



Article

Crude Slate, FCC Slurry Oil, Recycle, and Operating Conditions Effects on H-Oil[®] Product Quality

Dicho Stoyanov Stratiev ^{1,*}, Ivelina Kostova Shishkova ¹, Rosen Kocev Dinkov ¹, Ivan Petrov Petrov ¹, Iliyan Venkov Kolev ¹, Dobromir Yordanov ², Sotir Sotirov ², Evdokia Nikolaeva Sotirova ², Vassia Krassimirova Atanassova ³, Simeon Ribagin ³, Krassimir Todorov Atanassov ^{2,3}, Danail Dichev Stratiev ³ and Svetoslav Nenov ⁴

¹ LUKOIL Neftohim Burgas, 8104 Burgas, Bulgaria; Shishkova.Ivelina.K@neftochim.bg (I.K.S.); Dinkov.Rosen.K@neftochim.bg (R.K.D.); Petrov.Ivan.P@neftochim.bg (I.P.P.); Kolev.Iliyan.V@neftochim.bg (I.V.K.)

² Intelligent Systems Laboratory, University Prof. Dr. Assen Zlatarov, Professor Yakimov 1, 8010 Burgas, Bulgaria; dobromirj@abv.bg (D.Y.); ssotirov@btu.bg (S.S.); esotirova@btu.bg (E.N.S.); k.t.atanassov@gmail.com (K.T.A.)

³ Institute of Biophysics and Biomedical Engineering, Bulgarian Academy of Sciences, Academic Georgi Bonchev 105, 1113 Sofia, Bulgaria; vassia.atanassova@gmail.com (V.K.A.); sim_ribagin@mail.bg (S.R.); danail.stratiev@gmail.com (D.D.S.)

⁴ University of Chemical Technology and Metallurgy, Kliment Ohridski 8, 1756 Sofia, Bulgaria; s.nenov@gmail.com

* Correspondence: Stratiev.Dicho@neftochim.bg



Citation: Stratiev, D.S.; Shishkova, I.K.; Dinkov, R.K.; Petrov, I.P.; Kolev, I.V.; Yordanov, D.; Sotirov, S.; Sotirova, E.N.; Atanassova, V.K.; Ribagin, S.; et al. Crude Slate, FCC Slurry Oil, Recycle, and Operating Conditions Effects on H-Oil[®] Product Quality. *Processes* **2021**, *9*, 952. <https://doi.org/10.3390/pr9060952>

Academic Editor: Farid B. Cortés

Received: 7 April 2021

Accepted: 25 May 2021

Published: 27 May 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: This paper evaluates the influence of crude oil (vacuum residue) properties, the processing of fluid catalytic cracking slurry oil, and recycle of hydrocracked vacuum residue diluted with fluid catalytic cracking heavy cycle oil, and the operating conditions of the H-Oil vacuum residue hydrocracking on the quality of the H-Oil liquid products. 36 cases of operation of a commercial H-Oil[®] ebullated bed hydrocracker were studied at different feed composition, and different operating conditions. Intercriteria analysis was employed to define the statistically meaningful relations between 135 parameters including operating conditions, feed and products characteristics. Correlations and regression equations which related the H-Oil[®] mixed feed quality and the operating conditions (reaction temperature, and reaction time (throughput)) to the liquid H-Oil[®] products quality were developed. The developed equations can be used to find the optimal performance of the whole refinery considering that the H-Oil liquid products are part of the feed for the units: fluid catalytic cracking, hydrotreating, road pavement bitumen, and blending.

Keywords: ebullated bed hydrocracking; vacuum residue; atmospheric residue; intercriteria analysis; petroleum; H-Oil[®] product properties

1. Introduction

The ebullated bed vacuum residue H-Oil[®] hydrocracking proved commercially to be able of achieving 93% conversion of vacuum residue into gas (15.2%), naphtha (10.2%), diesel (47.2%), vacuum gas oil (25.1%), and unconverted hydrocracked vacuum residue, also known as vacuum tower bottom product (VTB) (5.85%) [1,2]. However, the naphtha, the diesel, the vacuum gas oil, and the VTB from H-Oil[®] are not finished marketable products and they require further processing. The naphtha and the diesel are hydrotreated to near zero sulphur level. The vacuum gas oil (VGO) is catalytically cracked. It was found that the properties of the H-Oil[®] VGO varied in a wide range, depending on H-Oil[®] feed structure and operation severity which affected the H-Oil[®] VGO reactivity during its processing in the fluid catalytic cracking (FCC) [3,4]. The H-Oil[®] feed structure consisted of straight run vacuum residue, FCC slurry oil (SLO) and recycle of partially blended fuel oil (PBFO). The PBFO is prepared from around 70% VTB and 30% FCC heavy cycle oil (HCO).

The VTB, is blended with cutter stocks (FCC cycle oils) to produce heavy fuel oil and it is also used as a feed component for production of road asphalt [5,6]. It was found that the properties of the VTB also varied in a wide range, depending on the crude blend processing and on the H-Oil[®] feed structure and operation severity [1]. This variation in VTB quality affects the processes of production of heavy fuel oil and road asphalt [5,6]. In an extreme case, the properties of the VTB were identical with those of asphaltenes produced from commercial deasphaltization units as reported by Naghizada et al. [7]. Considering the wide range of variation of the properties of the H-Oil[®] VGO and VTB, which influenced the performance of the other refinery units, their dependence on fluctuation of crude slate, the H-Oil[®] feed structure and H-Oil[®] operating conditions requires investigation in order to optimize the refinery performance. Besides, the lack of information about the properties variation of H-Oil[®] naphtha and diesel as a function of crude slate, the H-Oil[®] feed structure and H-Oil[®] operating conditions was another incentive to perform this study.

The aim of this work is to define how the crude slate, the FCC SLO, and the PBFO recycle processing, and the unit operating conditions affect the quality of naphtha, diesel, VGO, and VTB obtained in the LUKOIL Neftohim Burgas (LNB) refinery commercial H-Oil[®] hydrocracker.

2. Results and Discussion

Investigations have shown that density and Kw (Watson characterization factor) of heavy oils very well correlate with their contents of saturates [1,8], hydrogen, and aromatic carbon [9–11]. Therefore, density and Kw can be used as indicators for aromaticity and hydrogen deficiency of the heavy oils. Figure 1 presents graphs of the relations of density with Kw, and hydrogen content of the mixed H-Oil[®] feed, straight run vacuum residual oils (SRVROs), and H-Oil[®] atmospheric tower bottom product (ATB), and VTB. These data show a very strong relation between density, Kw, and hydrogen content for the H-Oil[®] ATB, and VTB, and a weaker relation for the SRVROs, and the H-Oil[®] mixed feed. The mixed feed demonstrates a lower slope of decreasing of Kw with enhancement of density than the SRVROs. Since Kw depends on average boiling and density [9] this phenomenon can be explained with a lower average boiling point of the mixed feed. The addition of FCC SLO and recycle of partially blended fuel oil (PBFO) to the straight run vacuum residue indeed decreases the average boiling point of the mixed feed. It is difficult to find a reasonable explanation why the correlations of Kw, density and hydrogen content for the H-Oil[®] residual oil products ATB, and VTB are stronger than those of the mixed feed, and the SRVROs.

The relations between 135 characterizing parameters for the 36 studied cases were investigated by the use of intercriteria analysis (ICrA). More information about the application of ICrA the reader can find in our recent studies [1,3]. ICrA defines the values of positive and negative consonance (μ) of the studied criteria (parameters) [1,3]. The meaning of $\mu = 0.75 \div 1.00$ denotes a statistically meaningful positive relation, where the strong positive consonance exhibits values of $\mu = 0.95 \div 1.00$, and the weak positive consonance exhibits values of $\mu = 0.75 \div 0.85$. Respectively, the values of negative consonance with $\mu = 0.00 \div 0.25$ means a statistically meaningful negative relation, where the strong negative consonance exhibits values of $\mu = 0.00 \div 0.05$, and the weak negative consonance exhibits values of $\mu = 0.15 \div 0.25$ [1,3].

