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# Investigation of the Effect of Severity Mode of Operation in the H-Oil Vacuum Residue Hydrocracking on Sediment Formation During Processing Different Feeds

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**Abstract**

Three Urals vacuum residual feeds and a feed blend of 70% Urals / 30% Middle East crude was studied at the LUKOIL Neftohim Burgas H-Oil commercial unit at different liquid hourly space velocities (LHSVs) and different reaction temperatures (TRXs). The hydrocracked oil sediment content was found to depend on two factors: the content of asphaltenes and the quality of the asphaltenes in terms of their solubility. The decrease of LHSV increased the asphaltene conversion and improved the asphaltene solubility reducing in this way the hydrocracked residue sediment content. The increase of TRX had a different effect on the hydrocracked residua obtained from the feeds 100% the Urals and 70%Urals/ 30%ME. It increased the vacuum tower bottom (VTB) product asphaltene content during hydrocracking of 100% Urals and did not change the VTB asphaltene content during hydrocracking of 70%Urals/30%ME feed. However, the increase of TRX deteriorated the asphaltene solubility and increased the VTB sediment content.

***Keywords***: *Vacuum residue, Hydrocracking, SARA, Asphaltenes, Sediments, Conversion.*

## 1. Introduction

Sediment formation is the biggest plague in the operation of an ebullated bed vacuum residue hydrocracker (EBVRHC) [1-12]. If a high rate of sediment formation occurs due to processing of a blend of different vacuum residual oils [9] (VRO), unsatisfied condition of the catalytic system[10], feed contaminants increase (metals, arsenic, nitrogen) or other reasons the reaction severity decrease must be applied to relax the system and run the unit at an acceptable level of sediments in the residual oils. Typically by increasing the reaction severity expressed by heightening the reaction temperature, the sediment level in the EBVRHC atmospheric tower bottom (ATB) product increases exponentially with the enhancement of conversion [13]. On the other hand, the augmentation of reaction severity expressed by liquid hourly space velocity (LHSV) decrease (reaction time extending) did not show the pattern of sediment increase with the reaction severity increase by heightening the reaction temperature as reported [14]. Asphaltenes were proved to be the main reason for sediment formation in the EBVRHC [10,15]. The reduction of their content has a big impact on the improvement in the sedimentation in the EBVRHC [14-16]. According to Rogel *et al.* [17], the asphaltenes are cracked and hydrogenated at a lower rate than the resins and oils. Therefore, the increase of the reaction temperature in the EBVRHC would be associated with an increase in the asphaltene content in the hydrocracked residual oils because the resins and oils would be cracked faster. As a result, the sediment content will go up because it correlates with the asphaltene content and with the asphaltene solubility profile [17]. However, there are reports indicating that the asphaltenes from some crudes like Buzurgan crude, for example, are hydrocracked faster than the whole vacuum residue by changing the reaction severity by lowering the liquid hourly space velocity (LHSV) at a reaction temperature of 427°C [18-19]. Another study showed that the asphaltenes from Arabian Heavy (Safaniya) vacuum residue were hydrocracked faster than the whole vacuum residue at the reaction temperature of 390°C and they were hydrocracked slower at a reaction temperature of 430°C [21]. The modification of the catalytic system by doping NiMo/$Al_2O_3$ catalyst with F showed an improvement in both VRO conversion and asphaltene conversion in both reaction temperatures 390 and 430°C [20]. The asphaltenes from Athabasca vacuum residue were reported to hydrocrack faster than the resins and oils at a reaction temperature of 395°C, and the reaction time of 2 hours [21]. It was shown that the asphaltenes and the whole vacuum residue from Arabian Heavy crude hydrocracked at almost the same rate by changing the reaction severity by variation of LHSV at constant reaction temperature [14]. It was shown that during EBVRHC of three different vacuum residual oils at three different reaction temperatures and constant LHSV for two of them the asphaltene conversion was higher than that of the whole vacuum residue in the vacuum residue conversion range 56-66% and asphaltene conversion range 69-76% [22]. It should be noted that in the study reported in [22] the increase of the reaction temperature was associated with a VRO conversion increase and asphaltene conversion decrease. The data reported in the literature suggests that the extent of conversion (removal) of the asphaltenes during EBVRHC depends on the reaction temperature employed and the reaction time. Since understanding the mechanism of the sediment formation in both modes of conversion increase (reaction temperature heightening and LHSV reduction) may give a notion how to struggle the sediment formation in the EBVRHC unit we investigated the performance of the EBVRHC H-Oil in LUKOIL Neftohim Burgas refinery during processing 100% Urals vacuum residual oils (VROs) and a VRO feed blend 70%Urals/30%ME crude at different LHSVs and constant reaction temperature and at different reaction temperatures and constant LHSV. The aim of this work is to discuss the obtained results.

## 2. Experimental

### 2.1. Materials

VRO feedstocks of the LUKOIL Neftohim Burgas (LNB) ebullated bed vacuum residue (EBVR) H-Oil hydrocracker, originating from Urals crude and from a blend 70%Urals crude /30%ME crude, were processed in the H-Oil hydrocracker during the study. Their physical and chemical properties are summarized in Table 1.

Table 1 Properties of the VRO feedstocks processed in the LNB H-Oil hydrocracker during the

| VRO Properties | Urals1 | Urals2 | Urals3 | 70%Urals3/30%ME | 100% ME VR |
|---|---|---|---|---|---|
| VRO $d_{15\,°C}$, g /cm $^3$ | 1.001 | 0.995 | 0.996 | 1.012 | 1.051 |
| VRO Concarbon content, wt.% | 18.3 | 17.3 | 17.5 | 19.4 | 23.8 |
| VRO sulphur, % | 2.6 | 2.9 | 3.0 | 3.9 | 5.9 |
| Saturates, wt.% | 22.1 | 22.4 | 25.6 | 21.6 | 12.3 |
| Aromatics, wt.% | 60.6 | 66.5 | 53.9 | 58.2 | 64.8 |
| Resins, wt.% | 9.3 | 4.9 | 7.8 | 6.9 | 4.9 |
| $C_7$-asphaltenes, wt.% | 8.0 | 6.3 | 12.7 | 13.3 | 18.0 |
| $C_5$-asphaltenes, wt.% | 17.6 |  | 22.2 | 20.6 | 27.7 |
| $d_{15}$-$C_5$ asphaltenes, g/cm$^3$ |  |  | 1.147 |  | 1.195 |
| $d_{15}$-$C_7$asphaltenes, g/cm$^3$ |  | 1.172 | 1.132 |  | 1.204 |
| Kin. viscosity of 70%SRVRO/30% FCC HCO, mm$^2$/s at 80°C | 199.8 |  | 220.9 |  | 368.9 |
| Softening point,°C |  | 42.4 | 40.1 |  | 50.3 |
| Penetration |  |  | 182.0 |  |  |
| V, ppm | 227 |  | 255 | 191 | 42 |
| Ni, ppm | 76 |  | 79 | 59 | 12 |

