

IMPACT OF SEVERITY IN THE H-OIL VACUUM RESIDUE HYDROCRACKING ON SEDIMENT FORMATION

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Abstract

The results of hydrocracking of several vacuum residual oils obtained in a pilot plant, in a laboratory Robinson Mahoney reactor unit, and in the commercial LUKOIL Neftohim Burgas ebullated bed H-Oil hydrocracker were discussed. It was found that during increasing of vacuum residue conversion by decreasing liquid hourly space velocity (LHSV) the asphaltene conversion increased simultaneously with the whole vacuum residue (VR) conversion enhancement. As a result the asphaltene content in the residual unconverted product continually decreased along with the sediment reduction during the reduction of the LHSV. The increase of VR conversion by raising the reaction temperature did not exhibit a simultaneous augmentation of the asphaltene conversion. By increasing the reaction temperature the asphaltene content in the ebullated bed vacuum residue hydrocracking (EBVRHC) residual oil raised and the same did the sediment content. The process of sediment formation is underestimated in the laboratory Robinson Mahoney reactor unit in contrast to the commercial EBVRHC unit, and the slope of increasing the sediment with the increase of the reaction temperature is much lower in the laboratory Robinson Mahoney reactor unit than in the commercial EBVRHC unit. The different asphaltenes, originating from different crudes exhibited different tendency to form coke like sediments. It was proved that the C₇-asphaltenes are the main contributor for sediment formation in the EBVRHC and their removal leads to zero sediment content in the EBVRHC residual oil.

Keywords: vacuum residue; ebullated bed hydrocracking; asphaltene; asphaltene conversion; sediment formation; SARA.

1. Introduction

The heavy oil hydrocracking is a process of high importance for the modern petroleum refining [1-5]. Sediment formation is the biggest plague in the operation of an ebullated bed vacuum residue hydrocracker (EBVRHC) [6]. If a high rate of sediment formation occurs due to processing of a blend of different vacuum residual oils [6], unsatisfied condition of the catalytic system [7], 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 (Figure 1).

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 shown in Figure 2.

The data in Figure 2 shows that the same level of sediments in the EBVRHC ATB can be observed when the vacuum residue conversion varies in the range 50-80% by varying the LHSV. As evident from Figure 1 the sediments increase by heightening reaction temperature

in the conversion range 50-80% is about tenfold, which supposes a different mechanism of sediment formation in both ways for conversion increase. Interestingly at a conversion of about 90% (Fig.2) by lowering the LHSV the sediments in the ATB are at the level of that obtained at a conversion of about 40%, which is lower than that observed in the conversion range 50-80%. Understanding the mechanism of the sediment formation in both modes of conversion increase (reaction temperature heighten and LHSV reduction) may give a notion how to struggle the sediment formation in the EBVRHC unit.

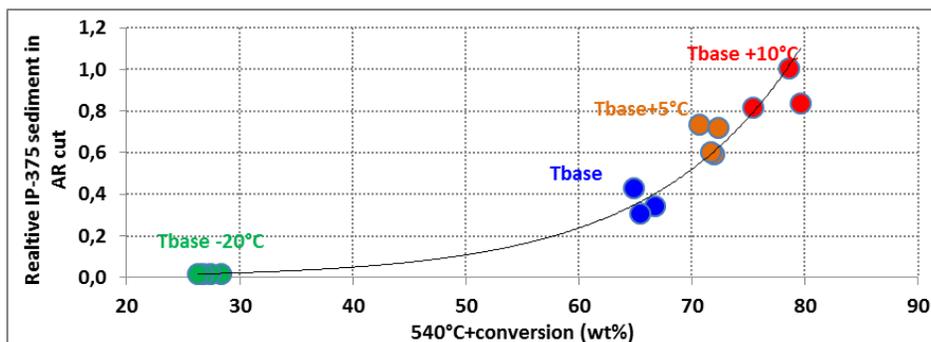


Figure 1. Relation of EBVRHC ATB sediment content to the conversion achieved by reaction temperature variation (The data of this graph is extracted from Ref 8).

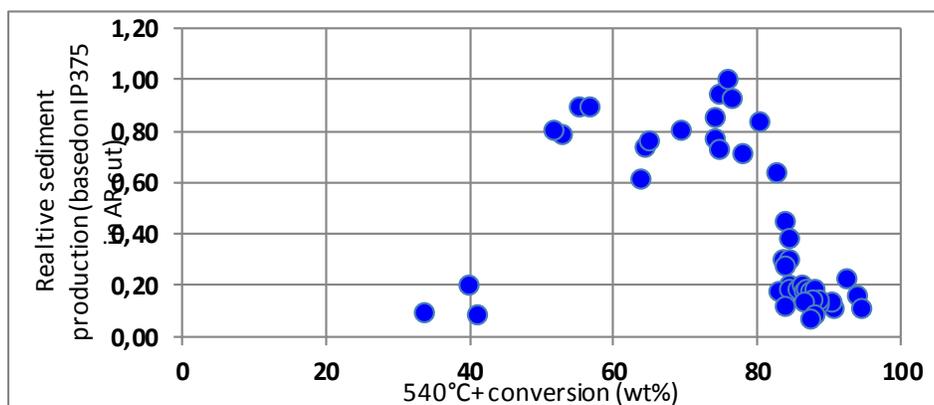


Figure 2. EBVRHC atmospheric tower bottom (ATB) product sediment content variation by changing conversion achieved by decreasing LHSV from 3 x base LHSV to base LHSV/3.5 (The data of this graph is extracted from Ref 8).

The aim of this work is to discuss the observations obtained during vacuum residue conversion increase by reaction temperature heightening and LHSV reduction concerning sedimentation in laboratory EBVRHC units and compare the laboratory results with those obtained at the LUKOIL Neftohim Burgas (LNB) commercial ebullated bed vacuum residue H-Oil hydrocracker during processing different vacuum residual oils.

2. Experimental

The experimental laboratory EBVRH results have been extracted from [8] and [9]. The commercial experimental results have been obtained at the LNB H-Oil hydrocracker. Properties of the vacuum residual oils employed in the laboratory experiments are shown in Table 1, while those used in the commercial experiments are summarized in Table 2. The operating conditions at the LNB H-Oil hydrocracker are given in [10].

Table 1. Properties of the vacuum residual oils studied in [8] and [9] and hydrocracked in laboratory (pilot) EBVRHC units

SRVRO properties	Arab Heavy SRVRO (ref. 8)	A (ref.8)	B (ref 8)	C (ref.8)
Density at 15°C, g/cm ³	1.024			
Concarbon, wt. %	21.6			
Sulphur, wt. %	4.89			
Nitrogen, wt. %	0.4495			
Ni+V, wt. ppm	218			
SARA, %				
Saturates	9.5	36.2	38.4	21.3
Aromatics	39.5	44.7	38.3	40.4
Resins	37.4	18.1	21.3	23.4
Asphaltenes	13.6	1	2	14.9

$$\text{Conversion (\%)} = \frac{\text{EBRHCFEED}_{540^{\circ}\text{C}+} - \text{EBRHCPRODUCT}_{540^{\circ}\text{C}+}}{\text{EBRHCFEED}_{540^{\circ}\text{C}+}} \times 100 \quad \text{eq. (1)}$$

where, EBRHCFEED_{540°C+} = weight of the EBRHC feed fraction boiling above 540°C, determined by high temperature simulated distillation, method ASTM D 7169; EBRHCPRODUCT_{540°C+} = weight of the EBRHC product fraction boiling above 540°C, determined by high temperature simulated distillation, method ASTM D 7169.

The C₅₋, and C₇₋ asphaltene conversions were calculated by the equation:

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

where, Feed Asp = Asphaltene (C₅, or C₇₋asphaltenes) content in the feed, %; Product Asp = Asphaltene (C₅, or C₇₋asphaltenes) content in the products, %.

Table 2. Properties of the vacuum residual oils studied in the commercial LNB EBVR H-Oil hydrocracker

SRVRO properties	Urals	El Bouri	Arab Heavy	Arab Medium
Density at 15°C, g/cm ³	1.0096	1.0495	1.047	1.030
Concarbon, wt. %	18.0	25.5	23.6	20.7
Sulphur, wt. %	2.9	3.3	5.8	5.4
Nitrogen, wt. %	0.45			
Ni+V, wt. ppm	334	154	163	183
SARA, %				
Saturates	22.4	12.0	12.4	11.8
Aromatics	66.5	57.9	61.9	68.3
Resins	4.9	12.6	4.4	5.3
Asphaltenes	6.3	17.5	21.3	14.6

In order to evaluate the effect of asphaltene content and the surrounding medium of the asphaltenes in H-Oil residual oil experiments were performed in the LNB Research Laboratory. A sample of LNB H-Oil vacuum tower bottom (VTB) product with properties shown in Table 3 was blended with fluid catalytic cracking (FCC) heavy cycle oil (HCO) in a ratio 68% (VTB)/32% (HCO) at the LNB H-Oil unit. Properties of the FCC HCO are given in [6]. The prepared in this way partially blended fuel oil (PBFO) was blended in different ratio with near zero sulphur jet fuel (NZSJ), near zero sulphur heavy diesel (NZSHD), diesel from H-Oil (H-Oil diesel), heavy atmospheric gas oil (HAGO) from H-Oil, heavy vacuum gas oil from H-Oil (HVGO). Properties of the diluents added to the LNB H-Oil PBFO are summarized in Table

3. Samples of the studied blends were analyzed for their total existent sediment content (TSE), and total sediment potential (after thermal aging - TSP), in accordance with the procedures IP 375, and IP 390 Procedure A. TSE and TSP of the studied blends are summarized in Table 4.

