. For example, a much higher increase in the saturates products of a maltene fraction was observed when it was treated with the molybdenum catalyst at hydrocracking (67%) compared to under thermal cracking (58%) conditions, as a likely result of

DOI: 10.1021/acs.energyfuels.7b00078
Energy Fuels 2017, 31, 3868−3877

the promotion of hydrogenation, hydrogenolysis, and ring opening reactions likely by MoS_2 formed in situ.

During the thermal and catalytic hydrocracking of the vacuum residue and its corresponding maltenes and asphaltenes fractions, sulfur and nickel and vanadium metals were rejected in the toluene-insoluble products (e.g., coke). This removal was more effective during the thermal treatment, but the catalytic treatment provided an increased Ni/V removal ratio as a result of a higher reactivity of V-containing complex aromatic species, which in the presence of hydrogen are more likely to undergo hydrogenation, hydrogenolysis, and ring opening reactions and remain in the liquid product.

An activated carbon pretreatment of the vacuum residue and its subsequent catalytic hydrocracking resulted in similar gas, toluene insolubles, and liquid yields to those obtained in the absence of such pretreatment. However, the activated carbon pretreatment improved the content of maltenes in the hydrocracked vacuum residue, possibly as a result of the conversion of reactive V-containing hydrocarbon complexes during the pretreatment step toward lighter compounds which distribute in the liquid product. Overall, the catalytic hydrocracking after activated carbon pretreatment of the vacuum residue also resulted in asphaltenes conversion (excluding the yield of toluene-insoluble solids) much higher (68.7%) than that in the pretreatment (46.8%) or catalytic hydrocracking (43.1%) alone. Overall, the results of this work show that model studies with vacuum residue asphaltene and maltene fractions can provide unique insights into the reactivity of these complex components toward the production of lighter hydrocarbons. The observed beneficial effect of activated carbon pretreatment of the vacuum residue for the catalytic hydrocracking in toluene solvent could serve as a basis for further studies of conversion of heavy vacuum residues to lighter hydrocarbon components in controlled solvent and catalytic environments.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: yovani_96@hotmail.com.
*E-mail: rvc1948@ku.edu.
*E-mail: bsubramaniam@ku.edu.
*E-mail: jjbravo@ku.edu.

ORCID

Bala Subramaniam: 0000-0001-5361-1954
Juan J. Bravo-Suárez: 0000-0002-6484-374X

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial support provided by ECOPETROL S.A-Colombian Petroleum Institute (ICP), Center for Environmentally Beneficial Catalysis (CEBC) at the University of Kansas (CEBC seed funds), the University of Kansas (J.J.B.-S. startup funds), the School of Chemical Engineering at the Industrial University of Santander (UIS), and Colciencias.