It should be pointed out that the VROs originating from Urals crude differed in their asphaltene content during the study. They are marked as Urals 1, Urals 2, and Urals 3. The VRO from the blend 70%Urals crude /30%ME crude was obtained by blending Urals 3 with the ME crude. The properties of the 100% ME crude are also given in Table 1. The catalyst employed in this study was a commercial Ni-Mo low sediment catalyst.

### 2.2. Procedures

All hydrocracking experiments were carried out at the LNB EBVR H-Oil hydrocracker. A simplified process diagram of the LNB EBVR H-Oil hydrocracker is presented in [9]. Details about the LUKOIL Neftohim Burgas H-Oil residue hydrocracker are given in [23]. The operating conditions in the LNB EBR H-Oil hydrocracker during processing the four vacuum residual oil feedstocks are summarized in [24].

The vacuum residue 540°C+ conversion was estimated by the equation:

$$\text{Conversion}\ \ (\%) = \frac{EBRHCFeed_{540°C+} - EBRHC\,\mathrm{Pr}oduct_{540°C+}}{EBRHCFeed_{540°C+}} \times 100 \qquad \text{eq. (1)}$$

where: EBRHCFeed540°C+ = mass flow rate of the EBVRHC feed fraction boiling above 540°C, determined by high temperature simulated distillation, method ASTM D 7169 of the feed and multiplied by the mass flow rate of the feed; EBRHCProduct540°C+ = mass flow rate of the EBVRHC product fraction boiling above 540°C, determined by high temperature simulated distillation, method ASTM D 7169 of the liquid product multiplied by the flow rate of the liquid product.

The $C_5$- and $C_7$-asphaltene conversions were calculated by the equation:

$$Asphaltene\ conversion, \% = \frac{\text{Feed Asp} - \text{Product Asp}}{\text{Feed Asp}} * 100 \qquad \text{eq. (2)}$$

where: Feed Asp = Asphaltene (C5, or C7-asphaltenes) content in the feed, % multiplied by the feed rate in t/h; Product Asp = Asphaltene (C5, or C7-asphaltenes) content in the liquid product, % multiplied by the liquid product rate in t/h.

### 2.3. Analyses

The H-Oil vacuum residual oil feedstocks were characterized for their SARA (saturates, aromatics, resins, asphaltenes) composition in accordance with the procedure described in[25]. The density of the $C_5$- and $C_7$-asphaltenes were measured indirectly from the densities of a series of solutions of asphaltenes and maltenes in toluene at different concentrations as described in [26]. Solutions of asphaltene in toluene at concentrations up to an asphaltene mass fraction of 3% were prepared. Solutions of vacuum residual oils in toluene at concentrations up to a maltene mass fraction of 6% were prepared. This way of acting was selected to avoid possible errors in the measurement of the densities of the investigated vacuum residual oils. It was documented in a previous work that errors could be registered in the measurement of vacuum residual oil density if no dilution with high aromatic solvent is applied [27]. The repeatability of $C_5$-asphaltenes was determined to be ±0.023 $g/cm^3$, while that of $C_7$-asphaltenes was ±0.036$g/cm^3$. Conradson carbon content of the studied vacuum residual oils was measured according to ASTM D189 - 06(2014) method. The measurement of the asphaltene content was performed in accordance with the procedure described in [28]. The total existent sediment content (TSE) of the residual oils studied in this work was measured in accordance with the procedure IP 375. The precision of the measurement of TSE expressed by the repeatability and reproducibility is summarized below:

$$r = 0.089\sqrt{HFT_{\mathrm{Result}}} \qquad \text{eq.(3)}$$

$$R = 0.294\sqrt{HFT_{\mathrm{Result}}} \qquad \text{eq.(4)}$$

## 3. Results and discussion

### 3.1. Hydrocracked residual oil properties that affect the sediment content

In order to verify that the $C_7$ asphaltenes are the main reason for sediment formation in the EBVRHC six residual oils obtained from the LNB H-Oil vacuum residue hydrocracker and two blends of H-Oil partially blended fuel oil (PBFO) with near zero sulfur diesel was deasphalted and the sediment content of the residual oils and the deasphalted oils was measured (Table 2). It should be pointed out here that the content of ash, a measure for the presence of inorganic matter in the sediments, and the content of toluene insolubles were also measured and subtracted from the total sediment content in order to determine the asphaltenes contribution to the sediment level.

Table 2. Data for sediment content of LNB H-Oil hydrocracked residual oils and their deasphalted oils (DAO)

| Nr | LNB H-Oil hydrocracked residual oils | $C_7$ asphaltenes, wt. % | Sediment content, wt.% | Ash content, % | Toluene insolubles, wt.% | DAO sediment content, wt.% | Sediment yield, % of asphaltenes | % of sediments coming from asphaltene agglomeration |
|---|---|---|---|---|---|---|---|---|
| 1 | H-Oil PBFO 10.12.18 | 11.4 | 0.04 | 0.03 | 0.001 | 0 | 0.1 | 17.5 |
| 2 | H-Oil ATB 16.07.18 | 8 | 0.4 | 0.03 | 0.001 | 0 | 4.6 | 91.3 |
| 3 | ATB 05.11.15 | 11.8 | 1.4 | 0.05 | 0.001 | 0 | 11.4 | 96.1 |
| 4 | ATB 28.12.16 | 9.8 | 0.6 | 0.05 | 0.001 | 0 | 5.6 | 91.8 |
| 5 | 40% H-Oil PBFO/60%NZSD | 4.6 | 0.6 | 0.03 | 0.001 | 0 | 12.4 | 94.8 |
| 6 | 60% H-Oil PBFO/40%NZSD | 6.8 | 0.5 | 0.06 | 0.001 | 0 | 6.5 | 88.8 |
| 7 | VTB 08.04.19 | 12.7 | 0.7 | 0.07 | 0.001 | 0 | 5.0 | 90.0 |
| 8 | ATB 08.04.19 | 7 | 0.2 | 0.04 | 0.001 | 0 | 2.3 | 81.6 |