Table 3. Physical and chemical properties of residual and distillate oils under study

	FCCPT Diesel	NZSJJet	NZSH Diesel	H-Oil HAGO	H-Oil HVGO	H-Oil Diesel	H-Oil VTB	PBFO*
Density at 15 °C, g/cm ³	0.8875	0.801	0.851	0.9284	0.9508	0.8525	1.0225	
Evaporate, %	High temperature simulated distillation ASTM D-7169, °C							
IBP 0,5	186	122	139	244	378	123	370	
10	248	162	193	338	432	165	514	
50	316	201	277	408	490	261	598	
90	369	233	353	475	541	349	693	
95	383	240	369	498	553	363	709	
FBP 99,5	419	247	407	551	574	385	734	
Conradson carbon content, wt. %							21.7	15.0
Saturates, wt. %	50	87	65.1	43	40	60	23.9	
Aromatics, wt. %	50	13	34.9	40	40.5	40	51.9	
Resins, wt. %				17	19.0		8.6	
Asphaltenes, wt. %					0.5		15.6	11.4
Sulphur, wt. %	0.09	0.0003	0.0008	0.567	0.832	0.128	1.36	1.27
TSE, %							0.31	0.04
Kin. viscosity at 120 (80°C), mm ² /s							179 (120°C)	92 (80°C)

*PBFO = (68%VTB/32%FCC HCO)

Table 4. Total sediment existent and total sediment potential of blends of the PBFO with distillate oils

Diluent % in the blend PBFO/FCC HCO	NZSH Diesel, TSE, %	NZSH Diesel, TSP, %	NZSJJet, TSE, %	H-Oil Diesel, TSE, %	FCCPT Diesel, TSE, %	H-Oil HAGO, TSE, %	H-Oil HVGO, TSE, %
0	0.04	0.04					
5	0.04	0.06					
10	0.05	0.53					
15	0.07	0.56					
20	0.16	0.82	0.35	0.09	0.08	0.04	0.04
30	0.40	1.00	0.70	0.13	0.17	0.06	0.06
40	0.46	1.24	0.92	0.25	0.24	0.09	0.08
60	0.61	1.31	1.12	0.50	0.41	0.17	0.16

3. Results and discussion

3.1. Effect of LHSV on conversion and sediment formation

By assuming an arbitrary value for the base reaction temperature of 420°C and arbitrary value for the LHSV of 0.25h⁻¹ one can estimate activation energy and the order of reaction from the data of ref. 8 as shown in Figure 3. The best fit for the reaction order is obtained with 1.3 order. This finding is in line with the data obtained from the operation of the LNB H-Oil vacuum residue hydrocracker, where 1.3 order was found to best describe the vacuum residue conversion at reaction temperature of 418°C as reported in [11].

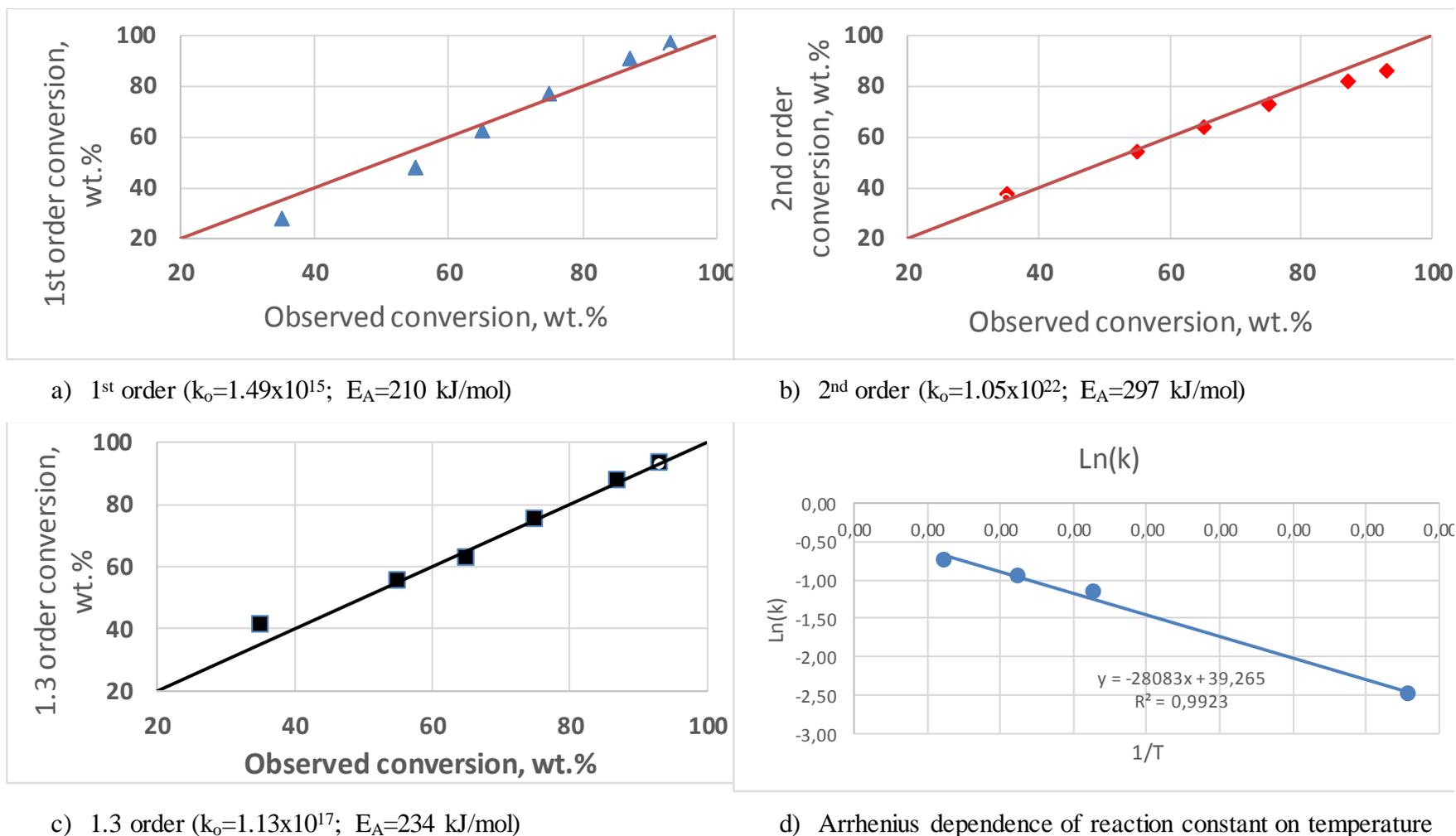
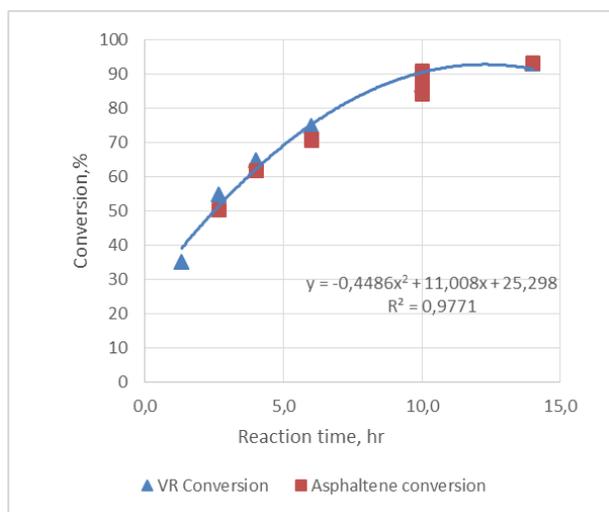
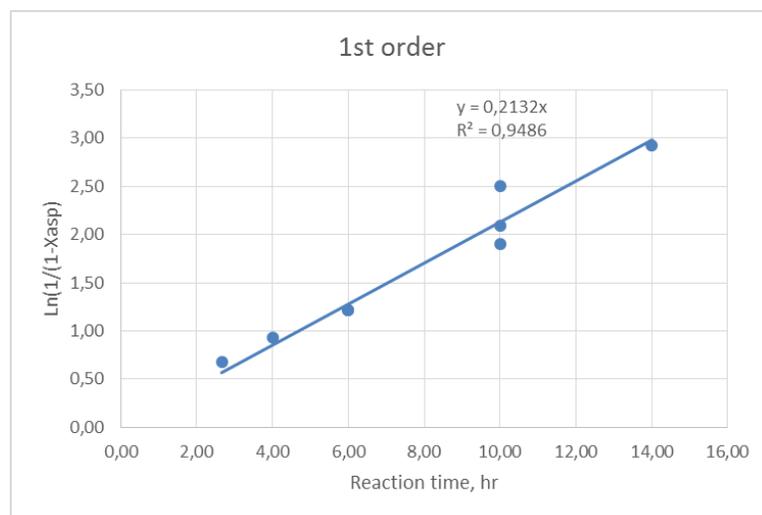


Figure 3. Agreement between observed conversion and 1st order (a), 2nd order (b) and 1.3 order (c) conversion and Arrhenius plot for the dependence of kinetic constant on reaction temperature for the data extracted from ref. 8.