REFERENCES

(1) Stratiev, D.; Dinkov, R.; Petkov, K.; Stanulov, K. *Pet. Coal* **2010**, *52*, 35−43.
(2) Pasquini, C.; Bueno, A. F. *Fuel* **2007**, *86*, 1927−1934.
(3) Li, S.; Zhang, Q.; Yao; Sun, X.; Fan, Q.; Chen, J. *Energy Fuels* **2007**, *21*, 1145−1150.
(4) Boduszynski, M. M. *Prepr. - Am. Chem. Soc., Div. Pet. Chem. - Meet. 224* **2002**, *47*, 329−331.
(5) Behrenbruch, P.; Dedigama, T. *J. Pet. Sci. Eng.* **2007**, *57*, 166−180.
(6) Yin, C.-X.; Stryker, J. M.; Gray, M. R. *Energy Fuels* **2009**, *23*, 2600−2605.
(7) Stoyanov, S. R.; Yin, C.-X.; Gray, M. R.; Stryker, J. M.; Gusarov, S.; Kovalenko, A. *Can. J. Chem.* **2013**, *91*, 872−878.
(8) Xu, C.; Hamilton, S.; Ghosh, M. *Fuel* **2009**, *88*, 2097−2105.
(9) Castañeda, L. C.; Muñoz, J. A. D.; Ancheyta, J. *Fuel* **2012**, *100*, 110−127.
(10) Rana, M. S.; Sámano, V.; Ancheyta, J.; Diaz, J. A. I. *Fuel* **2007**, *86*, 1216−1231.
(11) Topsøe, H.; Clausen, B. S.; Massoth, F. E. Hydrotreating Catalysis. In *Catalysis: Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 1996; pp 1−269.
(12) Fuhr, B. J.; Hawrelechko, C.; Holloway, L. R.; Huang, H. *Energy Fuels* **2005**, *19*, 1327−1329.
(13) Zhao, S.; Wang, R.; Lin, S. *Pet. Sci. Technol.* **2006**, *24*, 285−295.
(14) Long, J.; Shen, B.; Ling, H.; Zhao, J.; Lu, J. *Ind. Eng. Chem. Res.* **2011**, *50*, 11259−11269.
(15) Wang, L.; Peng, Q.; Li, S.; Du, L.; Cai, H. *J. Ind. Eng. Chem.* **2013**, *19*, 655−658.
(16) Shang, H.; Liu, Y.; Shi, J.-C.; Shi, Q.; Zhang, W.-H. *Fuel Process. Technol.* **2016**, *142*, 250−257.
(17) Ashtari, M.; Bayat, M.; Sattarin, M. *Energy Fuels* **2011**, *25*, 300−306.
(18) Ashtari, M.; Ashrafizadeh, S. N.; Bayat, M. *J. Pet. Sci. Eng.* **2012**, *82*−*83*, 44−49.
(19) Ching, M. J. T. M.; Pomerantz, A. E.; Andrews, A. B.; Dryden, P.; Schroeder, R.; Mullins, O. C.; Harrison, C. *Energy Fuels* **2010**, *24*, 5028−5037.
(20) Piskorz, J.; Radlein, D. S. A. G.; Majerski, P.; Scott, D. S. *Hydrotreating of heavy hydrocarbon oils in supercritical fluids*. U.S. Patent 5,496,464, March 5, 1996.
(21) Scott, D. S.; Radlein, D.; Piskorz, J.; Majerski, P.; deBruijn, T. J. W. *Fuel* **2001**, *80*, 1087−1099.
(22) Farcasiu, M.; Smith, C. *Energy Fuels* **1991**, *5*, 83−87.
(23) Farcasiu, M.; Smith, C. M.; Ladner, E. P. *Prepr. - Am. Chem. Soc., Div. Fuel Chem. - Meet. 202* **1991**, 1869−1877.
(24) Ovalles, C.; Rogel, E.; Lopez, J.; Pradhan, A.; Moir, M. *Energy Fuels* **2013**, *27*, 6552−6559.
(25) Ortiz-Moreno, H.; Ramírez, J.; Sanchez-Minero, F.; Cuevas, R.; Ancheyta, J. *Fuel* **2014**, *130*, 263−272.
(26) Hauser, A.; AlHumaidan, F.; Al-Rabiah, H.; Halabi, M. A. *Energy Fuels* **2014**, *28*, 4321−4332.
(27) Christensen, L. H.; Agerbo, A. *Anal. Chem.* **1981**, *53*, 1788−1792.
(28) Larson, M. L. *Method for making molybdenum naphthenate product*. U.S. Patent 3,598,847, August 10, 1971.
(29) Wallington, J. K. *Process for the preparation of certain molybdenum and vanadium salts*. U.S. Patent 3,362,972, January 9, 1968.
(30) Cavitt, S. B. *Process for hydrocarbon soluble metal salts*. U.S. Patent 3,595,891, July 17, 1971.
(31) Boeva, R. S.; Kotov, S. V.; Jordanov, N. *React. Kinet. Catal. Lett.* **1984**, *24*, 239−242.
(32) Wang, S.; Chung, K.; Masliyah, J. H.; Gray, M. R. *Fuel* **1998**, *77*, 1647−1653.
(33) Leon, A. Y.; Parra, M. J. *CT&F - Cienc. Tecnol. Futuro* **2010**, *4*, 101−112.
(34) Dinneen, G. U.; Smith, J. R.; Van Meter, R. A.; Allbright, C. S.; Anthoney, W. R. *Anal. Chem.* **1955**, *27*, 185−190.
(35) Pena, M. T.; Casais, M. C.; Mejuto, M. C.; Cela, R. *Anal. Chim. Acta* **2008**, *626*, 155−165.
(36) Behera, B.; Ray, S. S.; Singh, I. D. *Fuel* **2008**, *87*, 2322−2333.
(37) Poveda, J. C.; Molina, D. R. *J. Pet. Sci. Eng.* **2012**, *84*−*85*, 1−7.