As evident from the data in Table 2, all deasphalted oils had zero sediment content, and the contribution of the asphaltenes to the total sediment content formation in the studied H-Oil residual oils was in most cases higher than 90%. These data confirm that the $C_7$ asphaltenes are the main contributor to the sediment formation in the EBVRHC. It is clear that not all asphaltenes take part in the process of sedimentation; otherwise the sediment content would be equal to the asphaltene content of the hydrocracked residual oil plus the content of ash (inorganic material) and that of the toluene insoluble. In order to evaluate which part of the asphaltenes contributes to the sediment formation, the hydrocracked oil sediment content was divided by the $C_7$-asphaltene content and in this way, the sediment yield of $C_7$-asphaltenes was obtained.

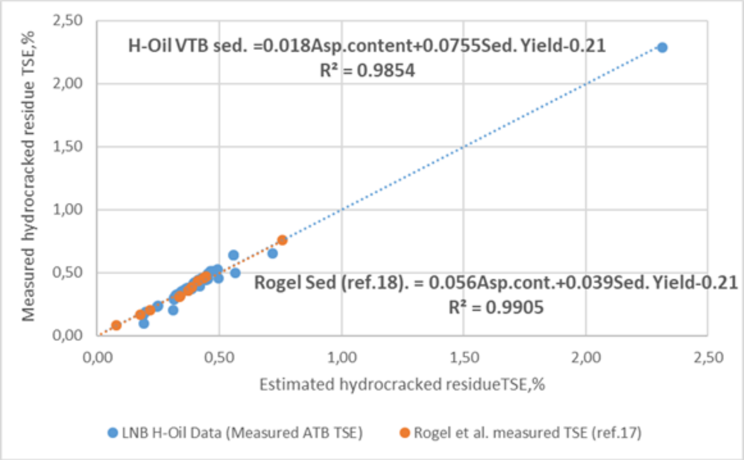


Figure 1 Agreement between measured and estimated, by regressions accounting the content of asphaltenes and the sediment yield of the asphaltenes, sediment content in hydrocracked residual oils

The data in Table 2 indicate that the yield of the sediments varies from 0.1 to 12.4% that suggests that the solubility of the asphaltenes in the studied residual oils significantly differs. The data for LNB H-Oil hydrocracked residual oils reported in other our studies [10,28] showed that the asphaltene content did not correlate with the hydrocracked residual oil sediment content neither it correlated with the ratio $C_7/C_5$ asphaltenes as developed in [12]. It was also shown in [28] that neither SARA analysis data nor asphaltene aromaticity measured by the asphaltene density correlated with the H-Oil hydrocracked residual oil sediment content.

The regression of the data for 42 LNB H-Oil hydrocracked residual oils asphaltene content and sediment yield of the asphaltenes indicated that these two parameters of the hydrocracked residual oils determined the sediment level in the H-Oil residual oils (Fig.1). The data for asphaltene content and the yield of sediments of the asphaltenes of 12 hydrocracked residual oils reported in the work of Rogel *et al.* [17] also showed that these two parameters: asphaltene content, and the yield of sediments of the asphaltenes define the sediment content in the hydrocracked residual oils (Fig.1).

Rogel *et al.* reported that a regression of the asphaltene solubility profile characteristics (the ratio of "the easy to dissolve to the difficult to dissolve") and the asphaltene content could predict the hydrocracked residual oil sediment content. Therefore, all approaches, which can decrease the asphaltene content and improve asphaltene solubility (sediment yield of asphaltenes), can decrease the sediment level in the hydrocracked residual oils.

### 3.2. Effect of LHSV and reaction temperature on sediment content during processing 100% Urals vacuum residue in the LNB H-Oil EBVRHC

Performing experiments at a commercial EBVRHC unit is very difficult because first, the quality of the feed could not be guaranteed as illustrated with the data for Urals VROs shown in Table 1, and second the operation of the unit is governed by this mode that is the most profitable. For that reason, collecting data at different LHSV and reaction temperature cannot be made in a planned mode. They can be extracted from the operation data of the commercial hydrocracker and then to analyze. The data in Table 1 shows that most physical and chemical properties (density, Conradson carbon content, saturated content, viscosity, metals content) of the three Urals VROs studied in this work were very close except their asphaltene content. The asphaltene content varied in a factor of two (between 6.3 and 12.7%). The Urals VROs were processed at LHSV of 0.12, 0.18, 0.23, and 0.25 $h^{-1}$, and reaction temperatures of 404, 410, and 418°C.