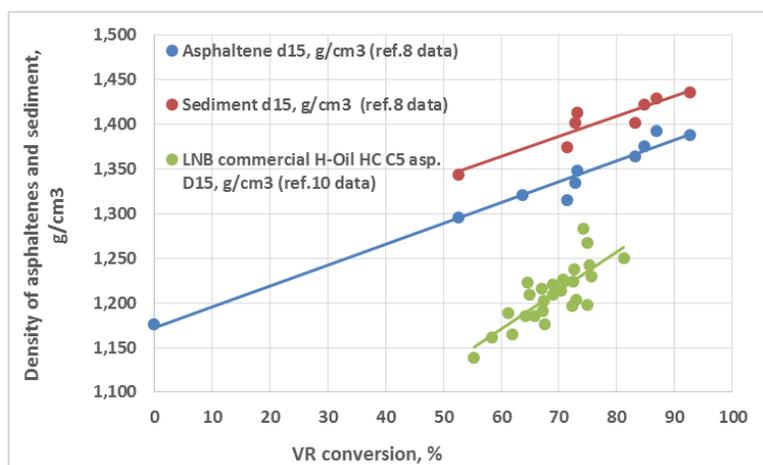


a)

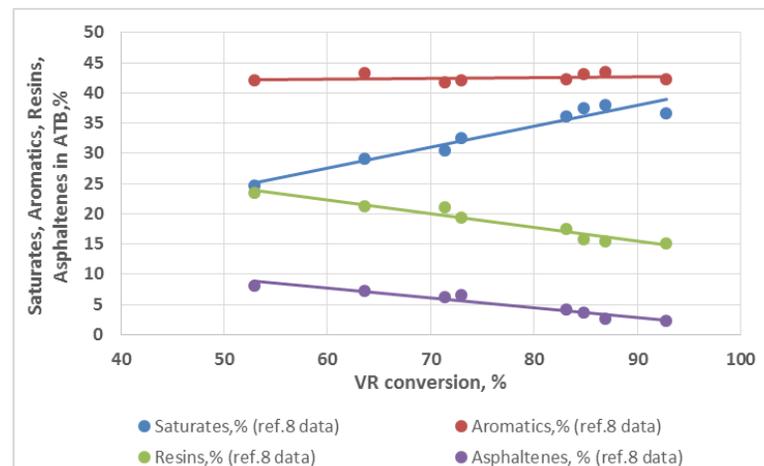


b)

Figure 4 Conversion of vacuum residue and asphaltenes as a function of reaction time (a); 1st order kinetics for asphaltene conversion (This data is extracted from ref.8)



a)



b)

Figure 5 Variation of asphaltene and sediment density (a), and SARA fractions content (b) in the atmospheric tower bottom (ATB) product by increasing conversion

The asphaltene conversion variation with time and the whole vacuum residue conversion with time is presented in Figure 4. The data in Figure 4a indicates that the VR conversion and the asphaltene conversion follow the same trend with variation of reaction time. The best fit for the kinetics of the asphaltene conversion was obtained by the first order (Figure 4 b).

Figure 5 presents graphs of variation of asphaltene and sediment density, and SARA fractions content in the atmospheric tower bottom (ATB) product by increasing conversion (lowering LHSV). The density was estimated from data for H/C atomic ratio of the asphaltenes and the sediments as given in ref. 8, and by the use of the relation of H/C and density established in [12]. The data for the commercial C₅ asphaltene density in Figure 5a are taken from [12]. The data in Figure 5a indicate that the increase of conversion leads to increasing of density of the asphaltenes and of the sediments in both laboratory and commercial vacuum residue hydrocrackers. Sediments are denser than the asphaltenes, which suggests that the sediments are formed from the most hydrogen deficient asphaltenes. The data in Figure 5a supposes that the aromaticity of the asphaltenes goes up with the increase of conversion probably due to cracking of the bridge structures in the asphaltene molecules and releasing of smaller fragments of saturates, mono-, and poly-nuclear aromatics boiling in the distillate range, and leaving the bigger aromatic structures, which have a lower hydrogen content in the unconverted asphaltene fraction [13]. The data in Figure 5b shows that the increase of conversion leads to a decrease of asphaltene content, and of resins content at the expense of saturate content increase in the ATB product. The variation of yields of ATB (>360°C) boiling range saturates, aromatics, resins and asphaltenes with reaction time as depicted in Figure 6 indicates a continuous decrease in the yields of asphaltenes, resins and aromatics. There is no decrease of saturates yield at low reaction times (between 2 and 6 hours) and then small reduction in saturates yield is observed.

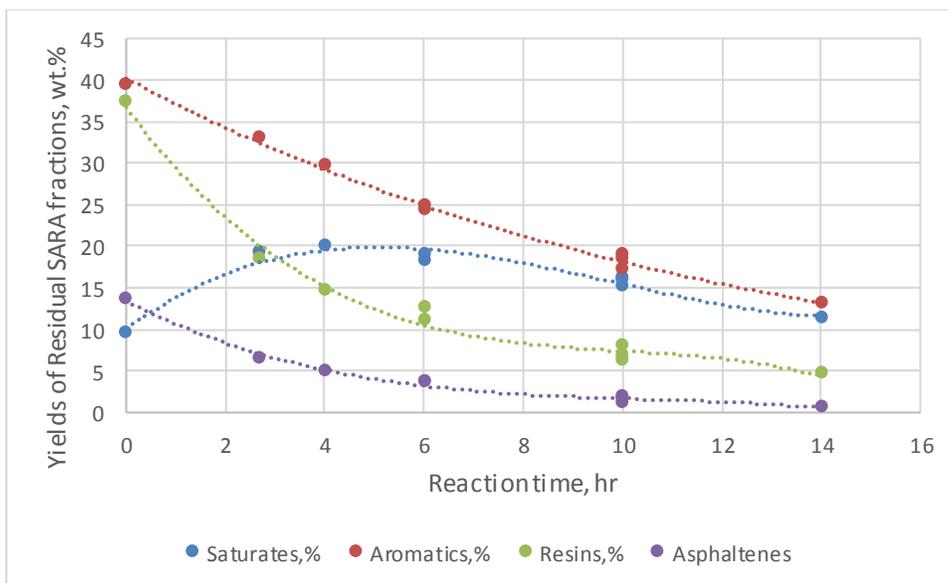


Figure 6. The variation of yields of ATB (>360°C) boiling range saturates, aromatics, resins and asphaltenes with reaction time (This data is extracted from ref.8)

The asphaltenes are converted to resins, saturates, and aromatics with prevalent yields of aromatics in the distillate range (boiling <538°C) as reported in [13-14]. The resins are converted mainly to aromatics [14]. The aromatics are converted to saturates according to the study of Felix and Ancheyta [14]. The increase of the saturate content in the ATB with extending reaction time could be a result of hydrogenation of aromatics and/or of a lower cracking reactivity of the saturates. The content of the aromatics in the ATB did not change because the aromatics were simultaneously formed from the asphaltenes and the resins cracking and depleted by their own cracking, and possibly by their hydrogenation to saturates.