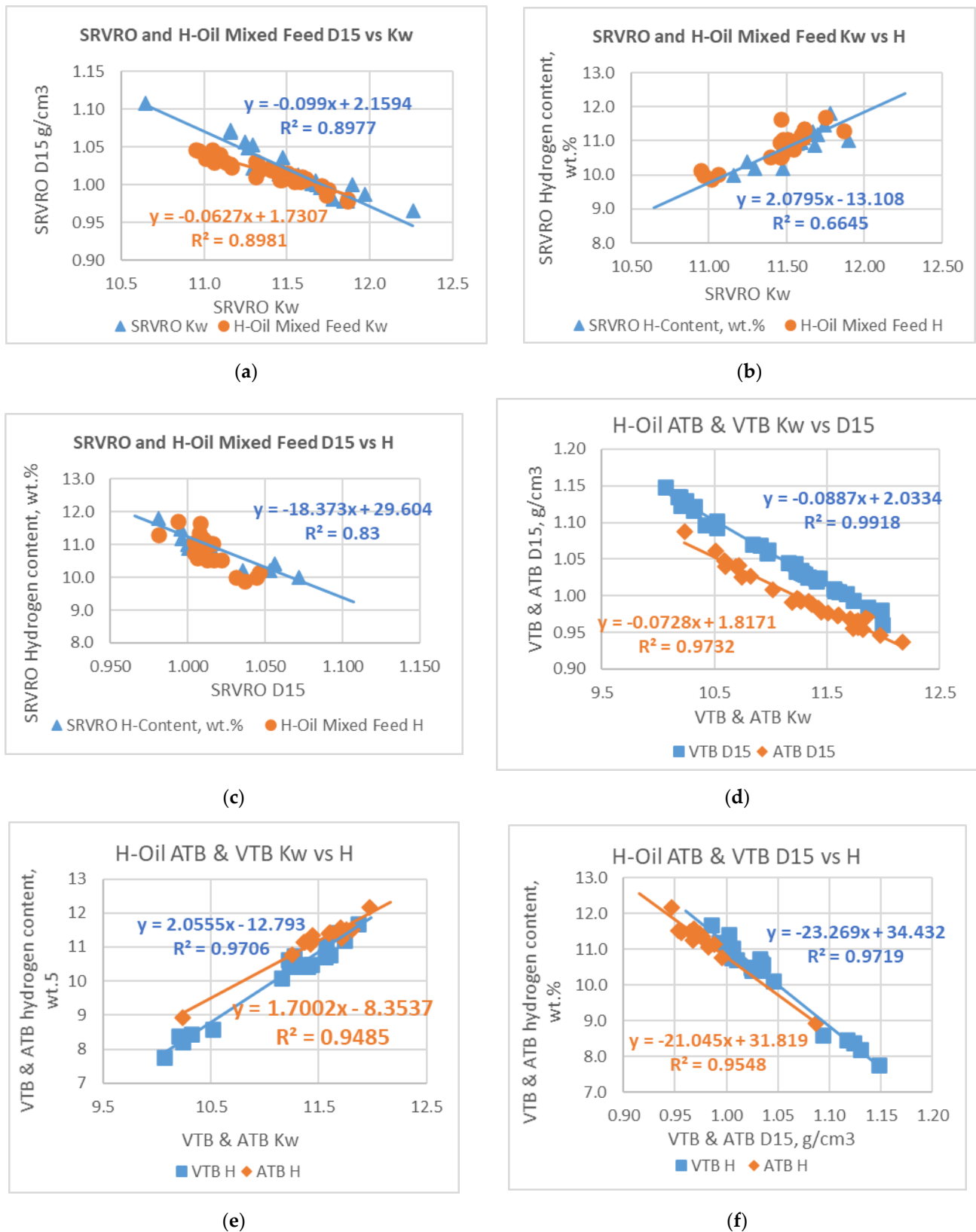


Figure 1. Correlations of Kw, density, and hydrogen content of H-Oil[®] mixed feed (a–c) SRVRO (a–c), and of H-Oil[®] ATB, and VT B (d–f).

The data in Table 1 confirm that for the studied 36 cases the density, and the Kw are equivalent substitutes of the contents of aromatic carbon, and hydrogen content for the H-Oil[®] gas oils. The consonances μ of Kw and aromatic carbon content for HAGO (heavy

atmospheric gas oil), LVGO (light vacuum gas oil), and HVGO (heavy vacuum gas oil) are 0.00. The consonances μ of density and hydrogen content for HAGO, LVGO, and HVGO are also 0.00. The average number of aromatic rings predicted by the aromatic ring index (ARI) strongly correlates with density of HAGO, LVGO, and HVGO ($\mu = 0.98$ – 0.99). The ARI of H-Oil[®] gas oils was found to affect conversion and coke yield during catalytic cracking of H-Oil[®] heavy oils [3].

Table 1. μ -value of ICRA for the evaluation of relations between H-Oil[®] gas oils parameters contents of aromatic carbon, and hydrogen, and density, and molecular weight.

	HAGO Kw	HAGO ARI	HAGO C _A	HAGO H	HAGO D15	LVGO D15	LVGO Kw	LVGO C _A	LVGO H	LVGO ARI	HVGO Kw	HVGO C _A	HVGO H	HVGO D15	HVGO ARI
HAGO Kw	1.00														
HAGO ARI	0.05	1.00													
HAGO C _A	0.00	0.96	1.00												
HAGO H	0.99	0.02	0.00	1.00											
HAGO D15	0.02	0.99	0.99	0.00	1.00										
LVGO D15	0.02	0.97	0.99	0.01	0.99	1.00									
LVGO Kw	0.99	0.08	0.02	0.97	0.03	0.02	1.00								
LVGO C _A	0.01	0.94	0.99	0.02	0.98	0.99	0.00	1.00							
LVGO H	0.99	0.04	0.01	0.99	0.01	0.00	0.99	0.00	1.00						
LVGO ARI	0.05	0.98	0.96	0.03	0.98	0.98	0.07	0.95	0.03	1.00					
HVGO Kw	0.93	0.11	0.07	0.93	0.02	0.04	0.97	0.03	0.96	0.11	1.00				
HVGO C _A	0.07	0.90	0.93	0.07	0.93	0.96	0.03	0.97	0.03	0.90	0.00	1.00			
HVGO H	0.93	0.09	0.06	0.94	0.06	0.04	0.97	0.03	0.97	0.09	0.99	0.00	1.00		
HVGO D15	0.07	0.91	0.94	0.06	0.94	0.97	0.03	0.97	0.03	0.92	0.01	1.00	0.00	1.00	
HVGO ARI	0.06	0.94	0.95	0.04	0.96	0.97	0.05	0.96	0.03	0.94	0.06	0.05	0.03	0.98	1.00

Table 2 presents the range of variation of the properties of the mixed feed and of the products: naphtha, diesel, heavy atmospheric gas oil (HAGO), light vacuum gas oil (LVGO), heavy vacuum gas oil (HVGO), ATB, and VTB for the studied 36 cases. These data indicate that the properties of mixed feed and of the liquid products vary in a rather wide range. Properties of the liquid products from H-Oil[®] are important because they control the reactivity of these streams during their further refining in processes like FCC and hydrotreatment [3,4,12,13] to produce finished marketable products. It was found in our earlier studies that the lower the Kw of H-Oil[®] gas oils the lower their crackability in FCC is [3]. The higher the density, and the aromatics content in the H-Oil[®] diesel the lower its reactivity during hydrotreatment [12–14]. It was reported in [1] and in [5,6,15] that the properties of H-Oil[®] VTB affect the process of production of road asphalt whose feed contains H-Oil[®] VTB. Therefore, understanding the factors controlling H-Oil[®] liquid products properties can allow optimization of the whole refinery performance.

Table 2. Variation in the properties of liquid H-Oil[®] EBVRHC products.

H-Oil Liquid Products Properties	Range	Mixed Feed	Naphtha	Diesel	ATB	HAGO	LVGO	HVGO	VTB
Sulphur, wt. %	Min	2.55	0.02	0.08	0.59	0.36	0.41	0.50	0.94
	Max	3.92	0.04	0.27	1.36	0.76	0.89	1.17	2.21
Density at 15 °C, g/cm ³	Min	0.979	0.698	0.841	0.915	0.899	0.902	0.921	0.961
	Max	1.046	0.727	0.875	1.087	0.958	0.985	1.013	1.148
Kw-characterizing factor	Min	10.9	12.0	11.4	10.2	11.1	10.9	10.9	10.1
	Max	11.9	12.5	12.1	12.2	11.9	11.9	12.0	12.0
Diesel Cetane Index	Min	-	-	38.2	-	-	-	-	-
	Max	-	-	67.1	-	-	-	-	-
Hydrogen content, wt. %	Min	9.9	-	-	8.9	11	10.3	9.8	7.8
	Max	11.7	-	-	12.2	12.6	12.5	12.2	11.7
Micro carbon residue, wt. %	Min	12	-	-	-	-	-	-	17.9
	Max	23.6	-	-	-	-	-	-	45.6
C ₅ asphaltenes, wt. %	Min	9.3	-	-	-	-	-	-	21.8
	Max	28.5	-	-	-	-	-	-	91
C ₇ asphaltenes, wt. %	Min	7.2	-	-	2.7	-	-	-	12.1
	Max	26.7	-	-	17.3	-	-	-	67
Nitrogen content, wt. %	Min	0.21	-	-	0.34	-	-	-	0.36
	Max	0.52	-	-	0.61	-	-	-	0.86
Nickel, ppm	Min	38	-	-	-	-	-	-	19
	Max	75	-	-	-	-	-	-	84
Vanadium, ppm	Min	110	-	-	-	-	-	-	39
	Max	245	-	-	-	-	-	-	191
Sodium, ppm	Min	12	-	-	-	-	-	-	7
	Max	41	-	-	-	-	-	-	95
Iron, ppm	Min	4	-	-	-	-	-	-	0.3
	Max	69	-	-	-	-	-	-	113
Diesel Mono-Aromatic Hydrocarbons, wt. %	Min	-	-	-	21.9	-	-	-	-
	Max	-	-	-	37.6	-	-	-	-
Diesel Di-Aromatic Hydrocarbons, wt. %	Min	-	-	-	3.9	-	-	-	-
	Max	-	-	-	10.9	-	-	-	-
Diesel Tri-Aromatic Hydrocarbons, wt. %	Min	-	-	-	0.7	-	-	-	-
	Max	-	-	-	12.2	-	-	-	-
MW, g/mol	Min	492	-	-	323	271	286	343	482
	Max	683	-	-	583	341	348	440	737
C _A , wt. %	Min	-	-	-	-	17.4	19	18.1	-
	Max	-	-	-	-	36	42.5	45.4	-
Aromatic ring index	Min	4.1	-	-	1.6	1.3	1.4	1.9	3.5
	Max	5.4	-	-	4.3	2.1	2.5	3.4	6.5

