

KINETICS AND CATALYSIS

APPLICATION OF EBULLATED-BED VACUUM RESIDUE HYDROCRACKING AT LUKOIL NEFTOHIM BURGAS

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This paper summarizes the experience gained over seven years of operating an H-Oil ebullated-bed vacuum residue hydrocracking unit. The following key factors in improving the performance of H-Oil process were identified, including feedstock quality, catalyst condition, as well as loading and utilization of the unconverted vacuum residue. The optimum combination of these four factors allowed a vacuum residue conversion rate of about 90% to be achieved. The challenge still remains to determine optimal approaches to using the unconverted vacuum residue produced at higher conversion rates.

Keywords: hydrocracking, vacuum residue, conversion, SARA, sedimentation.

The conversion rate of heavy oil residue is a factor that determines the economic efficiency of modern oil refining technologies. The selection of a particular technology for refinery residue treatment is a challenging issue, requiring consideration of such factors, as capital costs for operation and maintenance, product yield and quality, etc. Seven vacuum residue processing technologies have been evaluated at the LUKOIL Neftohim Burgas, including flexicoking, delayed coking, vacuum residue deasphaltization, thermal cracking of deasphalted oil and asphaltene flexicoking, vacuum residue deasphaltization and asphaltene gasification, fixed-bed vacuum residue hydrocracking, vacuum residue desulphurization (VRDS), and ebullated-bed vacuum residue hydrocracking to select the most suitable for application in the refinery. Following their analysis, ebullated-bed vacuum residue hydrocracking (H-Oil) with a vacuum residue (VR) conversion of ≥ 70 wt % was selected as the most promising technology.

The initial tests of a pilot vacuum residue hydrocracking unit operated on the feedstock of Russian Urals crude oil, indicated the sediment content in the atmospheric hydrocracking residue to range within the permissible limit of 0.3–0.4 wt % at a conversion rate of 70 wt %.

The H-Oil vacuum residue hydrocracking unit was launched in July 2015. However, during the initial employment of the H-Oil technology at the LUKOIL Neftohim Burgas, its performance did not correspond to the results obtained at the pilot unit (**Fig. 1**).

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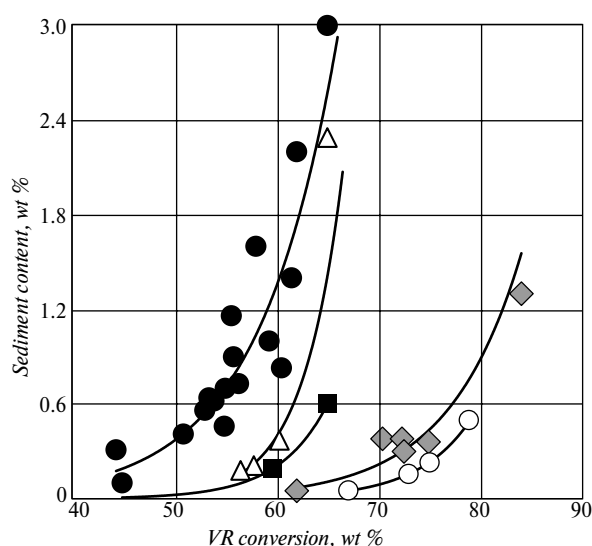


Fig. 1. Dependence of sediment content in the unconverted H-Oil vacuum residue on VR conversion rate when using VR mixtures obtained from oils of different origin: \triangle – Urals oil; \bullet – mixture of Urals oil, heavy Kazakh oil, Al-Buri oil, Val d’Agri oil; \blacksquare – mixture of Urals oil (64%), Basrah Heavy (15%) and fuel oil (21%); \circ – mixture of Urals oil (64%) and Kuwait oil (36%); \blacklozenge – mixture of Urals oil (70%) and Basrah Light (30%)

It was found that feedstock quality has a significant impact on the H-Oil performance. It can be seen from Fig. 1 that VRs from Middle Eastern oils are less prone to sediment formation during hydrocracking, thus enabling the unit to operate at higher reaction temperatures and to achieve higher conversion rates. **Table 1** shows that Middle Eastern oils tend to contain more sulfur, with their VR exhibiting lower amounts of saturated hydrocarbons and higher amounts of aromatic components.

The eight-fraction SAR-ADTM characterization method, developed by the Western Research Institute, was employed to determine the effect of VR quality on H-Oil characteristics [2]. The vacuum residues obtained from 24 different types of oil from five different groups, such as extra-light, light, medium, heavy, and extra-heavy, were investigated (**Table 2**).