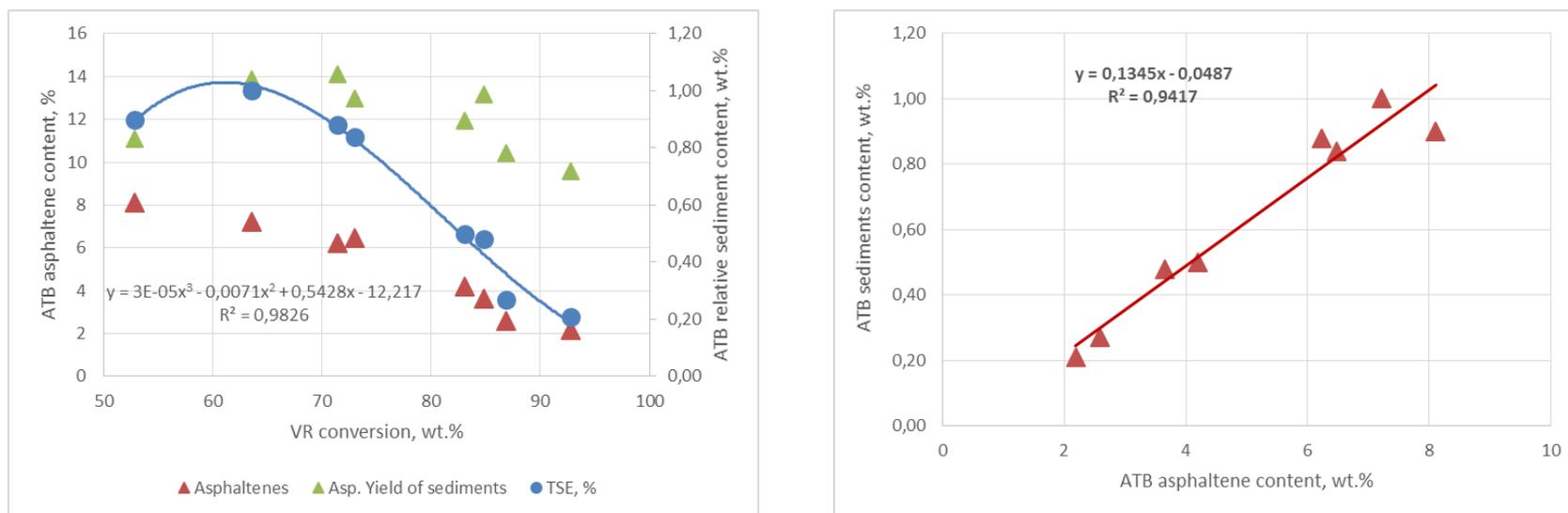


Figure 7. Variation of ATB asphaltene content, and sediment content, the yield of sediments of asphaltenes with conversion (a); and relation of sediments to asphaltene content in the ATB (b). (This data is extracted from ref. 8)

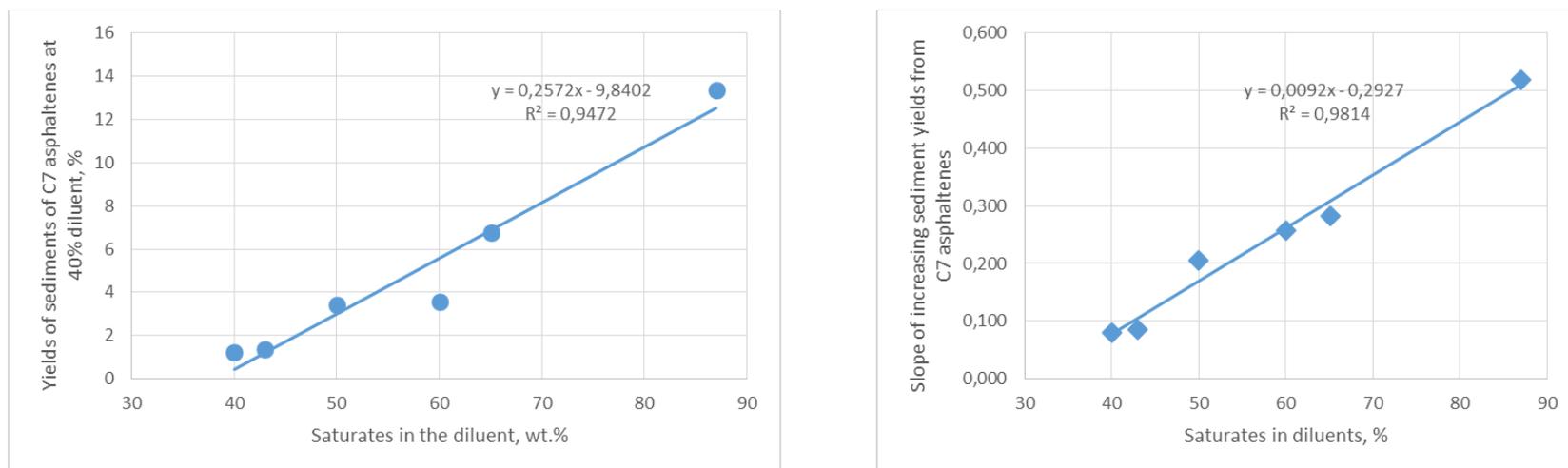


Figure 8. Relation of the yield of sediments of the asphaltenes in LNB H-Oil PBFO to the density of the diluent (a) and relation of the slope of increasing of the yield of sediments of the asphaltenes to the density of the diluent (b)

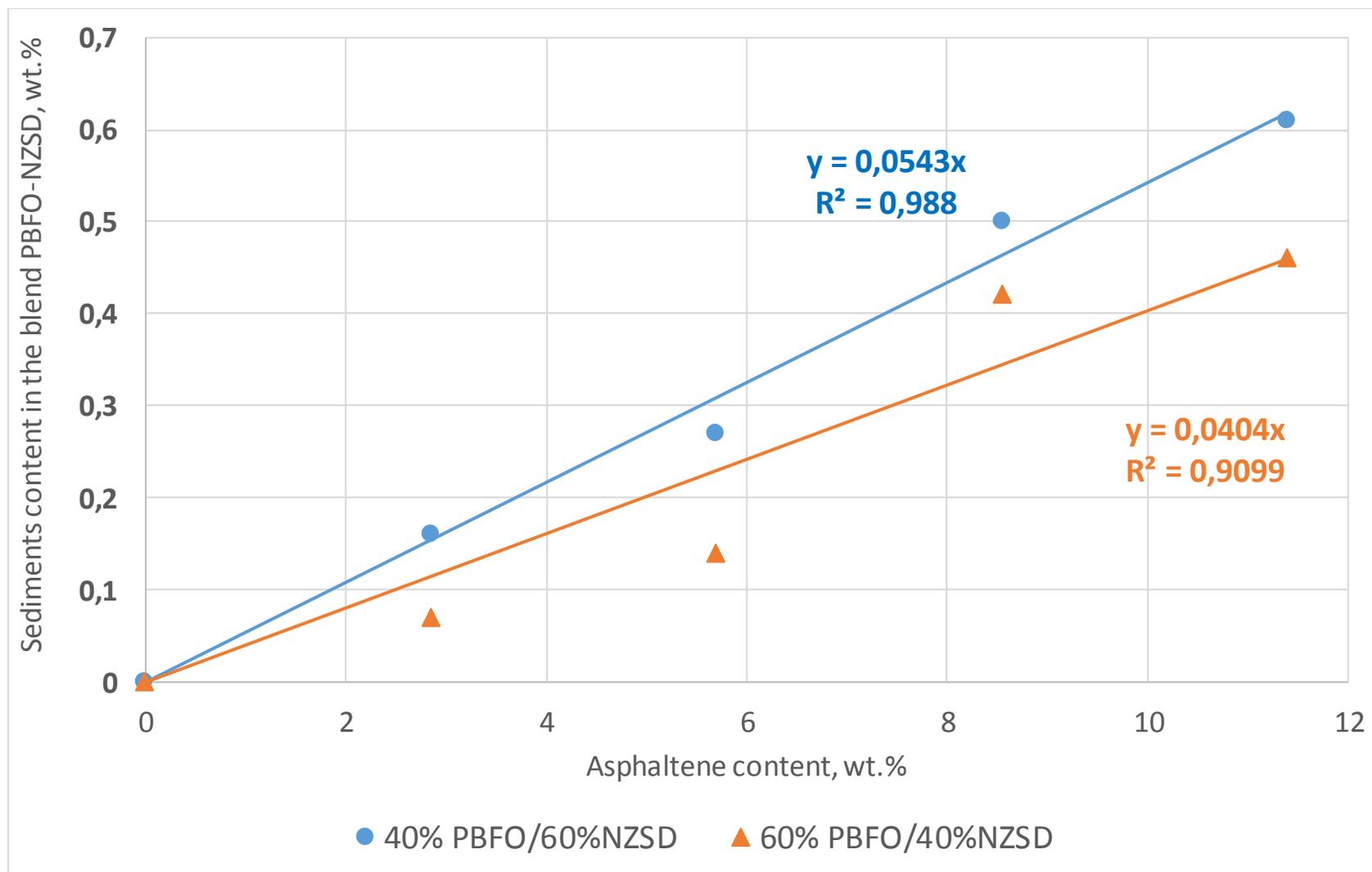


Figure 9. Relation of the asphaltene content in the H-Oil PBFO to the sediment content in the blends 40%PBFO/60% NZSH Diesel and 60%PBFO/40% NZSH Diesel