Table 3 shows some of the statistically meaningful relations between the H-Oil[®] feed properties, H-Oil[®] operating conditions and H-Oil[®] product properties established by the use of ICRA. It is evident from these data that the H-Oil[®] mixed feed Kw very strongly correlates with VTB density; ATB Kw, and HVGO Kw. The influence of the H-Oil[®] mixed feed Kw on the LVGO, HAGO, and diesel Kw factors decreases with reduction of molecular weight (average boiling point) of these three products (Figure 2). Figure 2 shows that there is a dependence of the consonance of mixed feed Kw and Kw of H-Oil[®] liquid products: diesel, HAGO, LVGO, HVGO, ATB, and VTB on the average boiling point of the liquid products. These data indicate that quality of the H-Oil[®] mixed feed affects mostly the quality of the hydrocracked heavy oil products, and the lighter products like diesel are weaker dependent on the H-Oil[®] residual feedstock quality, while the naphtha quality is not affected at all from the H-Oil[®] feed quality. The lighter products like diesel and naphtha are primary and secondary products and the secondary cracking reactions most probably decrease the dependence of their quality on the original vacuum residue feedstock quality.

Table 3. Some statistically meaningful relations (μ -value) between the H-Oil[®] feed properties, H-Oil[®] operating conditions and H-Oil[®] product properties established by the use of Intercriteria analysis.

	FR	WABT	Rec.	VTB D15	Diesel Kw	HAGO Kw	LVGO Kw	HVGO Kw	ATB Kw	Feed Kw
FR	1.00	-	-	-	-	-	-	-	-	-
WABT	0.43	1.00	-	-	-	-	-	-	-	-
Rec.	0.33	0.55	1.00	-	-	-	-	-	-	-
VTB D15	0.29	0.87	0.75	1.00	-	-	-	-	-	-
Diesel Kw	0.79	0.22	0.46	0.22	1.00	-	-	-	-	-
HAGO Kw	0.68	0.08	0.48	0.14	0.82	1.00	-	-	-	-
LVGO Kw	0.72	0.10	0.50	0.08	0.79	0.99	1.00	-	-	-
HVGO Kw	0.74	0.11	0.21	0.07	0.78	0.93	0.97	1.00	-	-
ATB Kw	0.73	0.13	0.19	0.04	0.77	0.86	0.94	0.96	1.00	-
Feed Kw	0.72	0.12	0.22	0.00	0.79	0.87	0.92	0.95	0.97	1.00

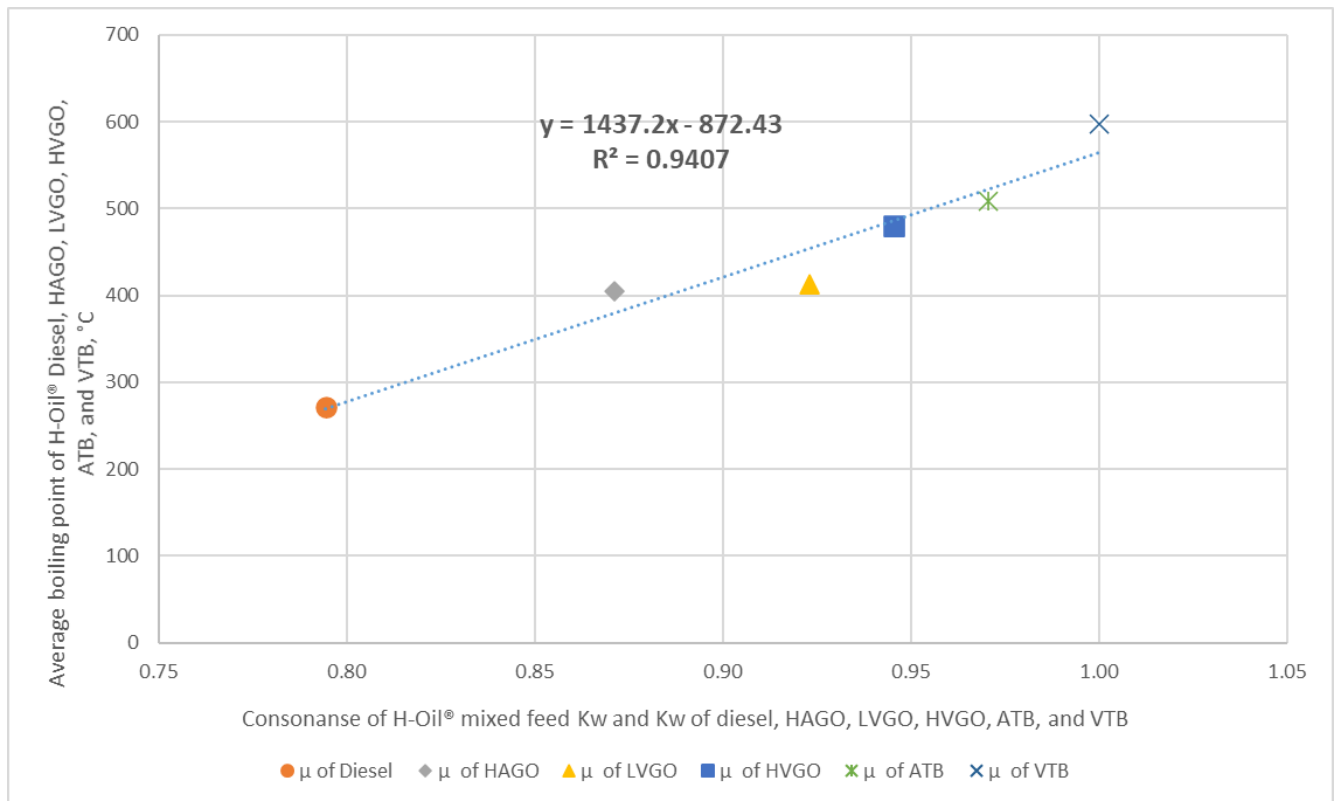


Figure 2. Dependence of the consonance of mixed feed Kw and Kw of H-Oil[®] liquid products on the average boiling point of the liquid products.

The data in Table 3 show that the mixed H-Oil[®] feed quality expressed by Kw controls the H-Oil[®] VTB properties since it is known that the H-Oil[®] VTB density strongly correlates with Concarbon (micro carbon) content [1] and as we will see later in this work it also correlates with softening point and viscosity. Thus, quality of the H-Oil[®] VTB will be strongly affected by the Kw of the feed, and from crudes which contain vacuum residue fractions with a lower Kw may be expected during H-Oil[®] hydrocracking to be produced VTB with a higher density. Figure 3 presents a graph of the Kw of the blended SRVROs, of the mixture blended SRVROs—FCC SLO, and of the mixed H-Oil[®] feed for the studied

36 cases. The blended SRVRO Kw was calculated on the base of Kw of the individual SRVROs originated from the different crude oils by the use of Equation (1) [16]:

$$Kw_{mix} = \sum_{i=1}^n X_i \cdot Kw_i \quad (1)$$

where:

Kw_{mix} = Watson characterization factor of the mixture;

X_i = weight fraction of i th pure component in the mixture;

Kw_i = Watson characterization factor of the of i th pure component in the mixture.

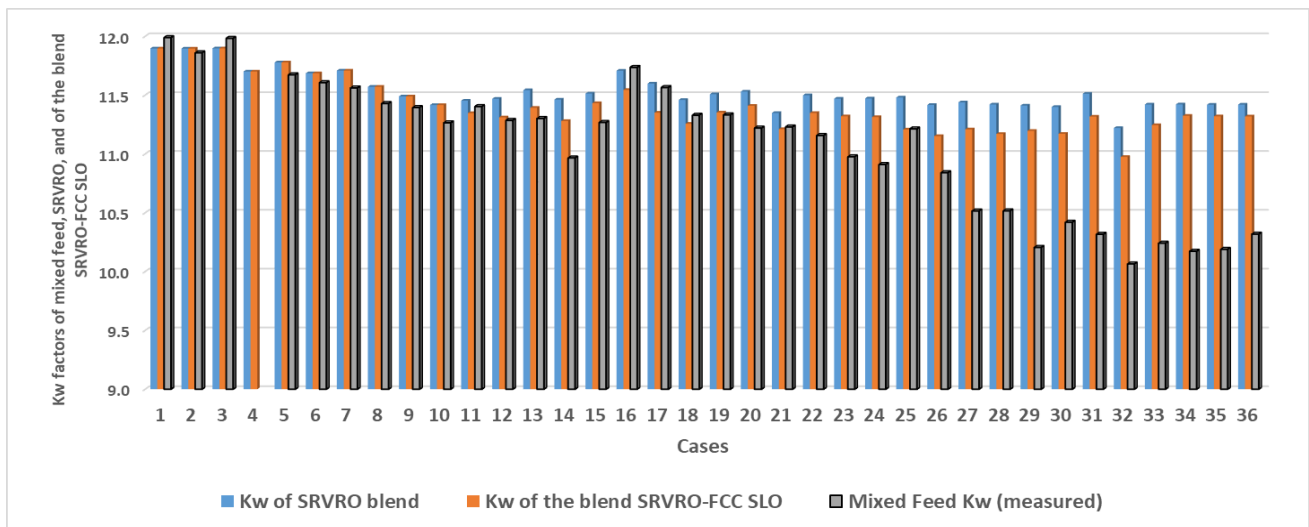


Figure 3. Kw for the blended SRVROs, the mixture SRVRO-FCC SLO, and for the mixed feed.