Table 1

Indicator	Oil grade					
	Urals	Arab Medium	Arab Heavy	Basrah Light	Basrah Heavy	Kirkuk
Density at 15°C, g/cm ³	0.877	0.872	0.889	0.878	0.905	0.873
Sulfur content, wt %	1.53	2.48	2.91	2.85	3.86	2.65
VR yield from oil, wt %	25.2	25.2	32	28.3	33.8	24.6
<i>Vacuum residue</i>						
Density at 15°C, g/cm ³	0.997	1.031	1.04	1.052	1.071	1.054
Conradson carbon residue	17.5	20.7	23.6	23.8	28.9	25.2
Sulfur content, wt %	3	5.4	5.8	5.9	7.1	5.9
Softening point, °C	40.1	44.7	51.2	50.3	68.6	58.1
Content, %:						
alkanes	18.2	9.2	6.2	7.9	7.4	9.5
Aro1	7.0	8.0	6.8	6.4	6.5	6.6
Aro2	20.7	25.4	23.5	22.7	23.9	23.3
Aro3	33.0	37.5	36.7	38.3	38.9	39.2
resins	14.0	11.0	13.6	14.4	13.4	10.2
asphaltenes, including	6.9	8.8	13.2	10.3	9.9	11.2
soluble in cyclohexane	2.4	2.4	3.3	2.8	3.0	2.3
soluble in toluene	4.4	6.1	9.5	7.2	6.6	8.4
soluble in dichloromethane	0.1	0.3	0.3	0.3	0.3	0.5

Note. Aro 1 – molecules with one aromatic ring; Aro 2 – aromatic molecules with two and three fused rings, a peri-condensed four-ring pyrene molecule, as well as molecules with three of five non-fused rings; Aro 3 – four-membered linear and cata-condensed aromatics and large polycyclic aromatic hydrocarbons with a wide range of conjugation and connectivity

Table 2

Fraction	Content, wt %	
	Minimum	Maximum
Saturated hydrocarbons	0.75	39.63
Aro1	1.89	11.07
Aro2	12.35	28.06
Aro3	22.38	44.84
Resins	5.81	23.39
asphaltenes, including	1.12	34.20
soluble in cyclohexane	0.25	8.14
soluble in toluene	0.74	25.57
soluble in dichloromethane	0.08	0.67

Following a regression analysis for 22 individual vacuum residues that underwent H-Oil cracking, the following equation was obtained:

$$C_{VR} = 65.04 - 0.5659VR_{Asp} - 0.1051VR_{Res} + 2.783VR_{Sul}, R = 0.983, \text{ error} - 0.78\%, \quad (1)$$

where C_{VR} is the conversion of straight-run VR, wt %; VR_{Asp} , VR_{Res} , VR_{Sul} are the contents of asphaltenes, resin, and sulfur in VR, respectively, wt %.

The results of regression analysis are presented in **Fig. 2**. It can be seen that the total content of asphaltenes, resins, and sulfur comprise the main factors affecting the conversion rate of vacuum residues in industrial ebullated-bed hydrocrackers under the same sedimentation rate. The effect of sulfur on VR conversion, as shown in Eq (1) agrees with the published data. Sulfides were found to be among the most highly-reactive chemical compounds, thus determining the cracking rate to a large extent [3].

The delaying effect of resin fractions and the total asphaltene content in VR on the hydrocracking conversion rate agrees well with the results reported in [4]. In this work, resins and asphaltenes were established to be the most difficult components to process via thermal conversion. Resin and asphaltene fractions contain large amounts of impurities of vanadium, nickel, and nitrogen [5, 6], which have a negative effect on both the catalyst activity [7, 8] and, consequently, the sediment formation rate [8].

Vacuum residues with high resin and asphaltene contents are expected to have poor conversion rates in the process of ebullated-bed vacuum residue hydrocracking. The higher sediment formation rate, which results from a more deactivated catalyst due to coke and metal deposition on its surface, requires more severe cracking conditions, thus ultimately decreasing the conversion rate.