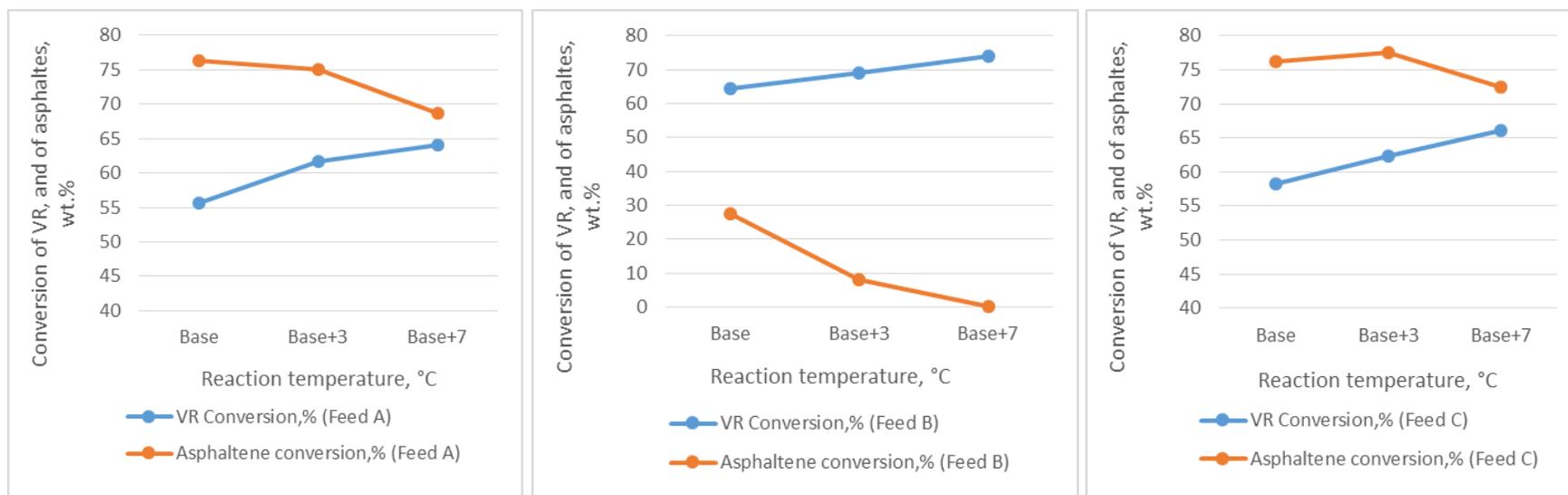


Figure 10. Variation of conversion of vacuum residue and asphaltene with reaction temperature increase for three VROs A (a), B (b), and C (c). (This data is extracted from ref.9)

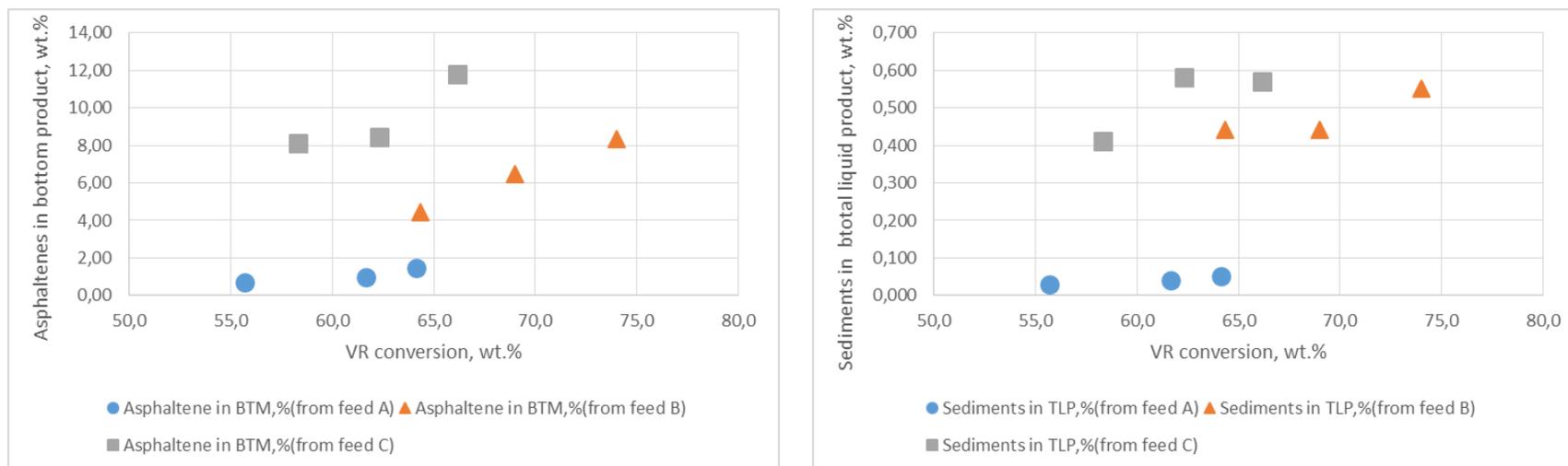


Figure 11. Asphaltene content in the bottom product (a) as a function of conversion and sediment content in the total liquid product (TLP) as a function of conversion. (This data is extracted from ref.9)

Regardless of the higher saturate and lower resins contents that should reflect the colloidal stability of the ATB it was found that the asphaltene content was the only factor that governed the sediment level in the ATB product by running the EBVRHC process at different LHSV (Figure 7). The yield of sediments of asphaltenes as evident from Figure 7a was about 12% (between 10 and 14%), that is 12% of the asphaltenes form sediments. No trend of variation of the yield of coke like sediments from the asphaltenes with the variation of reaction time was observed.

In order to understand the relation of saturates to sediment formation in the EBVRHC oil fractions having different saturate content as shown in Table 3 were added to PBFO, produced from the LNB EBVR H-Oil hydrocracker. As evident from the data in Table 4 the increase of the addition of diluents, which were richer of saturates than the PBFO, to the PBFO led to the sediment increase. The higher the saturate content of the diluent the higher the sediment content in the blend PBFO-diluent was. Understandably the increase of diluent content in the blend PBFO-diluent was related to a decrease of the asphaltene content, since the diluents did not contain asphaltenes. Nevertheless, the sediment content of the blend was higher when a higher amount of diluent was added to the PBFO. Therefore the yield of sediments from the asphaltenes raises with increasing the amount of the higher saturate content diluent in the blend. Figure 8a shows that the increase of the saturate content of the diluent linearly enhances the yield of sediments from the asphaltenes in the blend 60%PBFO/40% diluent. Figure 8b indicates that the slope of increasing of the yield of sediments from the asphaltenes also linearly increases with the saturate content of the diluent. In order to evaluate the effect of asphaltene content on the sediment level in the blends PBFO-diluent the PBFO was deasphalted and the deasphalted PBFO (DAPBFO) was blended with 40% and 60% of NZSH Diesel. The sediment content of both 40%DAPBFO/60% NZSH Diesel and 60%DAPBFO/40% NZSH Diesel was zero proving that the asphaltenes are the main reason for sediment formation in the EBVRHC. The increase of the asphaltene content in the H-Oil PBFO, achieved by blending PBFO with DAPBFO in different ratio, led to a linear enhancement of the sediment content in the blends 40%PBFO/60% NZSH Diesel and 60%PBFO/40% NZSH Diesel as shown in Figure 9. The data in Figure 9 again shows that the higher the amount of the high saturate diluent in the blend PBFO-Diluent, the higher the sediment content of the blend is. The blend 60%PBFO/40% NZSH Diesel has a slope of 0.0543 versus slope of 0.0404 of the blend 40%PBFO/60% NZSH Diesel. The yields of sediments from the asphaltenes from the data in Figure 9 completely fit to the data in Fig.8b. In the case with the increase of saturate content in the ATB with decreasing of LHSV, and enhancement of conversion no increase of sediment yield of asphaltenes was registered (Figures 5b and 7a). A possible explanation for the lack of influence of the increased saturate content on sediment yield of the asphaltenes could lie in the fact that the higher molecular saturates have a lower effect on asphaltene aggregation and consequently on sedimentation [15]. One may conclude that the asphaltene content and the saturate content, that affects the yield of sediments from the asphaltene, are both factors affecting sediment content in the EBVRHC residual oil. As we can see later in this work the nature of the asphaltenes has also a profound effect on the sediment level in the EBVRHC residual oil.