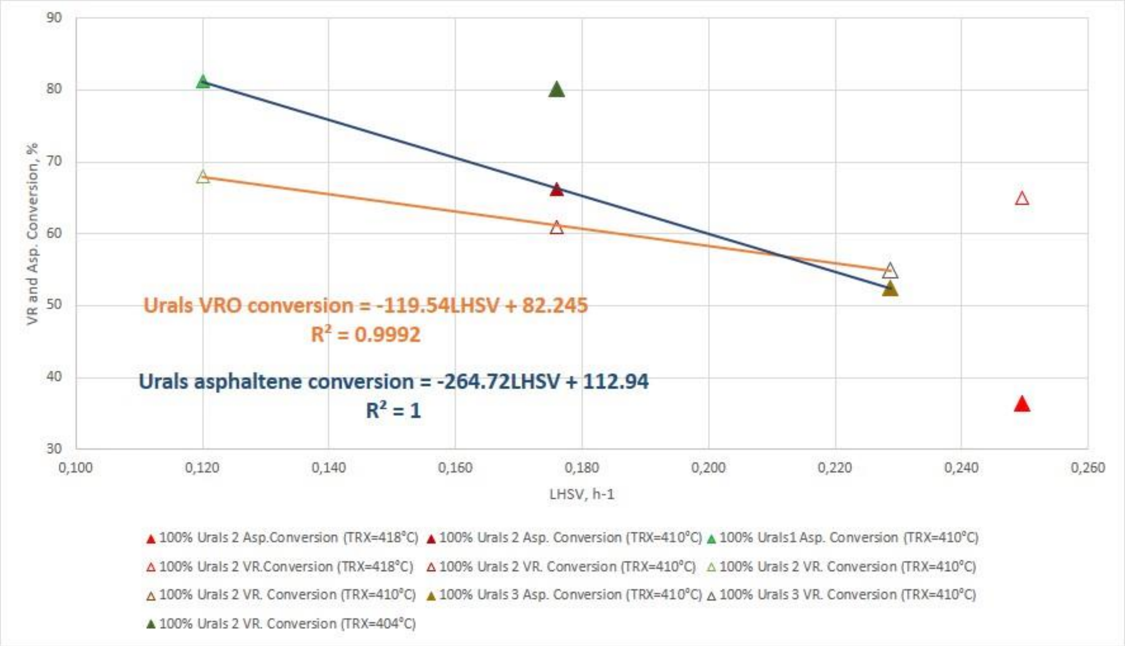
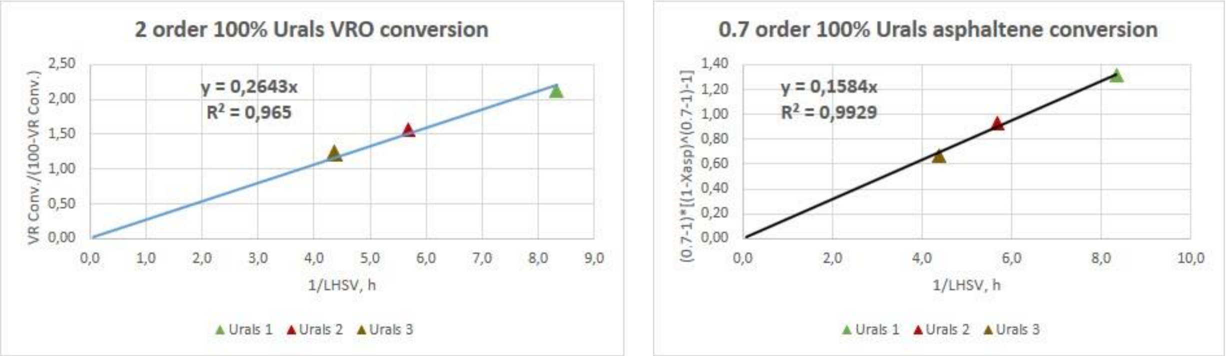


Figure 2. Variation of VRO and asphaltene conversions at different LHSVs and reaction temperatures (TRXs) during processing 100% Urals1, 100% Urals 2, and 100% Urals 3 in the LNB H-Oil hydrocracker

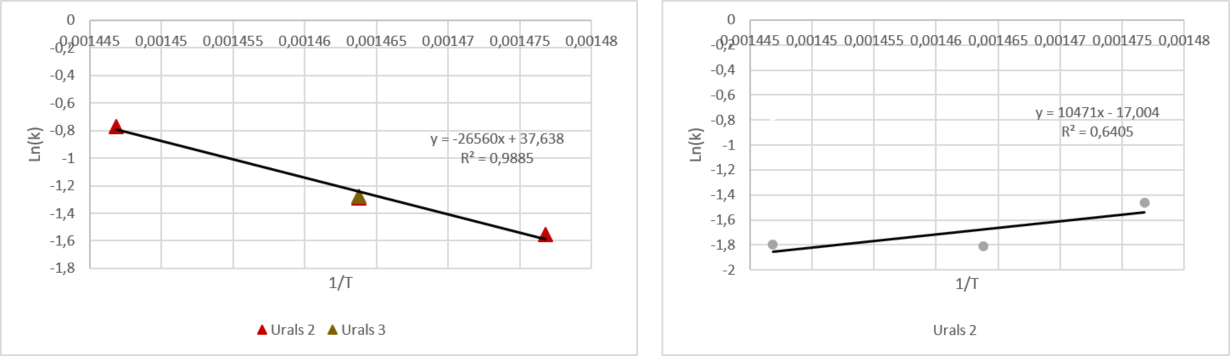
The LNB hydrocracker was not possible to run with 100% Urals VRO feed at a higher temperature due to the excessive sediment formation at a reaction temperature of 418°C. At a reaction temperature of 418°C and LHSV of 0.25 $h^{-1}$ the sediment content in the H-Oil VTB product reached 4.0%, and after a day running at such conditions, the vacuum tower of the

H-Oil hydrocracking unit had to be stopped for cleaning. For that reason, the data for running the unit at different LHSV was obtained at a reaction temperature of 410°C. There was also one data point at a reaction temperature of 404°C. Figure 2 summarizes the data of variation of VRO and asphaltene conversions at different LHSVs and reaction temperatures (TRXs) during processing 100% Urals1, 100% Urals 2, and 100% Urals 3 in the LNB H-Oil hydrocracker.The filled triangles designate the asphaltene conversions of the three Urals asphaltenes, while the empty triangles designate the Urals VRO conversions. This data shows that the slope of increasing the asphaltene conversion (slope = 265) is bigger than that of the VRO (slope = 120) at TRX of 410°C. The lower the TRX, the higher the asphaltene conversion of the Urals VROs was. At a LHSV of 0.18 and TRX of 404°C the asphaltene conversion was 80.2%, while at TRX of 410°C, the asphaltene conversion was 66.3%. The lowest was the asphaltene conversion at TRX of 418°C and LHSV of 0.25 h-1 = 36.4%. Figure 3 indicates kinetic plots for the conversion of 100% Urals VROs (Fig. 3a) and the 100% Urals asphaltenes (Fig. 3b). Interestingly regardless of the different asphaltene contents in the three 100% Urals VROs their points fit very well on the graphs in Fig.3. The H-oil 100% Urals VRO conversion data fits the second order kinetics, while the 100% Urals asphaltene conversion data fits the 0.7 order kinetics. Similar to the 100% Urals VROs the second order conversion for hydrocracking VROs have been reported for the VROs from Athatasca, Urals, Duru, and Arabian Light crudes studied in [18]. The second order was also reported for the thermal hydrocracking of an atmospheric residue in [29]. Concerning the asphaltene conversion kinetics, the literature reviewed in [29] on this matter showed that the order of the asphaltene conversion might vary between 0.5 and 2. Our data for the 100% Urals asphaltenes was within this range for the order of the asphaltene conversion.