The Kw of the mixture blended SRVROs—FCC SLO was computed by Equation (10) and the calculated Kw of the blended SRVROs, and the Kw of FCC SLO that varied between 9.6 and 9.8.

It is evident from the data in Figure 3 that the Kw of the mixed H-Oil[®] feed gradually decreases from Case 1 to Case 36. The blended SRVROs Kw for the studied 36 cases varied between 11.90 (Kw of Urals crude oil, the main crude oil for LNB refinery for this study) and 11.22 (Kw of the crude oil blend 41%Urals/34.5%Kirkuk/24.5%El Bouri; Case 32). The lowest Kw of the mixture blended SRVROs—FCC SLO was that of Case 32 and it was 10.97. The lowest Kw of the mixed H-Oil[®] feed was that of case 32, and it was 10.07. As apparent from the data in Figure 4 the sum of the FCC SLO and the recycle of PBFO can reach 43% of the fresh blended SRVRO feed. Considering that it has a substantially lower Kw (9.7 for FCC SLO, and 10.4 for the PBFO) it becomes clear that its effect on the mixed H-Oil[®] feed Kw will be appreciable. By the use of multiple linear regression for the studied 36 cases two equations were obtained relating Kw factors of FCC SLO and PBFO recycle to H-Oil[®] mixed feed Kw (Equation (2)), and Equation (3) that relates besides Kw factors of FCC SLO and PBFO recycle, and Kw of the blended SRVROs to the H-Oil[®] mixed feed Kw.

$$HOil \text{ mixed feed Kw} = 11.62 - 0.0253FCCSLO - 0.0142Rec. \quad (2)$$

R = 0.876, rel. av. error = 0.80%

$$HOil \text{ mixed feed Kw} = 1.43 + 0.866SRVROKw - 0.0206FCCSLO - 0.0137Rec. \quad (3)$$

R = 0.876, rel. av. error = 0.74%

where:

$SRVROKw$ = Kw of blended SRVROs originated from the processed crude oil blend;

$FCCSLO$ = per cent of FCC SLO in the H-Oil[®] mixed feed, wt.%;

Rec. = per cent of recycle of PBFO in the H-Oil[®] mixed feed, wt.%.

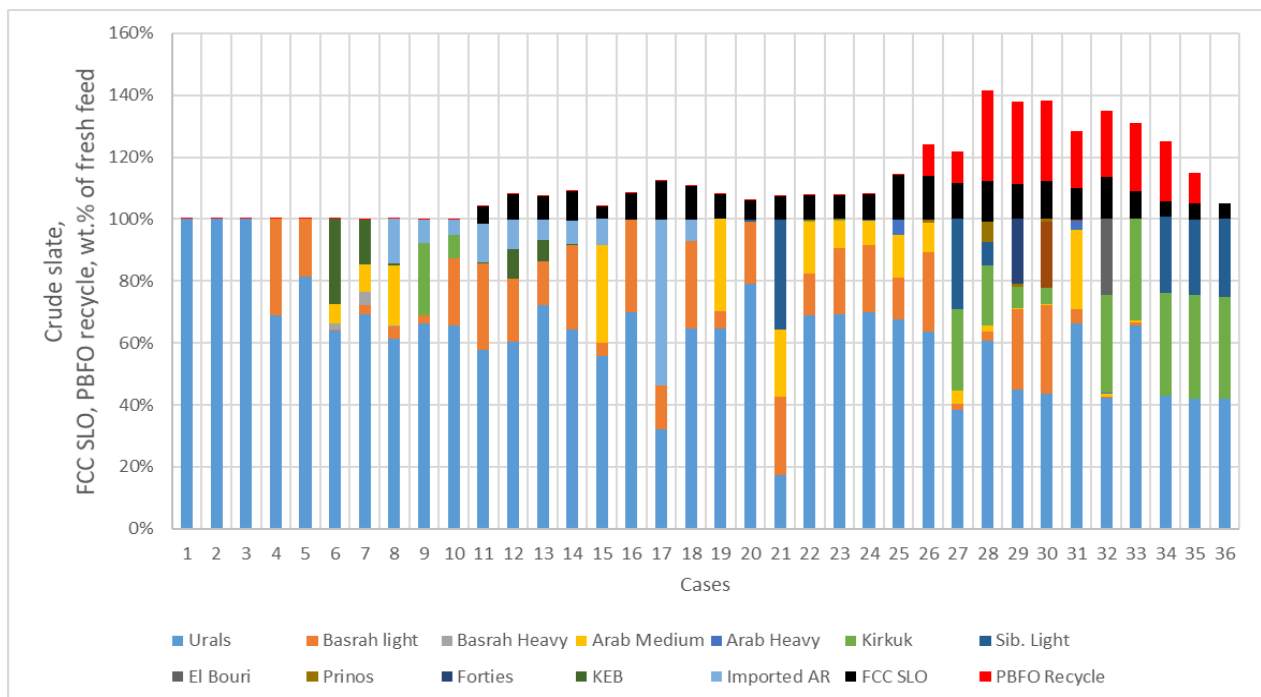


Figure 4. Crude slate processing, FCC SLO and Recycle of VTB share in the H-Oil[®] feed.

Equations (2) and (3) exhibit that for the studied 36 cases the H-Oil[®] mixed feed Kw predominantly depends on the shares of FCC SLO and of PBFO recycle. Understandably the FCC SLO has a bigger negative impact on the H-Oil[®] mixed feed Kw than that of the recycle because the FCC SLO has a lower Kw than that of the recycle. The influence of the blended SRVROs Kw on the H-Oil[®] mixed feed Kw seems to be negligible, because after inclusion of the blended SRVROs Kw in Equation (3) the relative average error of Equation (3) is slightly improved in comparison with that of Equation (2) (from 0.80 down to 0.74%).

The relation of the H-Oil[®] mixed feed to VTB density can be expressed by Equation (4)

$$VTB D15 = -0.178FeedKw + 3.074 \quad (4)$$

$$R = 0.992, \text{ av. rel. error} = 0.3\%$$

Interestingly the data in Table 3 also show that the feed Kw statistically meaningful intermediary negatively correlates with the hydrocracking reaction temperature. This at first glance strange correlation can be explained with the fact that the higher Kw vacuum residual oil feeds are lighter, and contain more saturates which negatively impact colloidal stability of the H-Oil[®] feed and as a consequence require lower reaction temperature to keep the ATB sediment content within the acceptable limits [1].

In order to evaluate the influence of H-Oil[®] unit through-put, hydrocracking reaction temperature, and shares of FCC SLO, and of PBFO recycle in the H-Oil[®] mixed feed on HVGO quality expressed by the Kw a multiple linear regression of the data was performed. Equation (5) shows the developed relation.

$$HVGOKw = 24.34 + 0.000841FR - 0.03034WABT - 0.004FCCSLO - 0.01326Rec. \quad (5)$$

$$R = 0.96, \text{ rel. av. error} = 0.68\%$$

where:

$$FR = \text{H-Oil}^{\text{®}} \text{ unit trough-put, t/h;}$$

$WABT$ = average weight average bed temperature of both reactors in LNB H-Oil[®] unit, °C.

Equation (5) indicates that HVGO Kw increases with enhancement of throughput, and reduction of reaction temperature, FCC SLO, and PBFO recycle contents in the mixed feed. Increasing H-Oil[®] feed rate decreases reaction time, that in turn diminishes the secondary cracking reactions and as a consequence a higher amount of aliphatic hydrocarbons from the HVGO boiling range are preserved, and they are known to have a higher Kw. As temperature increases, the rates of thermal cracking reactions increase more rapidly than the hydrogen addition counterparts [17], that in turn gives HVGO product with a lower amount of preserved aliphatic hydrocarbons leading to a product with a lower Kw. The FCC SLO, and the recycle of PBFO increase the aromaticity of the feedstock and from the more aromatic feedstock during hydrocracking a more aromatic lower Kw HVGO is obtained.