3.2. Effect of reaction temperature on conversion and sediment formation

The sediments formed in the LNB H-Oil hydrocracker as well as those formed in the laboratory EBVRH from ref. 8 are based on the presence of asphaltenes in the EBVRH residual oil products [7-8]. The conversion of asphaltenes as discussed in [14] leads to formation of gas, liquid, and coke like sediments which eventually lead to coke formation. As we saw earlier the conversion of both the whole VRO and the asphaltenes follow the same trend when conversion is increased by decreasing the LHSV (Figure 4a). It is clear that the reactivity of the asphaltenes can be different from the reactivity of the other SARA fractions as reported in [16]. The data in ref. 8 indicate that resins are less reactive than asphaltenes (reaction constant first order = 0.21h^{-1} for the asphaltenes versus 0.17h^{-1} for the resins, if 1st order kinetics is applied for the resins). Besides the hydrocracking of the resins is better described by second order kinetics. The reactivity of the different asphaltenes originating from different residual oils can

also be different as reported in [17]. Therefore the conversion of the asphaltenes could be equal, higher, or lower than that of the whole vacuum residue during EBVRHC. However, the increase of the vacuum residue conversion a result from reaction severity increase should be followed by an enhancement of asphaltene conversion too. If this is not the case and the asphaltene conversion decreases with the reaction severity augmentation when the vacuum residue conversion goes up this would be an indicator that asphaltene recombination may take place. This is what has been seen during catalytic hydrocracking of three VROs during the increase of reaction temperature as shown in Figure 10. The data in Figure 10 shows that for the feed A and C the asphaltenes are more reactive than the whole vacuum residual oil, while for the feed B the asphaltenes are less reactive. It is interesting to note that in the three cases, shown in Figure 10, the increase of the reaction temperature leads to increasing of the VR conversion. However, no increase in the asphaltene conversion is observed with reaction temperature heightening. Reactivity of the three studied feeds A, B, and C, measured by estimating their kinetic constants, assuming second order kinetics, and that the base reaction temperature is equal to 410°C is summarized in Table 5. It is evident from the data in Table 5 that feed B is the most reactive, followed by feed C, and the least reactive is feed A. The feed B is not only the most reactive but also has the highest activation energy, that means that its conversion will raise faster with the reaction temperature increase than the other two feeds. There is a decline in the asphaltene conversion with increasing of the reaction temperature as evident from the data in Figure 10. This is a distinction between the VR conversion increase by decreasing the LHSV and the VR conversion increase by increasing the reaction temperature. In the case with the increasing of the reaction temperature asphaltene recombination may take place. In contrast to the LHSV decreasing mode of operation the reaction temperature raising is associated with asphaltene increasing (Figure 11a) in the bottom product and sediment augmentation in the total liquid product (Figure 11b). From the data in Figure 12 it cannot be said that the increase of conversion by raising the reaction temperature is associated by changing of the yields of sediments from the asphaltenes.

Table 5. Reactivity of the feeds A, B, and C, expressed by their kinetic constants, and activation energies

Kinetic constant	Feed A	Feed B	Feed C
2nd order kinetic constant TRX=410°C)	0.314	0.451	0.350
2nd order kinetic constant TRX=413°C)	0.402	0.556	0.414
2nd order kinetic constant TRX=417°C)	0.447	0.712	0.489
ko	2.09E+14	1.38E+19	5.85E+13
Ea, kJ/mol	193.7	254.8	186.0

What is clear that the tendency of the asphaltenes to form sediments during EBVRHC is different for the three studied feeds, and that the heightening of the reaction temperature and consequently the conversion has not been related to an increased tendency of the asphaltenes to form coke like sediments. Based on this data set a conclusion could be made that the increase of reaction temperature leads to enhancement of VR conversion and concentration of asphaltenes in the bottom product that is related to a higher sediment formation. It should be pointed out here that the tendency of the asphaltene fractions obtained by hydrocracking of SRVROs to form coke like sediments could be different and the processing of feed blends in the EBVRHC could distort the picture shown in Figure 12. Figure 13 presents data for the dependence of the logarithm of the sediments on the logarithm of the reaction temperature obtained during hydrocracking of SRVROs in the pilot plant from ref. 8, assuming that the base reaction temperature = 420°C, in the laboratory unit from ref. 9 assuming that the base reaction temperature = 410°C, in the laboratory unit from ref. 11, and from the commercial LNB EBVR H-Oil hydrocracker

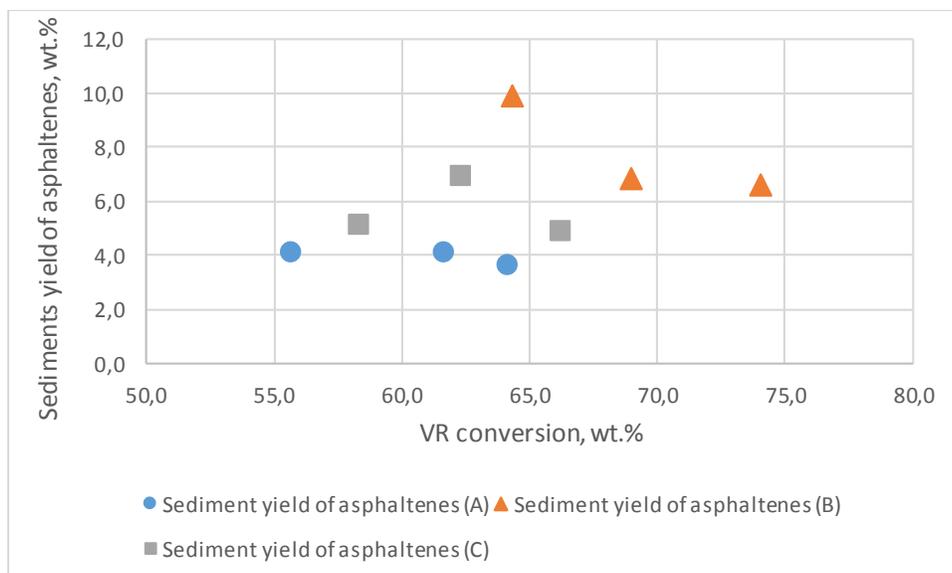


Figure 12. Variation of sediment yield of asphaltene for the three hydrocracked feeds with the increase of conversion by raising the reaction temperature (This data is extracted from ref. 9)

This data indicates an interesting match of the slope of increasing the logarithm of the sediments with the increase of the logarithm of the reaction temperature between the results from hydrocracking of Arab Heavy SRVRO in the pilot plant from ref. 8 (slope=56.3) with the commercial LNB EBVR H-Oil hydrocracker when four different feed blends were processed, a blend of SRVROs from the crudes REBCO, El Bouri and Kazakh Heavy, and the blends 80% REBCO/20% El Bouri, 70% REBCO/30% El Bouri, and 100% REBCO (slope = 56.97). The slopes observed with the three feeds (A, B, and C from ref. 9; Slopes = 32.8; 13.8; and 18.2 respectively) are much lower than those observed in the pilot plant from ref. 8 and in the commercial LNB EBVR H-Oil hydrocracker. The reason for this discrepancy could lie in the type of the reactor employed in ref. 9 (Robinson Mahoney reactor). A similar reactor was used in our earlier study [11] where the slope of sediments increase by raising the reactor temperature was much lower than that observed in the commercial LNB EBVR H-Oil hydrocracker as seen from the data in Figure 13 (The slope for the 100% REBCO VR feed was 56.967 in the commercial H-Oil VR hydrocracker versus 11.146 in the laboratory Robinson Mahoney reactor). Therefore a conclusion could be made that the laboratory Robinson Mahoney reactor could not simulate (it underestimates) the pattern of sediment increase by increasing reaction temperature during vacuum residue hydrocracking. Table 6 summarizes the data for the feed and VTB properties obtained during hydrocracking of different feed blends in the LNB EBVR H-Oil hydrocracker at different reaction temperatures.

This data shows that the increase of reaction temperature by 7°C for the feed blends 80% REBCO/20% El Bouri, and 70% REBCO/30% El Bouri and by 8°C for the feed 100% REBCO the content of asphaltene in the VTBs increases, the content of saturates decreases, and the content of aromatics increases. This is opposite of what has been observed during the increase of conversion by decreasing LHSV (Fig. 5b).

The increase of conversion by raising the reaction temperature leads to a decrease of the concentration of saturates and to an increase of the total amount of aromatic structures in the H-Oil VTB (aromatics+resins+asphaltene). The increase of the reaction temperature has also an effect on the tendency of the asphaltene to form coke like sediments. The tendency of the asphaltene to form coke like sediments goes up with the increase of the reaction temperature. The sediment yield of asphaltene increases from 18.1 to 21.2% for the feed 80% REBCO/20% El Bouri when the reaction temperature increases from 404 to 411°C. The sediment yield of asphaltene increases from 21.1 to 40.4% for the feed 70% REBCO/30% El Bouri for the feed when the reaction temperature increases from 402 to 409°C.