DOI: 10.1021/acs.energyfuels.7b00078
Energy Fuels 2017, 31, 3868−3877

(38) Stratiev, D.; Shishkova, I.; Tsaneva, T.; Mitkova, M.; Yordanov, D. *Fuel* **2016**, *170*, 115−129.
(39) Carauta, A. N. M.; Seidl, P. R.; Chrisman, E. C. A. N.; Correia, J. C. G.; Menechini, P. d. O.; Silva, D. M.; Leal, K. Z.; de Menezes, S. M. C.; de Souza, W. F.; Teixeira, M. A. G. *Energy Fuels* **2005**, *19*, 1245−1251.
(40) Parlov Vuković, J.; Novak, P.; Plavec, J.; Friedrich, M.; Marinić Pajc, L.; Hrenar, T. *Croat. Chem. Acta* **2015**, *88*, 89−95.
(41) Magendie, G.; Guichard, B.; Espinat, D. *Catal. Today* **2015**, *258* (Part 2), 304−318.
(42) Redelius, P.; Soenen, H. *Fuel* **2015**, *140*, 34−43.
(43) Wang, J.; Anthony, E. J. *Chem. Eng. Sci.* **2003**, *58*, 157−162.
(44) Guo, A.; Zhang, X.; Wang, Z. *Fuel Process. Technol.* **2008**, *89*, 643−650.
(45) Alvarez, E.; Marroquín, G.; Trejo, F.; Centeno, G.; Ancheyta, J.; Díaz, J. A. I. *Fuel* **2011**, *90*, 3602−3607.
(46) Kim, H.; Curtis, C. W. *Energy Fuels* **1990**, *4*, 206−214.
(47) Tye, C. T.; Smith, K. J. *Top. Catal.* **2006**, *37*, 129−135.
(48) Nguyen, T. S.; Tayakout-Fayolle, M.; Lacroix, M.; Gotteland, D.; Aouine, M.; Bacaud, R.; Afanasiev, P.; Geantet, C. *Fuel* **2015**, *160*, 50−56.
(49) Nguyen, M. T.; Nguyen, N. T.; Cho, J.; Park, C.; Park, S.; Jung, J.; Lee, C. W. *J. Ind. Eng. Chem.* **2016**, *43*, 1−12.
(50) Tye, C. T.; Smith, K. J. *Catal. Lett.* **2004**, *95*, 203−209.
(51) Rezaei, H.; Liu, X.; Ardakani, S. J.; Smith, K. J.; Bricker, M. *Catal. Today* **2010**, *150*, 244−254.
(52) Wiehe, I. A. *Ind. Eng. Chem. Res.* **1993**, *32*, 2447−2454.
(53) Jia, N.; Moore, R. G.; Mehta, S. A.; Ursenbach, M. G. *Fuel* **2009**, *88*, 1376−1382.
(54) Singh, J.; Kumar, S.; Garg, M. O. *Fuel Process. Technol.* **2012**, *94*, 131−144.
(55) Du, H.; Li, M.; Liu, D.; Ren, Y.; Duan, Y. *Appl. Petrochem. Res.* **2015**, *5*, 89−98.
(56) Duan, P.; Zhang, C.; Wang, F.; Fu, J.; Lü, X.; Xu, Y.; Shi, X. *Catal. Today* **2016**, *274*, 73−81.
(57) Liu, C.; Zhu, C.; Jin, L.; Shen, R.; Liang, W. *Fuel Process. Technol.* **1999**, *59*, 51−67.
(58) Ishihara, A.; Morita, S.; Kabe, T. *Fuel* **1995**, *74*, 63−69.
(59) Oviawe, A. P.; Nicole, D.; Gerardin, R. *Fuel* **1995**, *74*, 259−266.
(60) Wei, X.; Ogata, E.; Zong, Z.; Zhou, S.; Qin, Z.; Liu, J.; Shen, K.; Li, H. *Fuel Process. Technol.* **2000**, *62*, 103−107.
(61) Abourriche, A.; Oumam, M.; Hannache, H.; Adil, A.; Pailler, R.; Naslain, R.; Birot, M.; Pillot, J. P. *J. Supercrit. Fluids* **2009**, *51*, 24−28.
(62) Viet, T. T.; Lee, J. H.; Ma, F.; Kim, G. R.; Ahn, I. S.; Lee, C. H. *Fuel* **2013**, *103*, 553−561.
(63) Viet, T. T.; Lee, J.-H.; Ryu, J. W.; Ahn, I.-S.; Lee, C.-H. *Fuel* **2012**, *94*, 556−562.

DOI: 10.1021/acs.energyfuels.7b00078
Energy Fuels 2017, 31, 3868−3877