The relation between Kw of HVGO and Kw of LVGO is given by the regression Equation (6).

$$\begin{aligned} LVGOKw &= 0.983HVGOKw \\ R &= 0.965, \text{ av. rel. error} = 0.47\% \end{aligned} \quad (6)$$

The relation of Kw of LVGO and Kw of HAGO is presented by the regression Equation (7).

$$\begin{aligned} HAGOKw &= 1.011LVGOKw \\ R &= 0.970, \text{ av. rel. error} = 0.45\% \end{aligned} \quad (7)$$

The H-Oil[®] diesel quality expressed by its cetane index was found to depend on through-put, reaction temperature, and FCC SLO content in the H-Oil[®] mixed feed. This dependence is given in the regression Equation (8).

$$\begin{aligned} HOil \text{ Diesel Cetane Index} &= 212.1 + 0.6645FR - 0.42254WABT - 0.28432FCC \text{ SLO} \\ R &= 0.85, \text{ av. rel. error} = 6.7\% \end{aligned} \quad (8)$$

It is evident from Equation (8) that similarly to the H-Oil[®] HVGO (Equation (5)) the H-Oil[®] diesel cetane index (CI) increases with enhancement of throughput, and decreasing of reaction temperature, and FCC SLO content in H-Oil[®] mixed feed. The dependence of diesel CI on these variables, however, is lower than that of the H-Oil[®] HVGO which can be seen from the lower accuracy of the prediction of Equation (8), ten times as low as that of Equation (5). This suggests that other factors not included in Equation (8) can also affect the hydrocracked diesel fraction cetane index. The inclusion of the recycle of PBFO does not improve the accuracy of prediction that suggests that it does not have impact on H-Oil[®] diesel cetane index. The diesel fraction is difficult to crack at the hydrocracking conditions, although its secondary hydrocracking is documented in several researches [18–21]. The fact that the H-Oil[®] diesel cetane index decreases with augmentation of reaction temperature and extending of reaction time (feed through-put reduction) suggests that the diesel may undergo secondary cracking reactions which reduce the aliphatic hydrocarbons content in the diesel and increase the aromatics content. The higher aromatics content was found in our earlier study to correlate with a lower cetane index [22].

As mentioned earlier in this research the H-Oil[®] VTB density strongly correlates with Concarbon (micro carbon) content. Since the measurement of the viscosity of the H-Oil[®] VTB samples featured with high density and high Concarbon content was difficult to perform due to their high melting point solutions with FCC HCO containing 30% FCC HCO with kinematic viscosity of 11.6 mm²/s were prepared and their viscosity was measured. An ICrA matrix of the H-Oil[®] VTB properties studied in this work density, Concarbon content (CCR), kinematic viscosity of blends 70%VTB/30%FCC HCO, and softening point was prepared and shown in Table 4. As evident from the ICrA matrix in Table 4 all four studied H-Oil[®] VTB properties density, Concarbon content (CCR), kinematic viscosity of blends 70%VTB/30%FCC HCO, and softening point statistically meaningful strongly correlate with each other. Figure 5 exhibits graphs of the dependences of density, viscosity,

and softening point of H-Oil[®] VTB on Concarbon content. These data clearly indicate that viscosity, and softening point of the H-Oil[®] VTB exponentially increase with enhancement of Concarbon content and density. The relation of Concarbon content to density for the H-Oil[®] VTB and for the straight run vacuum residual oils shown in Figure 5a indicates that for the same value of density the H-Oil[®] VTB has a higher Concarbon content. Since the density correlates with the total aromatic structures content, and the Concarbon content correlates with the number of condensed aromatic rings [1] one may conclude that at the same content of aromatic structures the H-Oil[®] VTB could contain a higher amount of condensed aromatic rings.

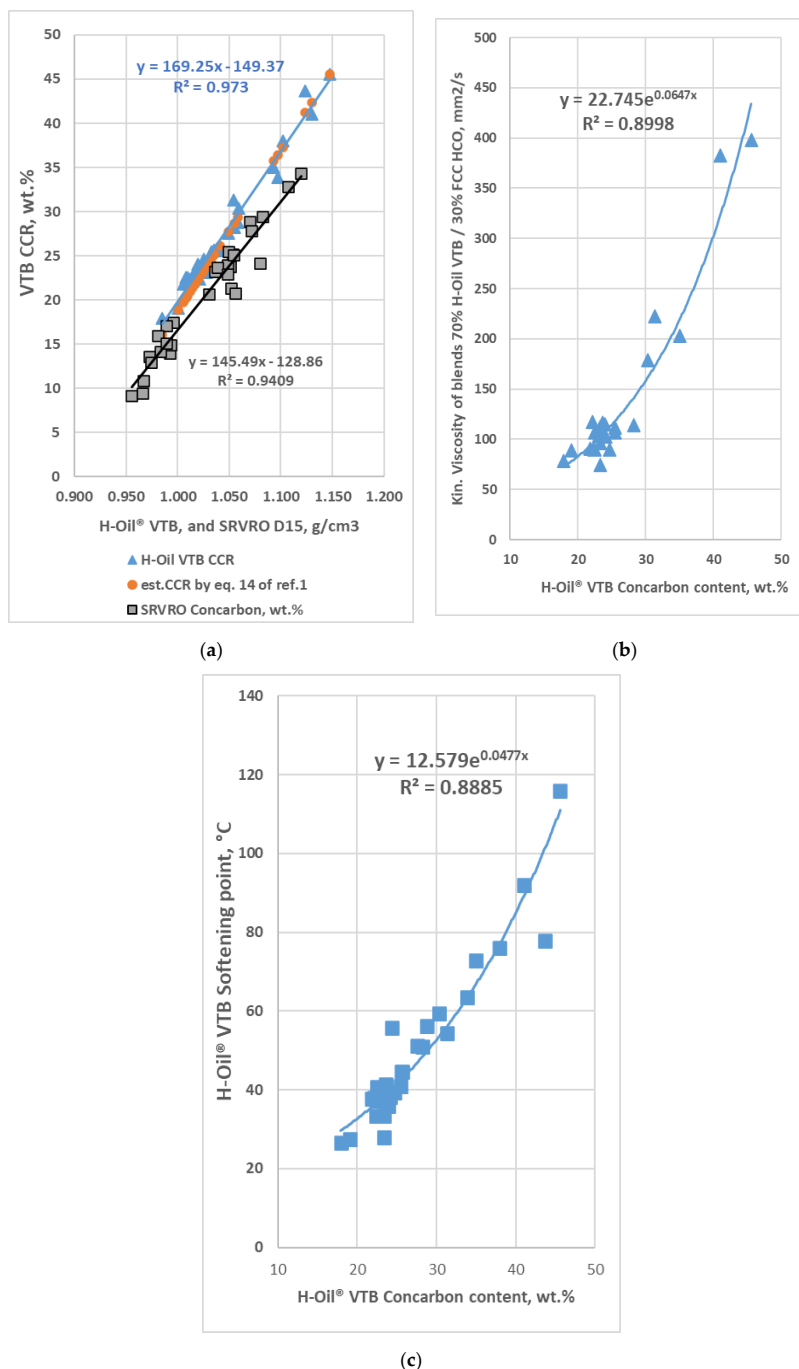
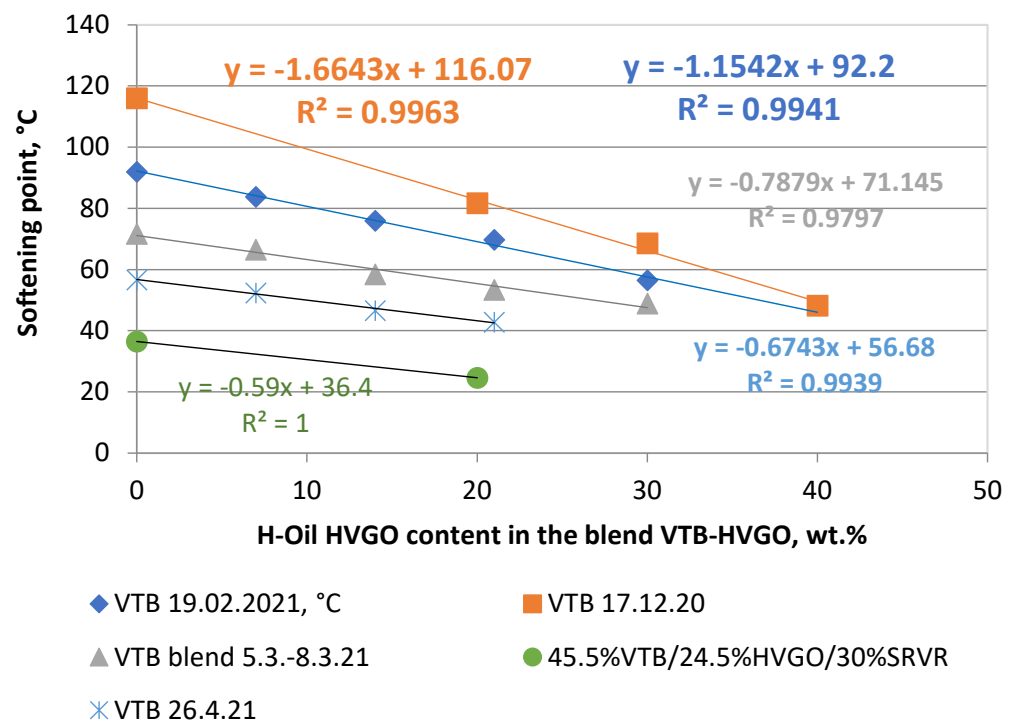


Figure 5. Dependence of density (a), viscosity (b), and softening point (c) of H-Oil[®] VTB on Concarbon content.