a b

Figure 3. Second order kinetic plot for the 100% Urals VRO conversion (a) and 0.7 order kinetic plot for the 100% Urals asphaltene conversion at a reaction temperature of 410°C (b)



a ($k_0$=2.219.10$^{16}$; Ea = 220.8 kJ/mole) b

Figure 4. Arrhenius plots for the dependence of kinetic constants on the reaction temperature for the 100% Urals VRO conversion (a) and for the asphaltene conversion (b)

Figure 4 shows Arrhenius plots for the dependence of kinetic constants on the reaction temperature for the 100% Urals VRO conversion (Fig. 4a) and for the asphaltene conversion (Fig. 4b). The activation energy for the 100% Urals VRO conversion was 221 kJ/mole, and the pre-exponential factor was $2.22 \times 10^{16}$ frac.$^{-1}$.h$^{-1}$ The behavior of the 100% Urals asphaltenes with the increase of TRX did not follow the Arrhenius equation. The slope of the curve in Fig. 4b is positive that should mean a negative value for the activation energy. This unusual behavior could be a result of the use of eq. 2 to calculate the asphaltene conversion

It is clear that in case of generating additional product asphaltenes, the estimated value of the asphaltene conversion would be lower. Therefore, the reduction of the value of the asphaltene conversion with increasing the reaction temperature could mean an acceleration of the reactions of asphaltene recombination leading to the generation of additional amount of product asphaltenes. The SARA data of the VTB products obtained during hydrocracking of 100% Urals 2, VRO summarized in Table 3 indicates that the reduction of the LHSV and of the TRX leads to increasing of saturating content and to decreasing of the content of aromatics, and asphaltenes, and sediments. The increase of TRX from 404 to 410°C was associated with an increase of asphaltenes from 2.3 to 5.5% and the sediments from 0.37 to 0.90%. The yields of sediments were the same at both TRXs = 16.3%. The increase of TRX from 410 to 418°C and the increase of LHSV from 0.176 to 0.250h$^{-1}$ led to increasing of asphaltene content from 5.5 to 12.0% and an increase of sediment content from 0.90 to 4.0%. The yield of sediments increased from 16.3% at TRX of 410°C and LHSV of 0.176 h$^{-1}$ to 33.4% at TRX of 418°C and LHSV of 0.250h$^{-1}$. Obviously, the increase of TRX and the increase of LHSV affected both the increase of asphaltene content and the yield of sediments of the Urals 2 asphaltenes. The VTB obtained from hydrocracking of the 100% Urals 3 VRO feedstock regardless of the highest asphaltene content (15.7%) did not have the highest sediment content. The reason for this is the very low sediment yield of the asphaltenes (3.2%) which is the lowest among all studied 100% Urals VROs. It seems that the asphaltenes from 100% Urals 3 VRO are more soluble irrespective of their highest content

Table 3. Variation of SARA and sediment contents of the H-Oil VTB during processing 100% Urals VROs

| Feed | TRX, °C | LHSV, h$^{-1}$ | Sat. % | Aro, % | Res. % | $C_7$-asp., % | VTB sed. content, % | Sed. yield, % |
|---|---|---|---|---|---|---|---|---|
| 100% Urals 2 | 418 | 0.250 | 22.1 | 60.6 | 5.4 | 12.0 | 4.00 | 33.4 |
| 100% Urals 3 | 410 | 0.229 | 34.5 | 44.2 | 5.6 | 15.7 | 0.50 | 3.2 |
| 100% Urals 2 | 410 | 0.176 | 39.0 | 50.9 | 4.6 | 5.5 | 0.90 | 16.3 |
| 100% Urals 2 | 404 | 0.176 | 50.0 | 44.1 | 3.7 | 2.3 | 0.37 | 16.3 |

### 3.3. Effect of LHSV and reaction temperature on sediment content during processing 70% Urals3/30%ME vacuum residue in the LNB H-Oil EBVRHC

The operation in the LNB H-Oil EBVRHC with the VRO feed blend 70%Urals 3 / 30% ME was much easier to study because this VRO feed blend had a much lower propensity to form sediments. The VRO feed blend 70%Urals 3 / 30% ME was processed at LHSV of 0.147, 0.189, 0.192, 0.234, and 0.250 h$^{-1}$, and reaction temperatures of 410, 411, 414, 416, 419, 421, and 425°C. Figure 5 shows the variation of conversion of 70% Urals 3/ 30% ME VRO and asphaltenes with the LHSV variation during H-Oil hydrocracking at 423°C. Similar to the hydrocracking of the 100% Urals the slope of increasing the asphaltene conversion of the 70% Urals 3/ 30% ME VRO feed (slope =164) is bigger than that of the VRO conversion (slope =71). However, at TRX of 423°C in the investigated range of LHSV variation the conversion of the asphaltenes was always lower than that of the VRO conversion.

Figure 6 indicates the second order kinetic plot for the 70% Urals 3/ 30% ME VRO conversion (6a) and 1.5 order kinetic plot for the 70% Urals 3/ 30% ME asphaltene conversion at the reaction temperature of 423°C. The blending of ME VRO with Urals 3 VRO did not change the kinetic order of the VRO conversion to lower boiling products. However, the blending of ME VRO with Urals 3 VRO had a very big impact on the conversion of the asphaltenes.