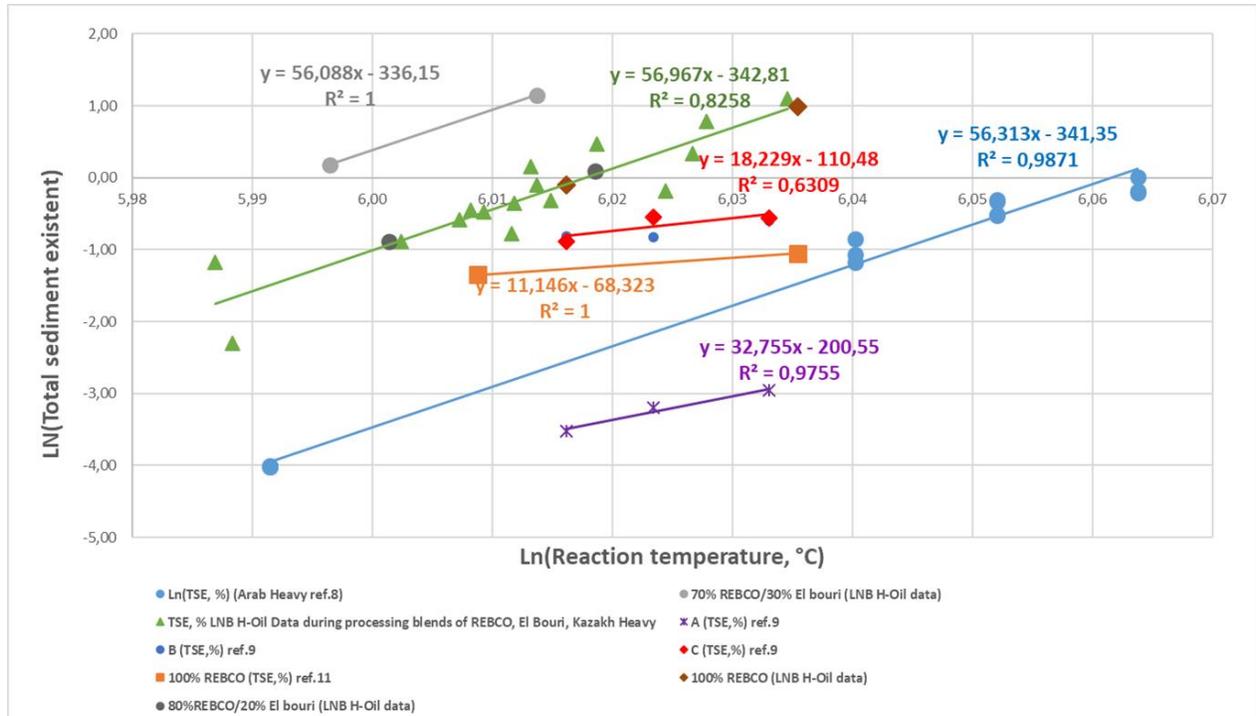


Figure 13. Relation of the logarithm of the sediments to the logarithm of the reaction temperature

Table 6. Data for the feeds and the vacuum tower bottom (VTB) products obtained during hydrocracking of three feed blends in the LNB EBVR H-Oil hydrocracking at different reaction temperatures

H-Oil Feed	80%REBCO/20%El Bouri		70%REBCO/30%El Bouri		100%REBCO		65%REBCO /24%AH/11%AM
TRX, °C	404	411	402	409	410	418	409
Feed hydrogen, wt. %	11.7		11.5	11.3	11.34	11.3	
Feed carbon, wt. %	86.9		86.8	87.7	86.88		
Feed nitrogen, wt. %	0.3		0.3	0.3	0.44	0.4	
Feed Sulphur, wt. %					2.9		
Feed Sat., wt. %	33.1		29.8	25.0	26.5	26.3	22.3
Feed Aro, wt. %	51.3		54.5	59.7	60.1	62.6	61.7
Feed Res., wt. %	9.4		8.0	6.9	7.1	4.8	8.0
Feed Asp., wt. %	6.2		8.5	8.3	6.2	6.3	7.9
VTB Sat., wt. %	52.2	42.0	36.6	33.5	40.2	25.8	25.6
VTB Aro, wt. %	41.9	48.1	51.4	54.9	49.7	56.9	61.6
VTB Res., wt. %	3.7	4.7	4.6	3.7	4.6	5.4	5.6
VTB Asp., wt. %	2.3	5.2	5.7	7.8	5.5	12.0	7.3
VTB TSE, wt. %	0.41	1.10	1.20	3.16	0.90	2.70	0.23
Asp. Yield, wt. %	18.1	21.2	21.1	40.4	16.3	22.6	3.2
Asp. Conversion, %	80.2	69.7	62.0	66.2	66.3	36.4	63.7
VTB hydrogen, wt. %	12.4	12.0	11.73	11.56	11.9	11.0	
VTB carbon, wt. %	88.2		88.39	89.24	88.8		
VTB nitrogen, wt. %	0.2		0.29	0.28	0.3	0.6	
VTB Sulphur, wt. %							
Feed Asp.H, wt. %	7.7		7.4	7.4	7.6		
Feed Asp.C, wt. %	85.1		85.8	86.7	85.3		
Feed Asp.N, wt. %	1.3		1.2	1.3	1.3		
Feed Asp.S, wt. %	2.8		3.8	4.7	3.7		
VTB Asp.H, wt. %	7.7		6.7	6.4	6.4	6.5	
VTB Asp. C, wt. %	90.0		89.9	90.5	89.9	90.0	
VTB Asp. N, wt. %	0.9		1.2	1.3	1.4	1.6	
VTB Asp. S, wt. %	1.3		2.1	2.6	1.7		

The sediment yield of asphaltenes increases from 16.3 to 22.6% for the feed 100% REBCO when the reaction temperature increases from 410 to 418°C. It is worth mentioning here that the tendency of the asphaltenes to form coke like sediments is different for the four different feeds processed in the LNB H-Oil hydrocracker. It increases in the order 65% REBCO/24%AH/11%AM (3.2%) < 100% REBCO (16.3%) < 80%REBCO/20%EIbouri (21.2%) < 70%REBCO/30%EIbouri (40.4%) at a reaction temperature of about 409°C. Therefore the asphaltene content only is not a reliable indicator for prediction of the sediment level in the EBVRHC residual oil. For example the asphaltene content in the VTB for the feed 70%REBCO/30%EIbouri at 409°C reaction temperature is 7.8%, almost the same as that in the VTB obtained for the feed 65% REBCO/24%AH/11%AM at 409°C reaction temperature (7.3%) but the difference in the sediment content is as high as 15 times. Therefore the nature of the asphaltenes has a profound effect on the sediment level in the EBVRHC residual oil. It can be seen from the data in Table 6 that the asphaltenes become more hydrogen deficient (more aromatic) after the hydrocracking. However, this hydrogen deficiency cannot explain the different tendency of the asphaltenes from different origin to form coke like sediments after hydrocracking.

As evident from the data in Table 6 the increase of the reaction temperature is not always associated by a decrease in the asphaltene conversion as the cases with the feeds 100% REBCO and 80%REBCO/20%EIbouri show. However, the augmentation of the asphaltene conversion in the case with the feed 70%REBCO/30%EIbouri is not as high as that of the whole VR conversion enhancement (4.2% asphaltene conversion increase versus 10% VR conversion raise, not shown in Table 6 by heightening the reaction temperature from 402 to 409°C). This suggests that the increase of the reaction temperature promotes the undesired reactions of asphaltene recombination due to the presence of a higher concentration of free asphaltene radicals a result from the higher reaction rate and the same number of available catalytic active sites which are capable of suppressing the asphaltene recombination. This results in a higher concentration of asphaltenes in the unconverted EBVRHC residual oil and in an increased part of the asphaltenes having the tendency to form coke like sediments. Figure 14 shows that the dependence of sediment level in the LNB H-Oil ATB (atmospheric tower bottom) on the reaction temperature is different for the residual oils obtained from the different feed blends.