Table 4. μ -value of ICRA for the evaluation of relations of H-Oil[®] VTB properties density, Concarbon content (CCR), kinematic viscosity of blends 70%VTB/30%FCC HCO, and softening point.

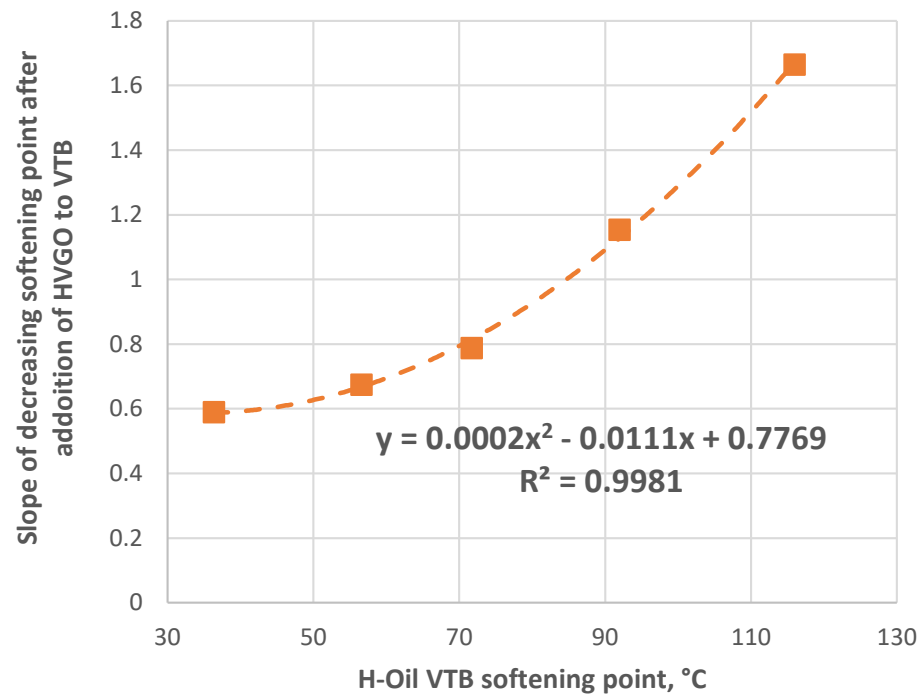
	VTB D15	VTB CCR	VTB VIS (70%VR/30%HCO) at 80 °C, mm ² /s	Softening Point, °C
VTB D15, g/cm ³	1.00	-	-	-
VTB CCR, wt.%	0.99	1.00	-	-
VTB VIS (70%VTB/30%HCO) at 80 °C, mm ² /s	0.92	0.95	1.00	
Softening point, °C	0.95	0.95	0.96	1.00

As the H-Oil[®] VTB having higher density, and higher Concarbon content possesses a higher softening point and it is more brittle undercutting of HVGO in the vacuum distillation column has been applied to decrease softening point and Fraas breaking point, and increase penetration to use this material as a feed for production of road asphalt [1,6]. In this study instead of undercutting H-Oil[®] HVGO we explored the feasibility to improve softening point of the harder H-Oil[®] VTB samples by blending them with H-Oil[®]. Figure 6 shows that the softening point of the H-Oil[®] VTB linearly decreases with augmentation of HVGO content in the blend H-Oil[®] VTB-HVGO (Figure 6a), and that the dependence of the slope of decreasing the softening point of the blend VTB-HVGO on the softening point of the pure VTB can be described by a second order polynomial (Figure 6b).



(a)

Figure 6. Cont.



(b)

Figure 6. Variation of H-Oil[®] VTB softening point with increasing of HVGO content in the blend VTB-HVGO (a), and dependence of the slope of decreasing of the softening point of the blend VTB-HVGO on the softening point of the pure VTB (b).

3. Materials and Methods

36 different cases of the operation of the LNB H-Oil[®] ebullated vacuum residue hydrocracking (EBVRHC) with crude slate (this is the crude slate processed in LNB refinery), share (per cent of total fresh vacuum residue feed) of FCC SLO, and of VTB recycle as shown in Figure 4 were studied. The variation of operating conditions and net conversion for the studied 36 cases is summarized in Table 5. A simplified diagram of the LNB H-Oil[®] hydrocracker where the investigations were performed is presented in Figure 7. A commercial supported Ni-Mo catalyst was employed throughout the study and for some of the cases a nano-dispersed catalyst was also used.

Table 5. Operating conditions in LNB H-Oil[®] hydrocracker for the studied 36 cases.

Case	Trough-Put, t/h	WABT, °C	FCC SLO, wt.% of Feed	Recycle, wt.% of Feed	Recycle Gas/Oil Ratio, R-1001 kg/t	Recycle Gas Hydrogen Content, wt (vol.) %	Net Conversion, wt.%	First Reactor Inlet Pressure, Bar	First Reactor Inlet H ₂ Partial Pressure, Bar
1	313	418	0	0	20.6	95.7	65.0	173	166
2	285	410	0	0	-	-	55.0	174	-
3	279	411	0	0	24.4	95.6	54.7	173	166
4	306	414	0	0	21.8	89	56.1	174	155
5	293	418	0	0	21.8	97.7	67.3	173	169
6	172	419	0	0	37.3	97.7	76.8	173	169
7	239	420	0	0	28.7	97	71.2	173	168
8	240	418	0	0	29.4	97.5	70.1	173	169
9	230	419	0	0	30.1	97.6	67.5	174	170
10	208	423	0	0	33.2	97	72.9	174	168
11	244	424	0	0	22.5	97.6	72.5	174	169
12	245	426	8	0	22.5	97.6	75.3	174	169
13	263	427	8	0	-	-	70.7	173	-
14	266	430	9	0	19.8	97.4	74.3	173	169
15	236	417	4	0	24.6	98.3	63.4	173	170

Table 5. Cont.

Case	Trough-Put, t/h	WABT, °C	FCC SLO, wt.% of Feed	Recycle, wt.% of Feed	Recycle Gas/Oil Ratio, R-1001 kg/t	Recycle Gas Hydrogen Content, wt (vol.) %	Net Conversion, wt.%	First Reactor Inlet Pressure, Bar	First Reactor Inlet H ₂ Partial Pressure, Bar
16	224	414	9	0	29.1	98.5	60.4	173	171
17	195	417	12	0	33.6	99.3	67.3	173	171
18	227	425	10	0	29.6	99.1	71.7	174	172
19	247	426	8	0	29.8	-	75.1	174	-
20	250	425	6	0	28.0	93	72.9	173	161
21	214	426	8	0	16.0	92.3	76.3	174	160
22	256	427	8	0	26.1	90.8	74.1	174	158
23	257	433	8	0	26.0	88.8	79.0	174	154
24	242	433	8	0	-	-	80.8	174	-
25	225	433	14	0	28.5	87.7	80.3	173	152
26	142	429	14	10	43.0	87.1	85.9	173	151
27	127	430	12	10.0	-	-	90.3	173	-
28	123	431	13	29.4	51.7	92.5	93.2	173	160
29	128	433	11	27	44.9	86.9	92.6	173	150
30	126	433	12	26	47.8	90.2	91.1	173	156
31	140	434	11	18	44.7	89.9	91.1	173	155
32	146	434	14	21	39.5	82.4	87.5	173	142
33	156	432	9	22	40.2	87.5	89.5	172	151
34	182	435	4.9	19.2	-	-	86.2	172	-
35	178	435	5.0	9.8	35.4	89.8	87.2	172	155
36	175	436	5.1	0.0	35.5	87.4	85.2	172	151

