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

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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) (5.8%) [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 deasphalitization 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 μ = 0.75 ÷ 1.00 denotes a statistically meaningful positive relation, where the strong positive consonance exhibits values of μ = 0.95 ÷ 1.00, and the weak positive consonance exhibits values of μ = 0.75 ÷ 0.85. Respectively, the values of negative consonance with μ = 0.00 ÷ 0.25 means a statistically meaningful negative relation, where the strong negative consonance exhibits values of μ = 0.00 ÷ 0.05, and the weak negative consonance exhibits values of μ = 0.15 ÷ 0.25 [1,3].
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 $\mu$ of Kw and aromatic carbon content for HAGO (heavy atmospheric gas oil), LVGO (light vacuum gas oil), and HVGO (heavy vacuum gas oil) are $0.95÷1.00$ and $0.75÷1.00$ respectively. Respectively, the values of negative consonance with $\mu = 0.00÷0.25$ means a statistically meaningful negative relation, where the strong negative consonance exhibits values of $\mu = 0.15÷0.25$ [1,3].

The correlations of Kw, density, and hydrogen content of H-Oil® mixed feed (a–c) SRVRO (a–c), and of H-Oil® ATB, and VTB (d–f).

**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 VTB (d–f).
atmospheric gas oil), LVGO (light vacuum gas oil), and HVGO (heavy vacuum gas oil) are 0.00. The consonances $\mu$ 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. $\mu$-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 |       | HAGO |       | HAGO |       | HAGO |       | HAGO |       | LVGO |       | LVGO |       | LVGO |       | LVGO |       | LVGO |       | HVGO |       | HVGO |       | HVGO |       | HVGO |       |
|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|------|-------|
|       | Kw   | ARI   | CA   | H     | D15  | Kw   | ARI   | CA   | H     | D15  | Kw   | ARI   | CA   | H     | D15  | Kw   | ARI   | CA   | H     | D15  | Kw   | ARI   | CA   | H     | D15  | Kw   | ARI   |
| HAGO  | 1.00 | 0.05  | 0.00 | 0.96  | 1.00 | 0.02  | 0.99  | 0.99  | 0.99  | 0.00 | 1.00 | 0.02  | 0.97  | 0.99  | 0.01  | 0.99  | 1.00 |
| LVGO  | 0.99 | 0.02  | 0.00 | 1.00 |
| HVGO  | 0.99 | 0.04  | 0.01 | 0.99  | 0.99  | 0.01  | 0.00  | 0.99  | 0.00 | 1.00 |
| LVGO  | 0.99 | 0.08  | 0.96 | 0.03  | 0.98  | 0.98  | 0.07  | 0.95  | 0.03  | 1.00 |
| LVGO  | 0.01 | 0.94  | 0.99 | 0.02  | 0.98  | 0.99  | 0.00  | 1.00  |
| LVGO  | 0.99 | 0.04  | 0.01  | 0.99  | 0.99  | 0.01  | 0.00  | 0.99  | 0.00  | 1.00 |
| LVGO  | 0.05 | 0.98  | 0.96 | 0.03  | 0.98  | 0.98  | 0.07  | 0.95  | 0.03  | 1.00 |
| HVGO  | 0.93 | 0.11  | 0.07  | 0.93  | 0.93  | 0.02  | 0.04  | 0.97  | 0.03  | 0.96  | 0.11  | 1.00 |
| HVGO  | 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  | 0.93 | 0.09  | 0.06  | 0.94  | 0.94  | 0.06  | 0.04  | 0.97  | 0.03  | 0.97  | 0.09  | 0.99  | 0.00  | 1.00 |
| HVGO  | 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  | 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 | 0.80 | 1.17 | 2.21|
| Density at 15 °C, g/cm³          | 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         | -       | -      | -   | -   | -   | -   | -   |
|       | Max   | 23.6       | -       | -      | -   | -   | -   | -   | -   |
| C₅ asphaltenes, wt.%             | Min   | 9.3        | -       | -      | -   | -   | -   | -   | -   |
|       | Max   | 28.5       | -       | -      | -   | -   | -   | -   | -   |
| C₇ 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 |
| C₅, 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]:

\[
K_{w_{mix}} = \sum_{i=1}^{n} X_i \cdot K_{w_i}
\]  

(1)

where:

- \(K_{w_{mix}}\) = Watson characterization factor of the mixture;
- \(X_i\) = weight fraction of ith pure component in the mixture;
- \(K_{w_i}\) = Watson characterization factor of the of ith pure component in the mixture.