Figures 3, 4 demonstrate changes in the content of different hydrocarbons in unconverted VR fractions depending on the conversion rate. It can be seen that the content of alkanes (saturates) in unconverted VR is low at very high conversion rates. This can be explained by separation of aliphatic alkane molecules from aromatic nuclei during cracking of asphaltenes and other heavy fractions. Eventually, under highest conversion rates, the content of saturates in unconverted VR is lower than that in the

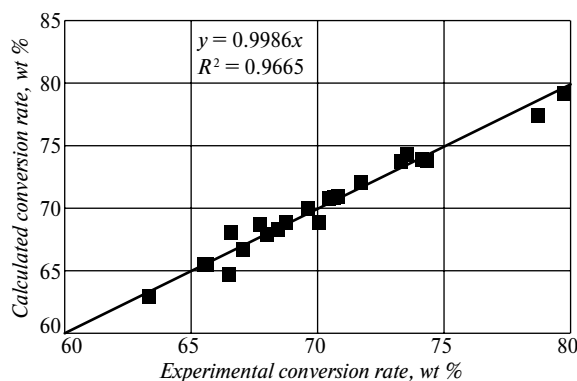


Fig. 2. Convergence between the experimental and calculated (in accordance with Eq (1)) conversion rate of straight-run VR

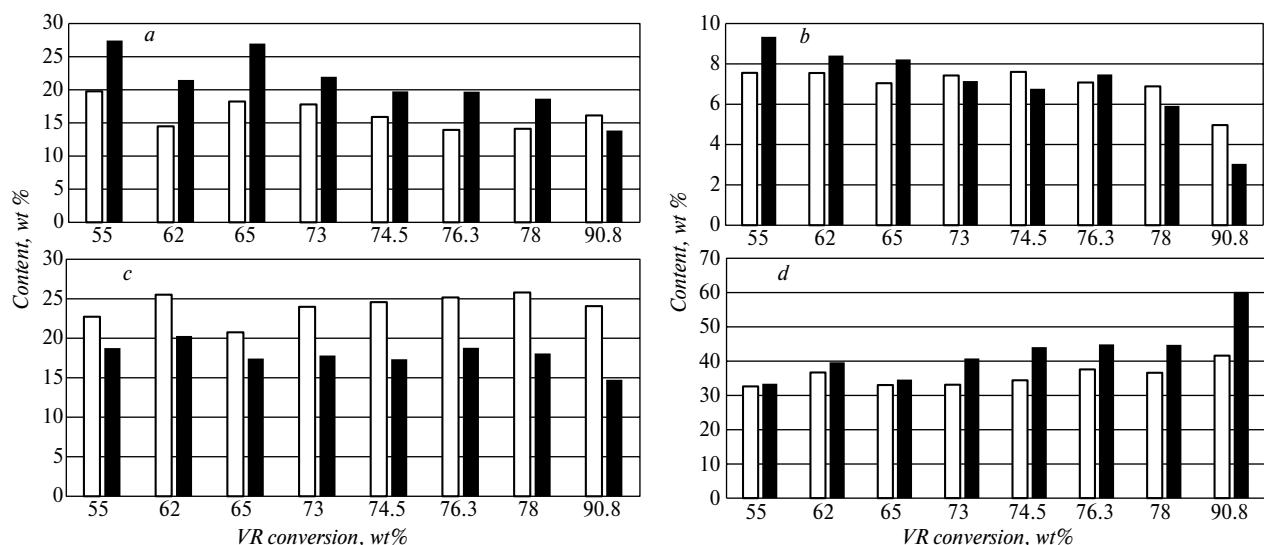


Fig. 3. Dependence of the content of saturates (a), Aro 1 (b), Aro 2 (c) and Aro 3 (d) in the feedstock (□) and in the VR (■) on the VR conversion rate

feedstock, which corresponds to further cracking of alkanes. A similar trend was observed for Aro 1, except that the decrease in the Aro 1 content in unconverted VR along with an increase in the conversion rate occurs earlier. This is consistent with the fact that Aro 1 compounds are highly similar to saturates in terms of containing single aromatic rings with a long alkane chain.

A further decrease in the content of saturates and Aro 1 in unconverted VR occurs under an increase in the conversion rate, since cracking of initial molecules or those obtained from larger molecules continues to decrease their molecular weight along with an increase in conversion, thereby facilitating their removal as lighter target fractions in the process of distillation. For the aromatic fractions containing fused ring systems, the content of Aro 2 in unconverted VR upon hydrocracking completion decreases with an increase in conversion followed by a growth in the Aro 3 fraction. Aro 2 are likely to be absent, since they consist of molecules with two or four fused rings and can be obtained by a cleavage of heavy radicals or as the original Aro 2 molecules. It seems that the cracking process also affects the aromatic rings, making the molecules in this fraction lighter and easier to distill, similarly to Aro 1. On the other hand, Aro 3 molecules have more than four condensed rings. Regardless of whether Aro 3 is the original fraction or obtained during hydrocracking at higher conversion rates, the large aromatic nuclei in this fraction are heavy