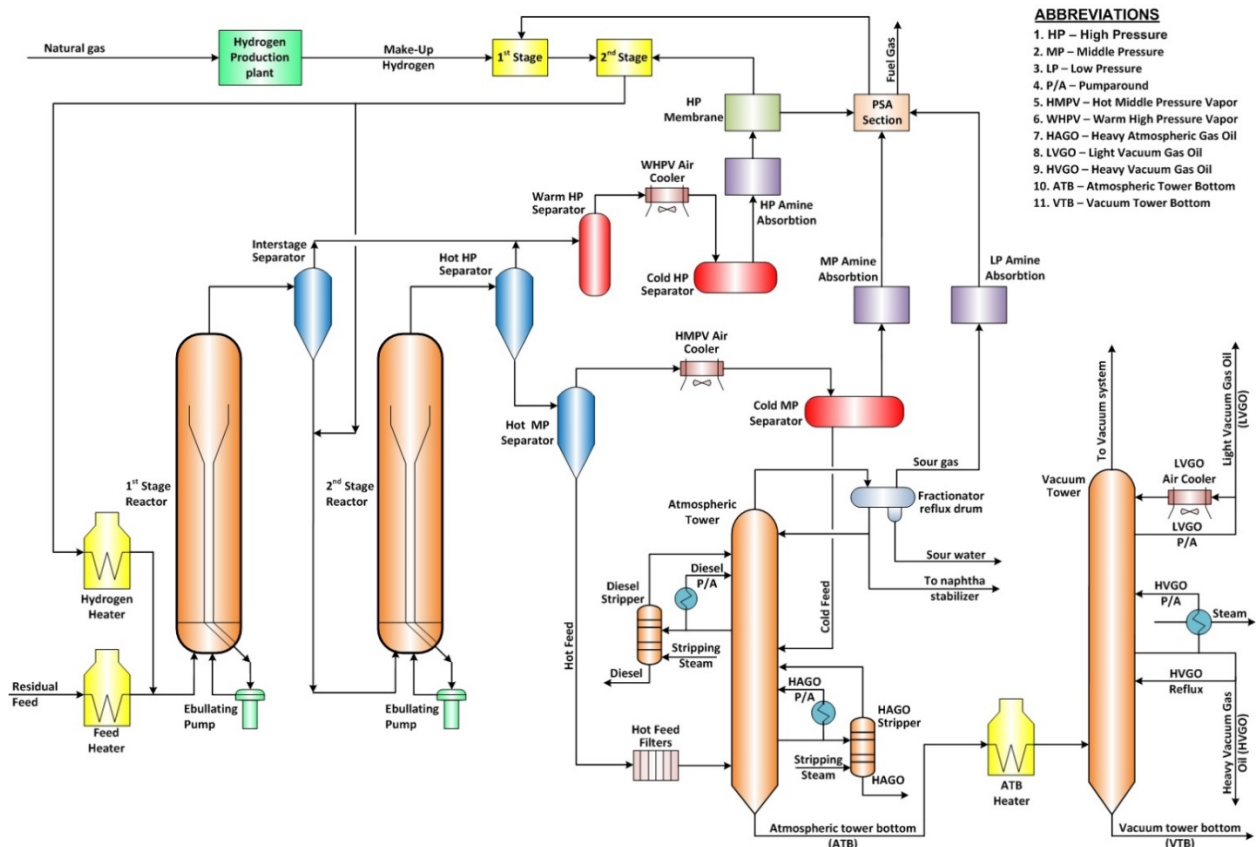


Figure 7. Process flow diagram of the LUKOIL Neftohim Burgas ebullated bed residue H-Oil[®] hydrocracker.

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

$$\text{Conversion}(\%) = \frac{\text{EBRHCFEED}_{540^{\circ}\text{C}+} - \text{EBRHCPRODUCT}_{540^{\circ}\text{C}+}}{\text{EBRHCFEED}_{540^{\circ}\text{C}+}} \times 100 \quad (9)$$

where:

$\text{EBRHCFEED}_{540^{\circ}\text{C}+}$ = 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;

$\text{EBRHCPRODUCT}_{540^{\circ}\text{C}+}$ = 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 methods used to characterize the mixed H-Oil[®] feed, and the liquid products: naphtha, diesel, HAGO, LVGO, HVGO, VTB, ATB are summarized in Table 6.

Table 6. Methods employed to measure properties of the LNB H-Oil[®] mixed feed and liquid products.

Density of Mixed Feed, g/cm ³	BDS EN ISO 3675
Sulfur of mixed feed, ATB, VTB, HAGO, LVGO, HVGO, Diesel wt.%	ASTM D 4294
Asphaltene (C ₇ , and C ₅) content, wt.%	ASTM D 6560
Micro carbon content, wt.%	EN ISO 10370
Specific viscosity, °E	ASTM D1665
Carbon content, wt.%	ASTM D 5291
Hydrogen content, wt.%	ASTM D 5291
Nitrogen content, wt.%	ASTM D 5291
Nickel, ppm	IP 501
Vanadium, ppm	IP 501
Sodium, ppm	IP 501
Iron, ppm	IP 501
High temperature simulation distillation (HTSD)	ASTM D7169
Density of naphtha, g/cm ³	BDS EN ISO 12185
Sulfur of naphtha, ppm	BDS EN ISO 20846
Distillation of naphtha and diesel	BDS EN ISO 3405
Density of diesel, g/cm ³	BDS EN ISO 3675
Diesel Aromatic hydrocarbons, wt.%	BDS EN 12916
Diesel Cetane Index	ASTM D4737

The Kw [9] was estimated based on information about density and distillation characteristics by the use of Equation (10).

$$Kw = \frac{\sqrt[3]{1.8 \left[\frac{T_{10} + T_{30} + T_{50} + T_{70} + T_{90}}{5} + 273.15 \right]}}{D15} \quad (10)$$

where:

T_{10} —boiling point of 10% of evaporate according to the HTSD, or physical distillation °C;

T_{30} —boiling point of 30% of evaporate according to the HTSD or physical distillation °C;

T_{50} —boiling point of 50% of evaporate according to the HTSD or physical distillation °C;

T_{70} —boiling point of 70% of evaporate according to the HTSD or physical distillation °C;

T_{90} —boiling point of 10% of evaporate according to the HTSD or physical distillation °C.

The aromatic carbon content of the HAGO, LVGO, and HVGO was estimated by Equation (11) (Conoco Philips Prediction method) [11].

$$C_A = 292.1SG - 0.043T_{50}^F - 212.2 \quad (11)$$

where:

C_A = Aromatic carbon content, wt.%;

SG = specific gravity;

T_{50}^F = boiling point of 50% of evaporate according to the HTSD, °F.

The hydrogen content of the HAGO, LVGO, and HVGO was estimated by Equation (12) (Conoco Philips Prediction method) [11].

$$H = -26.25SG + 0.0013T_{50}^F + 35.2 \quad (12)$$

The molecular weight of the studied H-Oil[®] mixed feed, HAGO, LVGO, HVGO, ATB, and VTB was estimated by the correlation of Goosens [23] (Equation (13)):

$$MW = 0.01077T_b^{[1.52869+0.06486Ln(\frac{T_b}{1078-T_b})]} / d \quad (13)$$

The correlation developed by Abutaqiya [24] was employed to estimate the average aromatic ring numbers in the average hydrocarbon structure of the investigated EBVRHC heavy oils, designated as ARI. ARI is estimated by Equations (14) and (15).

$$ARI = f(MW, FRI) = \frac{2[\frac{MW}{FRI} - (3.5149MW + 73.1858)]}{(3.5074MW - 91.972 - (3.5149MW + 73.1858))} \quad (14)$$

where:

MW = molecular weight of EBVRHC heavy oils, g/mol;

FRI = function of refractive index

$$FRI = \frac{(n_D^{20})^2 - 1}{(n_D^{20})^2 + 2} \quad (15)$$

where, n_D^{20} = refractive index at 20 °C.

The refractive index was estimated from density at 15 °C by the correlation developed in our earlier research [25] and shown in Equation (16).

$$n_d^{20} = 0.77887D15 + 0.80065 \quad (16)$$

4. Conclusions

135 parameters including H-Oil[®] operating conditions and H-Oil[®] feed and liquid product properties were evaluated by the use of Intercriteria analysis. It was found that the crude oils containing vacuum residue fractions with a lower Kw factor during ebullated bed hydrocracking produce hydrocracked vacuum residue with a higher density, higher Concarbon content, higher viscosity, and higher softening point. The addition of FCC slurry oil and recycle of partially blended fuel oil to the straight run vacuum residual oils decreases the H-Oil[®] mixed feed Kw that in turn leads to production of higher density hydrocracked vacuum residue, lower Kw gas oils, and lower cetane index diesel. The augmentation of H-Oil[®] reaction temperature enhances density and decreases Kw of VTB, and H-Oil[®] gas oils, and reduces the cetane index of diesel. The magnification of through-put amplifies the H-Oil gas oil Kw and diesel cetane index. All investigated factors controlling the properties of the liquid H-Oil[®] products: hydrocracked vacuum residue, hydrocracked gas oils, and hydrocracked diesel were found to have no impact on the properties of hydrocracked naphtha.

The developed in this work correlations can be used to evaluate the influence of crude oil properties, H-Oil[®] operating conditions, and the processing of FCC slurry oil, and recycle of partially blended fuel oil on the quality of the H-Oil[®] products: diesel, HAGO, LVGO, HVGO, and VTB. This information can be used to assess the impact H-Oil feed properties and operating conditions on the performance of the other refinery units which process the H-Oil[®] products mentioned above and to find the parameters which provide the optimal performance of the whole refinery.

Author Contributions: Conceptualization, E.N.S.; Data curation, R.K.D. and S.N.; Formal analysis, I.P.P. and D.Y.; Investigation, I.V.K.; Methodology, S.S.; Software, V.K.A., S.R. and D.D.S.; Supervision, K.T.A.; Writing—original draft, D.S.S. and I.K.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Asen Zlatarov University–Burgas, Project: Center of Excellence UNITE BG05M2OP001-1.001-0004 /28.02.2018 (2018–2023).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: Not applicable.

Acknowledgments: Krassimir Atanassov acknowledges the support from the project UNITE BG05M2OP001-1.001-0004 /28.02.2018 (2018–2023).