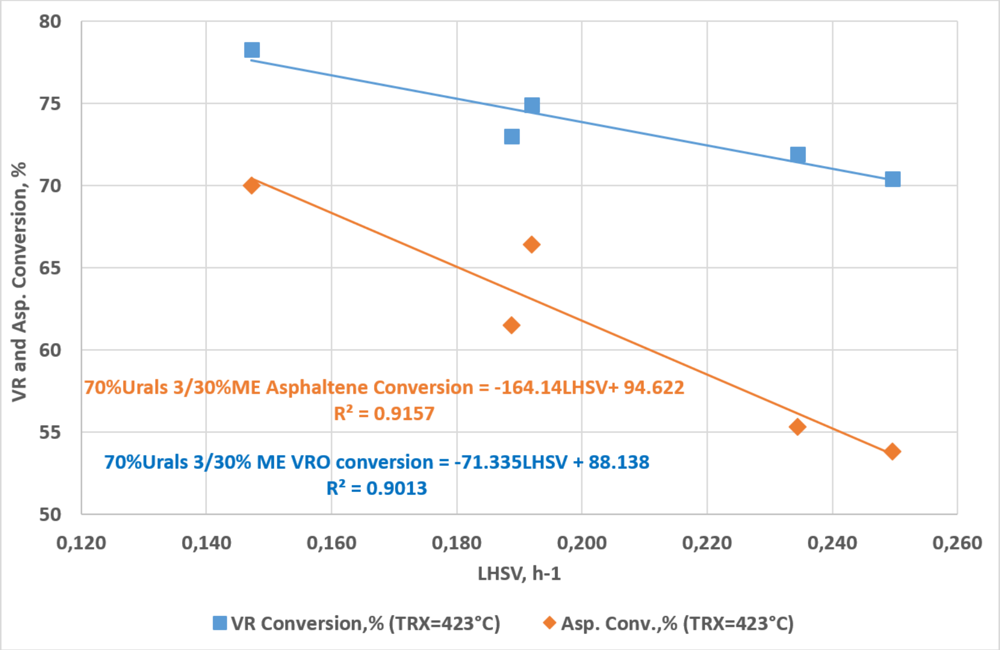
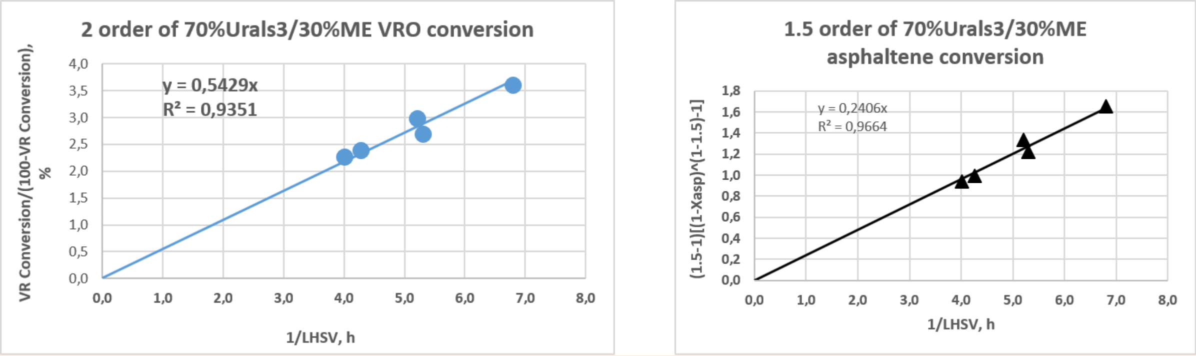


Figure 5. Variation of conversion of 70% Urals 3/ 30% ME VRO and asphaltenes with the LHSV variation during H-Oil hydrocracking at 423°C



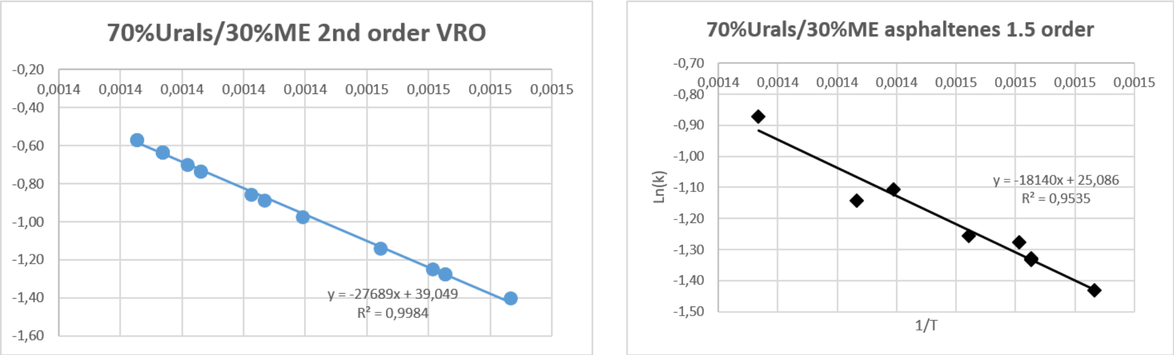
a

b

Figure 6 Second order kinetic plot for the 70% Urals 3/ 30% ME VRO conversion (a) and 1.5 order kinetic plot for the 70% Urals 3/ 30% ME asphaltene conversion (b) at reaction temperature of 423°C

The conversion of the asphaltenes at 423°C and LHSV of 0.250h$^{-1}$ was 53.8% for the feed 70%Urals 3/30% ME, while that of the 100% Urals 2 at the same LHSV and TRX of 418°C was 36.4%. The sediment content in the 70% Urals 3/ 30% ME hydrocracked VTB product was 0.61% versus 4.0% in the 100% Urals 2. It seems that the conversion of the 70% Urals 3/ 30% ME asphaltenes is higher than that of the 100% Urals asphaltenes at elevated temperature. However, the kinetic order of the of the 70% Urals 3/ 30% ME asphaltene conversion at 423°C is twice as high as that of the 100% Urals asphaltene conversion at 410°C. The 1.5 order of the 70% Urals 3/ 30% ME asphaltene conversion at 423°C suggests that these asphaltenes consist of species with different reactivities [30]. The more reactive species react rapidly, and the mixture becomes progressively more refractory, i.e., less reactive, thus giving rise to a higher overall reaction order [27]. The lower the reaction order the easier is the feed to convert [30]. Therefore the 100% Urals asphaltenes are easier to convert at 410°C than the 70% Urals 3/ 30% ME asphaltenes do at 423°C. If the 100% Urals asphaltenes are easier to convert at 410°C their lower conversion at 418°C would definitely mean the presence of recombination reactions between the 100% Urals asphaltene species. The addition of the ME