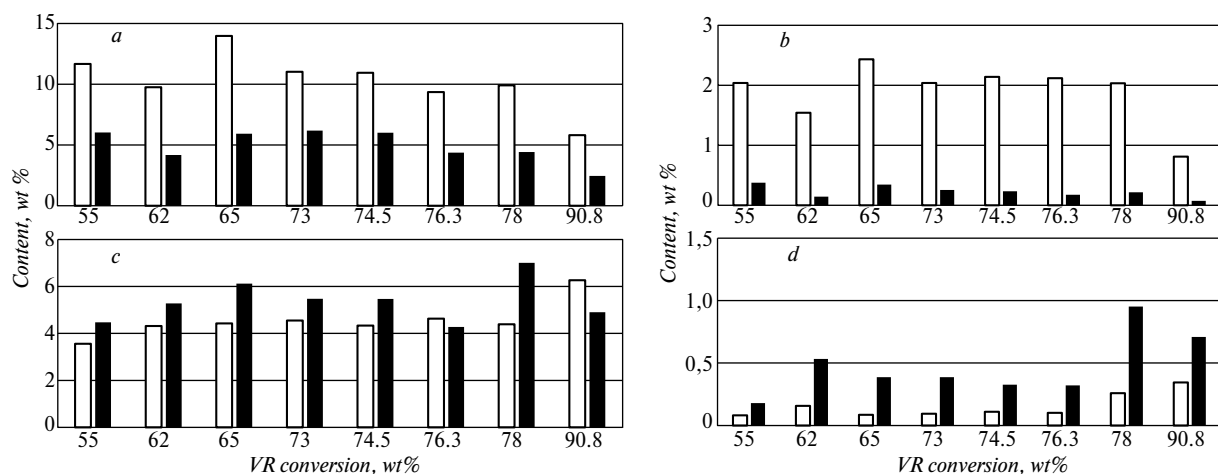


Fig. 4. Dependence of the content of resins (a) and asphaltenes soluble in cyclohexane (b), toluene (c) and dichloromethane (d) in the feedstock (□) and in the VR (■) the VR conversion rate

enough to become part of the target distillates. The relationship between the content of saturates, Aro 1, Aro 2, and Aro 3 and the conversion rate of an ebullated-bed vacuum residue hydrocracking unit can be expressed by the following regression equations:

$$VTB_{Sat} = 33.28 + 0.617046 F_{Sat} - 0.30778C, R = 0.946, \text{ error} - 5.5\%, \quad (2)$$

$$VTB_{Aro1} = 10.32 + 0.759841 F_{Aro1} - 0.11986C, R = 0.974, \text{ error} - 4.7\%, \quad (3)$$

$$VTB_{Aro2} = 13.62 + 0.597046 F_{Aro2} - 0.14038C, R = 0.94, \text{ error} - 2.4\%, \quad (4)$$

$$VTB_{Aro3} = -32.84 + 1.233803 F_{Aro3} + 0.439633C, R = 0.977, \text{ error} - 3.6\%, \quad (5)$$

where VTB_{Sat} , VTB_{Aro1} , VTB_{Aro2} , and VTB_{Aro3} are the content of saturates, Aro1, Aro2, and Aro3 in unconverted VR, respectively; F_{Sat} , F_{Aro1} , F_{Aro2} , and F_{Aro3} are the content of saturates, Aro1, Aro2, and Aro3 in the feedstock, respectively; C is the conversion rate.

Eq (2)–(5) reflect the data of Fig. 3, indicating a decrease in the content of saturates, Aro 1, and Aro 2 in unconverted VR upon a decrease in their content in the feedstock and an increase in conversion. The content of Aro 3 in unconverted VR also decreases with its decrease in the feedstock, although increasing under higher conversion rates. This might be connected with a decomposition of archipelago asphaltene structures followed by the formation of more than four-ring aromatic molecules.

Figure 4 shows that the content of resins and asphaltenes soluble in cyclohexane in unconverted VR is lower than that in the feedstock, while the content of asphaltenes in unconverted VR is higher than that in the feedstock.