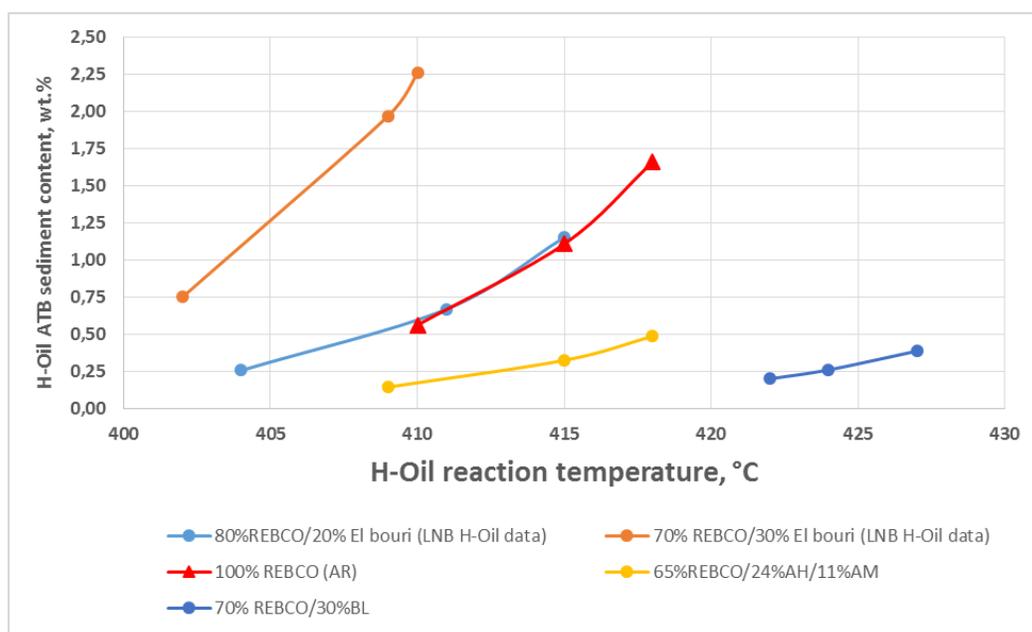


Figure 14. Dependence of H-Oil ATB sediment content on reaction temperature for different feed blends processed at the LNB EBVR H-Oil hydrocracker

Irrespective of the different level of the sediments in these distinct LNB H-Oil ATBs their increment with reaction temperature rising follows the same slope of exponential increase as indicated in eq.3.

$$\ln(ATB \text{ sed. content}) = 56\ln(TRX) + B \quad \text{eq.3}$$

where, ATB sed. content = sediment content in the atmospheric tower bottom, wt.%; TRX = Reaction temperature, °C; B = intercept (it can be calculated from a given set of TRX and ATB sediment content).

Therefore one could estimate the sediment content that a H-Oil residual oil would have at any reaction temperature on the base of data for the H-Oil residual oil sediment content and the reaction temperature at which this sediment content is measured. The improvement of the catalyst condition as shown in in our recent work [7], or delivering additional catalytic active sites, as is the case with the use of nano-catalysts in the EBVRHC [18-19] can allow increasing the reaction temperature without increasing the sediment formation due to promoting the reactions of suppression the sediment formation as is the case with the increase of conversion by decreasing the LHSV.

4. Conclusions

Different pattern of sediment formation is observed when the conversion in an EBVRHC is increased by reaction temperature heightening and LHSV decreasing. The decrease of LHSV is associated by a continuous increase of asphaltene conversion, a decrease of asphaltene and resin content and increase of saturate content in the converted residual oil. The reduction in the residual oil asphaltene content leads to a reduction in its sediment content. The increased saturate content has no effect on the tendency of the asphaltenes to agglomerate and to form coke like sediments most probably because of the lower influence of the higher molecular, higher boiling saturates on the aggregation of the asphaltenes. It was proved that the asphaltenes (C₇ asphaltenes) are the main reason for sediment formation in the EBVRHC residual oils. Their removal leads to zero sediment content in the deasphalted EBVRHC residual oil. By adding lower molecular weight, lower boiling, high saturate content oil fractions to EBVRHC residual oil its sediment content increases linearly with the saturate content of the added oil fraction. The residual oil sediment content also linearly increases with the increase of asphaltene content. The increase of reaction temperature leads to increased sediment content in the EBVRHC residual oil due to concentration of the asphaltenes and due to an increase of their tendency to form coke like sediments. The Robinson Mahoney reactor laboratory EBVRHC unit does not simulate well the process of sediment formation in the commercial EBVRHC unit. It underestimates the slope of sediment increase with the increase of reaction temperature. The asphaltenes coming from different origin demonstrate different behavior during hydrocracking. They exhibit different reactivity, and different tendency to form sediment. During ebullated bed hydrocracking they become more hydrogen deficient. Their conversion could become higher or lower with the increase of reaction temperature but sediment content in the VTB product goes up due to asphaltene concentration and their enhanced tendency to form coke like sediments.

References

- [1] Bridjanian H, Samimi AK. Bottom of the barrel, an important challenge of the petroleum refining industry. *Petroleum and Coal*, 2011; 53(1): 13-21.
- [2] Kumar A, Sinha S. Steady state modelling and simulation of hydrocracking reactor. *Petroleum & Coal*, 2012; 54(1): 59-64.
- [3] Bahmani M, Mohadecy RS, Sadighi S. Pilot plant and modeling study of hydrocracking, hydrodenitrogenation and hydrodesulphurization of vacuum gas oil in a trickle bed reactor. *Petroleum & Coal*, 2009 51 (1), 59-69.
- [4] Bahmani M, Sadighi S, Mashayekhi M, Mohadecy SRS, Vakili D. Maximizing naphtha and diesel yields of an Industrial hydrocracking unit with minimal Changes. *Petroleum & Coal*, 2007; 49(1): 16-20
- [5] Khorasheh F, Zainali H, Chan EC, and Gray MR. Kinetic modeling of bitumen hydrocracking reactions. *Petroleum & Coal*, 2001; 43 (3-4): 208-218.

- [6] Stratiev D, Dinkov R, Shishkova I, Sharafutdinov I, Ivanova N, Mitkova M, Yordanov D, Rudnev N, Stanulov K, Artemiev A, Barova I, Chushkov B. What is behind the high values of hot filtration test of the ebullated bed residue H-Oil hydrocracker residual oils?, *Energy Fuels*, 2016; 30: 7037–7054.
- [7] Stratiev D, Shishkova I, Nikolaychuk E, Anastasov M, Stanulov K, Toteva V. Effect of catalyst condition on sedimentation and conversion in the ebullated bed vacuum residue H-Oil hydrocracking. *Pet. Sci. Technol.*, 2019; 37, 12: 1463-1470.
- [8] Dreillard M, Marques J, Barbier J, Feugnet F. Deep conversion of vacuum residue while limiting sediment formation, *Petrophase Conference - 11th July 2018, The Chateaux at Deer Valley*.
- [9] Nakashima N Update on H-Oil Unit Fouling Mitigation Study, *Criterion EB workshop on Sep 26, 2018, Vancouver, Canada*.
- [10] Stratiev D, Shishkova I, Nikolaychuk E, Dinkov R, Stoilov G, Argirov G, Yankov V, Nedelchev A, Yordanov D, Tankov I, Mitkova M, Ijlstra W, Holmes B, Caillot M. Feed Properties Effect on the Performance of Vacuum Residue Ebullated Bed H-Oil Hydrocracking, *Oil Gas European Magazine*, article in press in.
- [11] Stratiev DS, Dinkov RD, Shishkova IK, Nikolaychuk EV, Mitkova MS, Nikolova R, Yordanov D, Tankov I, Ijlstra W, McNamara D, Nguyen HD, Chapot S Laboratory and commercial investigation of ebullated bed residue hydrocracking performance during processing of Urals crude vacuum resid and its blends with vacuum gas oil and atmospheric residue, *Int. J. Oil, Gas and Coal Technology*, 2019; 22(1): 16-39.
- [12] Stratiev D, Shishkova I, Tsaneva T, Mitkova M, Yordanov D. Investigation of relations between properties of vacuum residual oils from different origin, and of their deasphalted and asphaltene fractions. *Fuel*, 2016; 170: 115–29.
- [13] Karimi A, Qian K, Olmstead WN, Freund H, Yung C, Gray MR. Quantitative evidence for bridged structures in asphaltenes by thin film pyrolysis, *Energy Fuels*, 2011; 25: 3581–3589.
- [14] Félix G, Ancheyta J. Comparison of hydrocracking kinetic models based on SARA fractions obtained in slurry-phase reactor. *Fuel*, 2019; 241: 495–505.
- [15] Ancheyta J, Trejo F, Rana MS. *Asphaltenes: Chemical Transformation during Hydroprocessing of Heavy Oils*, first ed., CRC Press, 2017.
- [16] Fotain PD. *Étude de la réactivité des résidus pétroliers en hydroconversion*, PhD Thesis. l'Université Bordeaux 1 (October 2010).
- [17] Usui K, Kidena K, Murata S, Nomura M, Trisunaryanti W. Catalytic hydrocracking of petroleum-derived asphaltenes by transition metal-loaded zeolite catalysts, *Fuel*, 2004 ; 83 : 1899–1906.
- [18] US patent, US 2017/0081599A1, Publication date: Mar.23, 2017.
- [19] Kunnas J, Smith L. Improving residue hydrocracking performance, *PTQ*, 2011, Q3. www.digit refining.com/article/1000387 .

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