VRO asphaltenes to the Urals asphaltenes may retard the recombination reactions of the Urals asphaltenes and the reactions of conversion of the Urals asphaltenes at all. The data for 70% Urals 3/ 30% ME VRO and the asphaltene conversions obtained at constant LHSV of 0.176 h$^{-1}$ and different TRX was used to estimate activation energies and pre-exponential factors. Figure 7 shows Arrhenius plots for the dependence of kinetic constants on the reaction temperature for the 70% Urals 3/30%ME VRO conversion (7a) and for the asphaltene conversion (7b). In contrast to the data for the 100% Urals asphaltene conversion where the increase of TRX was associated with asphaltene conversion decrease the 70% Urals 3/30%ME asphaltene conversion increases with TRX heightening with an activation energy of 150.8 kJ/mole



a ($k_0$=9.09.10$^{16}$; Ea = 230.2 kJ/mole)

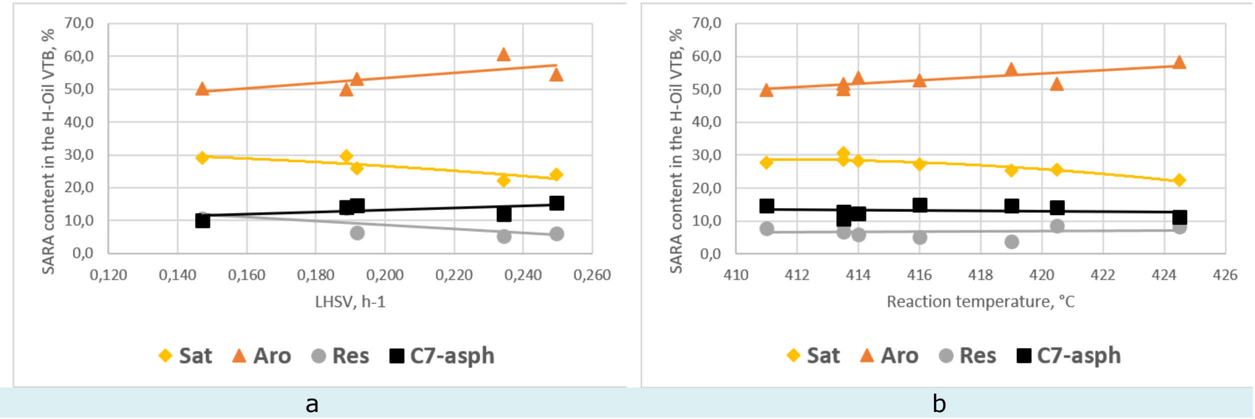
b ($k_0$=7.84.10$^{10}$; Ea = 150.8 kJ/mole)

Figure 7. Arrhenius plots for the dependence of kinetic constants on the reaction temperature for the 70% Urals 3/30%ME VRO conversion (a) and for the asphaltene conversion (b)

The activation energy of the 70% Urals 3/30%ME VRO conversion is 230.2 kJ/mole. The addition of the ME VRO to the Urals VRO increases the activation energy from 220.8 to 230.2 kJ/mole.

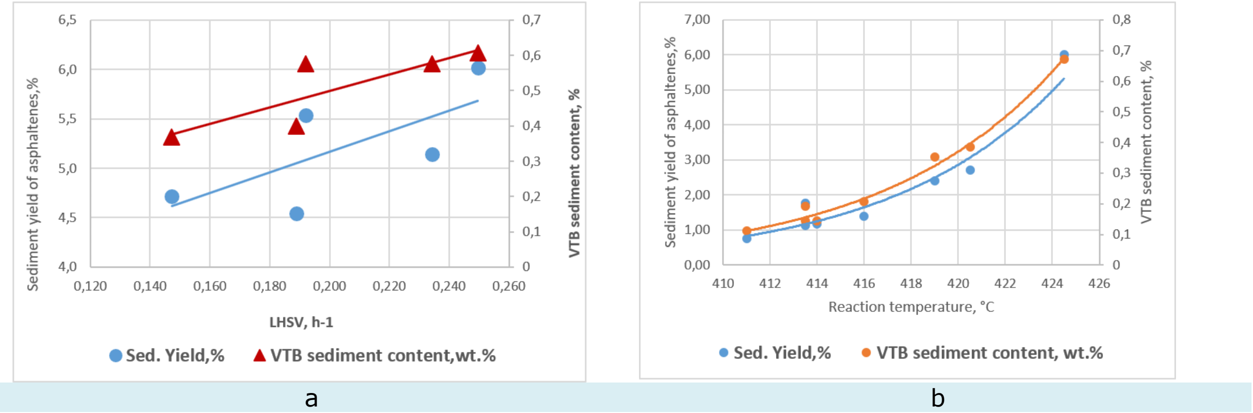
Figure 8 depicts graphs of variation of SARA composition of the H-Oil VTBs obtained by hydrocracking of the feed 70%Urals3/30%ME at different LHSVs and constant TRX of 423°C (Fig. 8a), and at different TRX and constant LHSV of 0.176h$^{-1}$ (Fig. 8b). It is evident from the data in Fig. 8a that the increase of the LHSV is associated with a decrease of saturates and resins contents, and increasing of asphaltene and aromatics content. A similar trend in variation of SARA fractions contents in ATB during hydrocracking of Arabian Heavy VRO at different LHSVs and constant TRX has been reported in [14] for the saturates and asphaltene contents. In [14], the resin content decreased with LHSV decrease, while the aromatics content remained unchanged. The difference observed in these two SARA fractions variation with alteration of LHSV could be explained by the distinct SARA analysis procedures employed in this work and in [14], as shown in [31]. The data in Fig. 8a suggests that the aromatics are hydrogenated to saturates and the asphaltenes are hydrocracked to resins with the reduction of the LHSV [32]. Fig. 8b shows that heightening the TRX leads to an increase of aromatics content and a decrease of the saturates content, while the resins and asphaltenes contents remained unaltered in the VTB. This data suggests that the increase of TRX may decrease the hydrogenation of the aromatics to saturates, or the activation energy of the saturate hydrocracking to be higher than that of the aromatics hydrocracking promoting the hydrocracking reactions of the saturate fraction to a greater extent than those of the aromatics with the increase of TRX [33].