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.

\[
H_{Oil \text{ mixed feed } Kw} = 11.62 - 0.0253FCCSLO - 0.0142Rec.
\]

R = 0.876, rel. av. error = 0.80% (2)

\[
H_{Oil \text{ mixed feed } Kw} = 1.43 + 0.866SRVROKw - 0.0206FCCSLO - 0.0137Rec.
\]

R = 0.876, rel. av. error = 0.74% (3)

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.%.

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)

$$VTB\ D15 = -0.178\ FeedKw + 3.074$$
$$R = 0.992, \ av. \ rel. \ error = 0.3\%$$  \hspace{1cm} (4)

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.

$$HVGOKw = 24.34 + 0.000841\ FR - 0.03034\ WABT - 0.004\ FCCSLO - 0.01326\ Rec.$$  \hspace{1cm} (5)

where:

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

$$WABT = \ \text{hydrocracking \ reaction \ temperature, \ }^\circ\text{C}.$$
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).

\[
LVGOKw = 0.983HVGOKw \\
R = 0.965, \text{ av. rel. error } = 0.47\%
\] (6)

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

\[
HAGOKw = 1.011LVGOKw \\
R = 0.970, \text{ av. rel. error } = 0.45\%
\] (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).

\[
HOil Diesel Cetane Index = 212.1 + 0.6645FR - 0.42254WABT - 0.28432FCC SLO \\
R = 0.85, \text{ av. rel. error } = 6.7\%
\] (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. 1 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, g/cm³ | VTB CCR, wt.% | VTB VIS (70%VTB/30%HCO) at 80 °C, mm²/s | Softening Point, ºC |
|----------------|---------------|-----------------------------------------|---------------------|
| 1.00           | -             | -                                       | -                   |
| 0.99           | 1.00          | -                                       | -                   |
| 0.92           | 0.95          | 1.00                                    | -                   |
| 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 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).

\[
y = -1.6643x + 116.07 \quad R^2 = 0.9963
\]
\[
y = -1.1542x + 92.2 \quad R^2 = 0.9941
\]
\[
y = -0.7879x + 71.145 \quad R^2 = 0.9797
\]
\[
y = -0.59x + 36.4 \quad R^2 = 1
\]
\[
y = -0.6743x + 56.68 \quad R^2 = 0.9939
\]
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 % | Net Conversion, wt.% | First Reactor Inlet Pressure, Bar | First Reactor Inlet H₂ 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 Hydrogen Content, wt. (vol.) % | Net Conversion, wt.% | First Reactor Inlet Pressure, Bar | First Reactor Inlet H₂ 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                     | -                                | -                                       | 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:

\[
\text{Conversion}(\%) = \frac{\text{EBRHCFeed}_{540\,^\circ\text{C}+} - \text{EBRHCProduct}_{540\,^\circ\text{C}+}}{\text{EBRHCFeed}_{540\,^\circ\text{C}+}} \times 100
\] (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.

| Property / Method | BDS EN ISO 3675 |
|-------------------|-----------------|
| Density of Mixed Feed, g/cm\(^3\) |  |
| 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 D 1665 |
| 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) | BDS EN D7169 |
| Density of naphtha, g/cm\(^3\) | BDS EN ISO 3675 |
| 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 D 4737 |

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

\[
Kw = \sqrt[3]{1.8 \left[ \frac{T_{10} + T_{30} + T_{50} + T_{70} + T_{90}}{5} \right]^5 + 273.15} 
\] (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].