The content of asphaltenes soluble in toluene exceeds that in the feedstock in six out of the nine cases studied. The toluene-asphaltene fraction is an intermediate fraction, during which some molecules form resins and asphaltenes soluble in cyclohexane. These are converted to new toluene-soluble asphaltenes by losing their aliphatic side chains, which contribute to their solubility, while the amount of toluene-soluble asphaltenes is reduced by asphaltenes soluble in dichloromethane. At higher conversion rates, new toluene-soluble asphaltenes are converted to dichloromethane-soluble asphaltenes, which are eventually converted to coke under further conversion. Eq (6)–(8) show that the content of resins (soluble in cyclohexane) and asphaltenes (soluble in dichloromethane) contained in unconverted VR depends solely on the content of these fractions in the feedstock:

$$VTB_{Res} = 0.5026 F_{Res} - 0.233, R = 0.885, \text{ error} - 9.8\%, \quad (6)$$

$$VTB_{ch} = 0.10872 F_{ch} - 0.00401, R = 0.864, \text{ error} - 18.6\%, \quad (7)$$

$$VTB_{CH_2Cl_2} = 3.5294 F_{CH_2Cl_2}, R = 0.96, \text{ error} - 19.4\%, \quad (8)$$

where F_{Res} , F_{ch} , and $F_{CH_2Cl_2}$ are the content of resins and asphaltenes in the feedstock, soluble in cyclohexane and dichloromethane, respectively.

Along with the feedstock quality, the catalyst condition is another significant factor that affects the conversion rate and efficiency of an H-Oil plant [9]. Thus, changes in the feedstock quality can result in changes in the VR conversion rate of up to 20 wt % [10], while the catalyst condition can cause a difference of up to 14 wt % [9, 11].

A previously unreported phenomenon was observed during operation of the H-Oil ebullated bed hydrocracking unit at the LUKOIL Neftohim Burgas, concerning the transformation of the catalyst into a black powder in the first reactor. The powder consisted of vanadium sulfide and iron sulfide [11]. This phenomenon was observed for the first time at the beginning of 2018, during the first maintenance operation of the unit following three years of its operation. The second maintenance performed at the end of 2021 again showed the presence of a black powder in the first reactor. The ratio between the metals in the composition of this powder was similar to that in the vacuum residue, implying that its source should have been the feedstock. It turned out that the vanadium and iron sulfides in the black powder in the first ebullated bed reactor exhibited catalytic functions. The parameters of hydrodesulfurization, hydrodemetallization, Conradson carbon residue (CCR) conversion, and hydrodeasphaltization apparently remained unchanged during the cycle when the black powder was being formed.

Since the catalyst was converted into a black powder in the first reactor, which was revealed during maintenance works at the beginning of 2018 and at the end of 2021, this catalyst could not be used for loading. Therefore, the first reactor was loaded with a fresh catalyst. Hence, new cycles of the H-Oil unit were started with a fresh catalyst in the first reactor and with

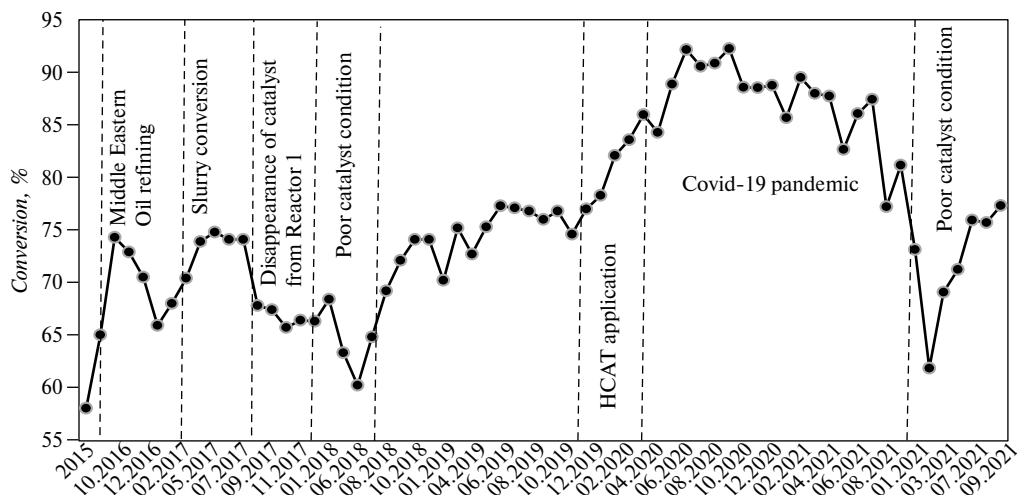


Fig. 5. Dynamics of VR conversion at the H-Oil unit during seven years of operation

the spent catalyst in the second reactor. This resulted in an unbalanced catalyst activity, thus promoting the sediment formation and equipment fouling.