Figure 9 shows graphs of variation of VTB sediment content and the yield of sediments of asphaltenes by changing LHSV at 423°C TRX (Fig. 9a), and by altering the TRX at constant LHSV of 0.176h$^{-1}$ (Fig. 9b).



a b

Figure 8. SARA fractions variation by changing the LHSV at 423°C TRX (a), and by alteration the TRX at constant LHSV of $0.176h^{-1}$ (b)



a b

Figure 9. VTB sediment content and the yield of sediments of asphaltenes variation by changing LHSV at 423°C TRX (a), and by altering the TRX at constant LHSV of $0.176h^{-1}$ (b)

This data indicates that the increase of LHSV increases the VTB sediment content and the yield of sediments of the asphaltenes. Therefore, the increase of sediment content in the VTB with augmentation of LHSV is due to the increase of asphaltene content as seen from the data in Fig. 8a and the decrease of the asphaltenes solubility. The increase of TRX as evident from the data in Fig. 9b leads to an exponential increase of the VTB sediment content and of the yield of sediments of the asphaltenes. Considering that the asphaltene content in the VTB remained unaltered with heightening the TRX one may conclude that the exponential increase of the VTB sediment content during hydrocracking the VRO feed 70% Urals 3/30%ME is due to the exponential decrease of the solubility of the asphaltenes expressed by the yield of sediments of the asphaltenes. The data published in the literature showed that the VROs from the Middle East crudes demonstrate a lower than second order kinetics for the VRO conversion [14,18-19]. For example, the data for hydrocracking of VRO from Buzurgan crude (Iraq origin) fits 1.5 order kinetics for the VRO conversion [18-19]. The data for hydrocracking a VRO from Arabian Heavy crude fits 1.3 order kinetics for the VRO conversion. Based on the reasoning discussed in [27] the lower reaction order would mean an easy feed to convert. Therefore, the ME VROs could be considered more reactive in the hydrocracking process. The pilot plant tests with the ME VRO employed in this study showed that it is more reactive than the Urals VRO. At the same operating conditions, that particular VRO exhibited 10% higher conversion. However, its addition in the amount of 30% to the feed blend with 70% Urals did not show an improvement in the LNB H-Oil feedstock reactivity. The reaction order was not changed, and the conversion was not altered at the same operating conditions. The big difference was observed in the sedimentation performance of the VRO blend 70% Urals / 30% ME. It seems that the ME VRO suppresses the reactions of the recombination of the Urals asphaltenes observed at elevated temperatures. This allowed operation at higher TRX and higher VRO conversion while maintaining a reasonable low sediment content in the hydrocracked residual oils when the feed blend 70% Urals / 30% ME was hydrocracked in the LNB H-Oil commercial unit. Comparing the behavior of both feeds 100% the Urals and 70% Urals 3/30%ME in this work one can see that the increase of the TRX was associated with a decrease of the asphaltene solubility. However, the asphaltene content in the hydrocracked residual oils obtained from the 70% Urals 3/30%ME VRO did not change with augmentation of TRX, while that in the hydrocracked residual oils obtained from the 100% Urals VRO increased with the increase of TRX. This along with the lower solubility of the hydrocracked residual oil asphaltenes obtained from 100% Urals, contributed to the significantly higher sediment content.

The improvement in the sedimentation during EBVRHC can be achieved by increasing asphaltene solubility trough the addition of high aromatic FCC gas oils [13,34], the use of asphaltene dispersants [35-38], improving catalyst condition by increasing catalyst addition rate [12], use of a better catalyst [20], use of nano-catalyst [39-40]. The improvement in the sedimentation during EBVRHC can be also achieved through the reduction of the asphaltene content by the use of feed deasphaltization [17], increase asphaltene conversion by the use of a better catalyst [20], increase asphaltene conversion by the use of nano-catalyst [39-40].

## 4. Conclusions

It was confirmed that the $C_7$ asphaltenes in the hydrocracked residual oils are the main reason for the formation of sediments in the EBVRHC. The hydrocracked oil sediment content was found to depend on two factors: the content of $C_7$ asphaltenes and the quality of the asphaltenes in terms of their solubility (yield of sediment of the asphaltenes). The increase of reaction temperature reduces the asphaltene solubility, and depending on the feed can increase asphaltene content. Both of these factors contribute to a higher sediment content in the hydrocracked residual oils. The decrease of LHSV reduces the asphaltene content in the hydrocracked residual oils and improves the asphaltene solubility. Both these factors contribute to a lower sediment content in the hydrocracked residual oils.

Two types of VRO feed (100% Urals and 70% Urals/30%ME) for EBVRHC were processed in the LNB H-Oil hydrocracker. The conversion of both VRO feeds can be described by second order kinetics. The addition of the ME VRO to the Urals VRO led to an increase in VRO conversion activation energy. The asphaltene conversion of the feed 70% Urals/30%ME can be described by 1.5 order kinetics, while that of the feed 100 Urals can be described by 0.7 order kinetics. The 100% Urals asphaltene conversion did not obey the Arrhenius equation for the dependence of reaction rate constant on TRX for the operating conditions studied in this work. The probable reason for this finding is the presence of recombination reactions of the asphaltenes leading to the generation of an additional amount of product asphaltenes, which accelerate with the increase of TRX. The hydrocracking of 100% Urals feed at elevated TRX increases the asphaltene content in the VTB product, while the hydrocracking of 70% Urals/30%ME at elevated TRX does not increase the asphaltene content in the VTB product. The addition of the ME VRO to Urals VRO has a profound effect on the sedimentation due to improving the asphaltene solubility and retarding the recombination reactions of the Urals asphaltenes.

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