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

where:

- \(C_A\) = Aromatic carbon content, wt.%;
- \(SG\) = specific gravity;
$T_{SO}^{F}$ = 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].

$$H = -26.25SG + 0.0013T_{SO}^{F} + 35.2$$ (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)):

$$MW = 0.01077T_{k}^{\left[1.52869 + 0.06486\ln\left(\frac{T_{b}}{1078} - T_{b}ight)\right]} / d$$ (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).

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

where:

- $MW$ = molecular weight of EBVRHC heavy oils, g/mol;
- $FRI$ = function of refractive index

$$FRI = \frac{\left(n_{D}^{20}\right)^{2} - 1}{\left(n_{D}^{20}\right)^{2} + 2}$$ (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).

$$n_{D}^{20} = 0.77887D15 + 0.80065$$ (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.
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Nomenclature

| Abbreviation | Description |
|--------------|-------------|
| 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/cm³ |
| d            | relative density at 15 °C, g/cm³ |
| EBVRHC       | Ebullated bed vacuum residue hydrocracking |
| FCC          | Fluid catalytic cracking |
| FR           | H-Oil® unit throughput (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 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, mm²/s
$Xi$  weight fraction of $i$th pure component in the mixture

References

1. 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]
2. 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.
3. 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]
4. 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]
5. 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]
6. Stratiev, D.; Shishkova, I.; Dinkov, R.; Kirilov, K.; Yordanov, D.; Nikolova, R.; Veli, A.; Tavlueva, 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]
7. Naghizada, N.; Prado, G.H.C.; de Klerk, A. Uncatalyzed Hydrogen Transfer during 100–250 °C Conversion of Asphaltene. *Energy Fuels* 2017, 31, 6800–6811. [CrossRef]
8. 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]
9. Watson, K.M.; Nelson, E.F.; Murphy, G.B. Characterization of Petroleum Fractions. *Ind. Eng. Chem.* 1935, 27, 1460–1464. [CrossRef]
10. 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 asphalts and asphaltene fractions. *Fuel* 2016, 170, 115–129. [CrossRef]
11. Choudhary, T.V.; Meier, P.F. Characterization of heavy petroleum feedstocks. *Fuel Process. Technol.* 2008, 89, 697–703. [CrossRef]
12. 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.
13. 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]
14. 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]
15. 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.
16. Gharagheizi, F.; Fazeli, A. Prediction of the Watson Characterization Factor of Hydrocarbon Components from Molecular Properties. *QSAR Comb. Sci.* 2008, 27, 758–767. [CrossRef]
17. 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).
18. Sánchez, S.; Rodríguez, M.A.; Ancheyta, J. Kinetic model for moderate hydrocracking of heavy oils. *Ind. Eng. Chem. Res.* 2005, 44, 9409–9413. [CrossRef]
19. Loria, H.; Trujillo-Ferrer, G.; Sosa-Stull, C.; Pereira-Almao, P. Kinetic modeling of bitumen hydproprocessing at in-reservoir conditions employing ultradispersed catalysts. *Energy Fuels* 2011, 25, 1364–1372. [CrossRef]
20. Martinez, J.; Ancheyta, J. Kinetic model for hydrocracking of heavy oil in a CSTR involving short term catalyst deactivation. *Fuel* 2012, 100, 193–199. [CrossRef]
21. Asaei, 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]
22. Sharafutdinov, I.; Stratiev, D.; Shishkova, I.; Dinkov, R.; Pavlova, A.; Petkov, P.; Rudnev, N. Dependence of cetane index on aromatic content in diesel fuels. *OGE* 2012, 38, 148–152.
23. Goossens, A.G. Prediction of Molecular Weight of Petroleum Fractions. *Ind. Eng. Chem. Res.* 1996, 35, 988. [CrossRef]
24. Abutaqyia, M. Advances in Thermodynamic Modeling of Nonpolar Hydrocarbons and Asphaltene Precipitation in Crude Oils. Ph.D. Thesis, Rice University, Houston, TX, USA, 2019.
25. 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]