The VR conversion rate ranged considerably over the seven years of operation of the H-Oil unit at the LUKOIL Neftohim Burgas (Fig. 5).

The start of refining Middle Eastern oil along with a decrease in the liquid hourly space velocity from 0.25 to 0.19 h⁻¹ increased the VR conversion from 55 to 71 wt % [10]. The addition of a catalytic cracking slurry in the amount of 8 wt % improved the conversion rate from 71 to 74 wt % [10]. Moreover, the use of nanodispersed HCAT catalyst produced a further increase in the conversion rate from 74 to 80 wt % [10]. Due to a drop in the market demand caused by the Covid-19 pandemic, and as a consequence, a decrease in the H-Oil unit through-put and a decrease in the liquid hourly space velocity from 0.19 to 0.10 h⁻¹, the

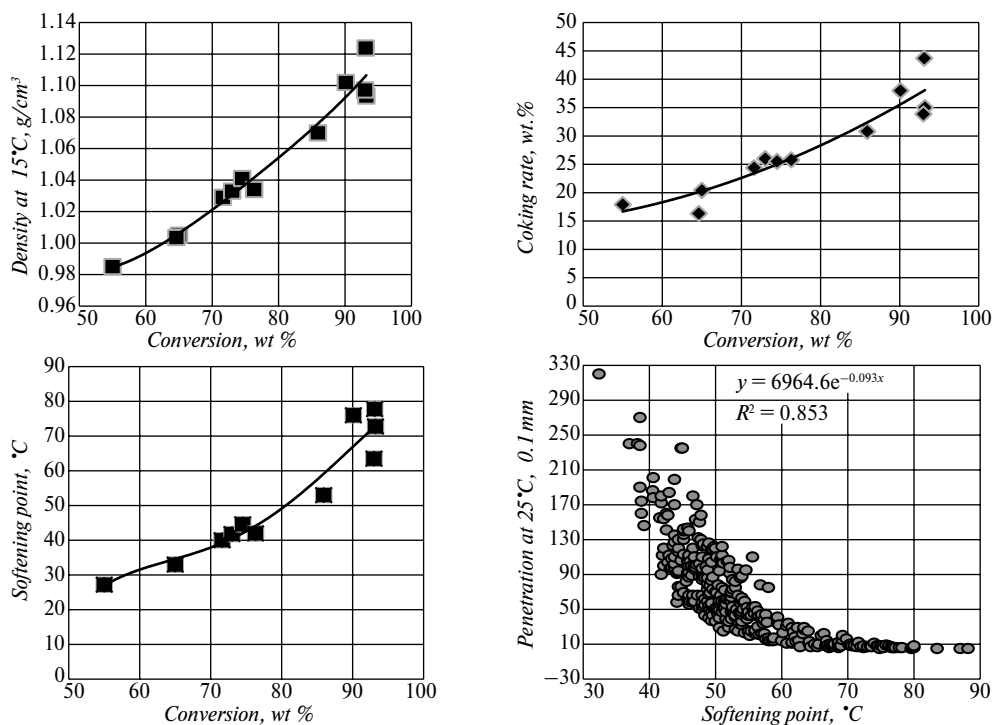


Fig. 6. Effects of H-Oil conversion on the properties of unconverted VR and the dependence of the unconverted VR penetration on the softening temperature

conversion rate increased from 80 to 93 wt % [10]. The properties of the unconverted VR also changed due to changes in the cracking severity and the associated changes in the conversion rate (Fig. 6). These rearrangements complicated the production of fuel oil with a density below the maximum limit of 1.025 g/cm³ and Conradson carbon content below 18 wt %. The higher softening point and lower penetration also challenged the use of the hydrocracked VR as a potential source for the production of road pavement bitumen.

In summary, we found that proper feedstock selection has a major impact on the rate of sediment formation, thereby affecting the cracking severity and the conversion rate. Feedstock with a higher sulfur content and a lower resin and asphaltene content contributes to higher conversion rates. An optimal activity balance of catalysts loaded into the first and second reactor can impede sediment formation and enable operation at higher reaction temperatures to reach higher conversion rates. However, higher conversion rates lead to a higher Conradson carbon content, higher density, higher softening point, and lower penetration of the unconverted VR. This fact complicates the use of hydrocracked VR in the production of bunker oil and road bitumen. New areas of application should be found for the unconverted VR obtained at higher conversion rates.

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