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

ATB	atmospheric tower bottom product
ARI	Aromatic ring index (average ring number) in the average EBVRHC heavy oil hydrocarbon structure;
CA	Aromatic carbon content, wt.%
CCR	Conradson carbon content, wt.%
CI	Cetane index
D15	Density at 15 °C, g/cm ³
d	relative density at 15 °C, g/cm ³
EBVRHC	Ebullated bed vacuum residue hydrocracking
FCC	Fluid catalytic cracking
FR	H-Oil [®] unit trough-put (feed low rate), t/h
FRI20	function of refractive index
H	hydrogen content, wt.%
HAGO	Heavy atmospheric gas oil
HCO	Heavy cycle oil
HTSD	High temperature simulated distillation
HVGO	Heavy vacuum gas oil
ICrA	InterCriteria Analysis
nd20	refractive index
Kw	Watson characterization factor
Kwi	Watson characterization factor of the of ith pure component in the mixture
LNB	LUKOIL Neftohim Burgas refinery
LVGO	Light vacuum gas oil
μ	consonance
MW	molecular weight, g/mol
PBFO	Partially blended fuel oil
SG	specific gravity
SLO	Slurry oil
SRVRO	Straight run vacuum residual oil
T50F	boiling point of 50% of evaporate according to the HTSD, °F
Tb	normal boiling point or 50 wt % of evaporate according to the HTSD, K
T10	boiling point of 10% of evaporate according to the HTSD, or physical distillation, °C
T30	boiling point of 30% of evaporate according to the HTSD or physical distillation, °C
T50	boiling point of 50% of evaporate according to the HTSD or physical distillation, °C
T70	boiling point of 70% of evaporate according to the HTSD or physical distillation, °C
T90	boiling point of 10% of evaporate according to the HTSD or physical distillation, °C
Rec.	per cent of PBFO recycle in the H-Oil [®] mixed feed, wt.%.
VGO	Vacuum gas oil
VTB	Vacuum tower bottom product (equivalent to unconverted hydrocracked vacuum residue)

WABT	average weight average bed temperature of both reactors in LNB H-Oil [®] unit, °C
VIS	kinematic viscosity at 80 °C, mm ² /s
Xi	weight fraction of ith pure component in the mixture

References

- Stratiev, D.; Nenov, S.; Shishkova, I.; Georgiev, B.; Argirov, G.; Dinkov, R.; Yordanov, D.; Atanassova, V.; Vassilev, P.; Atanassov, K. Commercial Investigation of the Ebullated-Bed Vacuum Residue Hydrocracking in the Conversion Range of 55–93%. *ACS Omega* **2020**, *51*, 33290. [CrossRef] [PubMed]
- Stratiev, D.; Nenov, S.; Shishkova, I.; Dinkov, R.; Argirov, G.; Georgiev, B.; Yordanov, D.; Atanassova, V.; Vassilev, P.; Atanassov, K. Non-linear least-squares method for modeling vacuum residue hydrocracking selectivity data. submitted for publication in *Oxidation Communications*.
- Stratiev, D.; Shishkova, I.; Ivanov, M.; Dinkov, R.; Georgiev, B.; Argirov, G.; Atanassova, V.; Vassilev, P.; Atanassov, K.; Yordanov, D.; et al. Catalytic cracking of diverse vacuum residue hydrocracking gas oils. *Chem. Eng. Technol.* **2021**, *44*, 1–13. [CrossRef]
- Stratiev, D.; Shishkova, I.; Ivanov, M.; Dinkov, R.; Georgiev, B.; Argirov, G.; Atanassova, V.; Vassilev, P.; Atanassov, K.; Yordanov, D.; et al. Role of Catalyst in Optimizing Fluid Catalytic Cracking Performance During Cracking of H-Oil-Derived Gas Oils. *ACS Omega* **2021**, in press. [CrossRef] [PubMed]
- Dinkov, R.; Kirilov, K.; Stratiev, D. Feasibility of Bitumen Production from Unconverted Vacuum Tower Bottom from H-Oil Ebullated Bed Residue Hydrocracking. *Ind. Eng. Chem. Res.* **2018**, *57*, 2003. [CrossRef]
- Stratiev, D.; Shishkova, I.; Dinkov, R.; Kirilov, K.; Yordanov, D.; Nikolova, R.; Veli, A.; Tavlieva, M.; Vasilev, S.; Suyunov, R. Variation of Oxidation Reactivity of Straight Run and H-Oil Hydrocracked Vacuum Residual Oils in the Process of Road Asphalt Production. *Road Mater. Pavement Des.* **2021**, 1–25. [CrossRef]
- Naghizada, N.; Prado, G.H.C.; de Klerk, A. Uncatalyzed Hydrogen Transfer during 100–250 °C Conversion of Asphaltenes. *Energy Fuels* **2017**, *31*, 6800–6811. [CrossRef]
- Stratiev, D.S.; Marinov, I.M.; Shishkova, I.K.; Dinkov, R.K.; Stratiev, D.D. Investigation on feasibility to predict the content of saturate plus mono-nuclear aromatic hydrocarbons in vacuum gas oils from bulk properties and empirical correlations. *Fuel* **2014**, *129*, 156–162. [CrossRef]
- Watson, K.M.; Nelson, E.F.; Murphy, G.B. Characterization of Petroleum Fractions. *Ind. Eng. Chem.* **1935**, *27*, 1460–1464. [CrossRef]
- 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*, 115–129. [CrossRef]
- Choudhary, T.V.; Meier, P.F. Characterization of heavy petroleum feedstocks. *Fuel Process. Technol.* **2008**, *89*, 697–703. [CrossRef]
- Herrera, P.S.; Oballa, M.C.; Somogyvari, A.F.; Monnier, J. Catalyst selection for hydrotreating diesel fuel from residue hydrocracking. *ACS Prepr.* **1992**, *37*, 1855–1863.
- Wandas, R.; Chrapek, T. Hydrotreating of middle distillates from destructive petroleum processing over high-activity catalysts to reduce nitrogen and improve the quality. *Fuel Process. Technol.* **2004**, *85*, 1333–1343. [CrossRef]
- Tomášek, J.; Matějovský, L.; Lamblová, M.; Blažek, J. Properties and Composition of Products from Hydrotreating of Straight-Run Gas Oil and Its Mixtures with Light Cycle Oil over Sulfidic Ni-Mo/Al₂O₃ Catalyst. *ACS Omega* **2020**, *5*, 27922–27932. [CrossRef] [PubMed]
- Dinkov, R.; Stratiev, D. Studying The Evolution of H-OIL Hydrocracked Residual Oil Properties In The Conversion Range 65–93%, and the Opportunity To Produce Road Asphalt From H-OIL VTB. *Oxid. Commun.* **2021**, *5*, 33290–33304.
- Gharagheizi, F.; Fazeli, A. Prediction of the Watson Characterization Factor of Hydrocarbon Components from Molecular Properties. *QSAR Comb. Sci.* **2008**, *27*, 758–767. [CrossRef]
- Chabot, J.; Shiflett, W. Residuum Hydrocracking: Chemistry and Catalysis. Available online: <https://www.digitalrefining.com/article/1002340/residuum-hydrocracking-chemistry-and-catalysis#YK9AZaFRVPY> (accessed on 6 April 2021).
- Sánchez, S.; Rodríguez, M.A.; Ancheyta, J. Kinetic model for moderate hydrocracking of heavy oils. *Ind. Eng. Chem. Res.* **2005**, *44*, 9409–9413. [CrossRef]
- Loria, H.; Trujillo-Ferrer, G.; Sosa-Stull, C.; Pereira-Almao, P. Kinetic modeling of bitumen hydroprocessing at in-reservoir conditions employing ultradispersed catalysts. *Energy Fuels* **2011**, *25*, 1364–1372. [CrossRef]
- Martínez, J.; Ancheyta, J. Kinetic model for hydrocracking of heavy oil in a CSTR involving short term catalyst deactivation. *Fuel* **2012**, *100*, 193–199. [CrossRef]
- Asaee, S.D.S.; Vafajoo, L.; Khorasheh, F. A new approach to estimate parameters of a lumped kinetic model for hydroconversion of heavy residue. *Fuel* **2014**, *134*, 343–353. [CrossRef]
- Sharafutdinov, I.; Stratiev, D.; Shishkova, I.; Dinkov, R.; Pavlova, A.; Petkov, P.; Rudnev, N. Dependence of cetane index on aromatic content in diesel fuels. *OGEM* **2012**, *38*, 148–152.
- Goossens, A.G. Prediction of Molecular Weight of Petroleum Fractions. *Ind. Eng. Chem. Res.* **1996**, *35*, 985. [CrossRef]
- Abutaqiya, M. Advances in Thermodynamic Modeling of Nonpolar Hydrocarbons and Asphaltene Precipitation in Crude Oils. Ph.D. Thesis, Rice University, Houston, TX, USA, 2019.
- Stratiev, D.; Shishkova, I.; Tankov, I.; Pavlova, A. Challenges in characterization of residual oils. A review. *J. Petrol. Sci. Eng.* **2019**, *178*, 227–250. [CrossRef]