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INVESTIGATION OF RELATIONS OF PROPERTIES OF STRAIGHT RUN AND H-OIL UNCONVERTED VACUUM RESIDUAL OILS

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Abstract

24 straight run vacuum residual oils (SRVROs) and 28 H-Oil vacuum tower bottom products (VTBs) obtained during processing different blends of the 24 SRVROs in the LUKOIL Neftohim Burgas (LNB) ebullated bed vacuum residue (EBVR) H-Oil hydrocracking unit were analyzed for their physical and chemical properties. It was found that in both primary and secondary vacuum residual oils (VROs), the density and the Conradson carbon content strongly correlate. The properties of H-Oil VTB Conradson carbon content and density correlate with the VTB hydrogen content and H/C atomic ratio in the same manner as the SRVROs. It was also confirmed that the VRO saturate content can be predicted from data of VRO density and the use of the second order polynomial fits for both SRVROs and H-Oil VTBs. It was established that the lower density VROs have a lower density, a higher hydrogen content of asphaltenes, resins and of aromatics than those of the higher density VROs. The H-Oil VTBs have higher density asphaltenes and lower density maltenes than the SRVROs, which can explain the lower colloidal stability of the H-Oil VTBs. Dissimilar to the SRVROs the H-Oil VTB viscosity does not correlate with the asphaltene content. Instead, it correlates with the saturated content. While the SRVRO softening point strongly correlates with its viscosity, such a relation does not exist for the H-Oil VTBs, which suggests different rheological properties of the H-Oil VTBs in contrast to these of the SRVROs.

Keywords: *Vacuum residue; Vacuum residue hydrocracking; SARA; Asphaltenes; correlations.*

1. Introduction

The International Maritime Organisation (a branch of the UN) has stated that as of the 1 January 2020 all ships must reduce their sulphur emissions from 3.5% thresholds to 0.5%. The regulation has already been passed, and any attempt to change the regulation would potentially take another 22 months (i.e. the regulation will go through on the stated date). The aim of this regulation is to reduce the emission of sulphur dioxide (which results in acid rain and environmental damage) [1].

This new regulation presents a big challenge for the petroleum refining industry since the available technologies for the time being are not capable of providing solutions for the production of residual oil bunker fuel whose sulphur content must be less than 0.5%. Therefore new ways for utilization of the unconverted residual oils from the residue conversion processes have to be searched. In order to find a new application of the unconverted residual oils, one needs to know more about their properties and the relations between them.

This study is a continuation of our recent work [1] in which the effect of vacuum residual feedstock properties on the ebullated bed vacuum residue H-Oil hydrocracking (EBVRHC) conversion at approximately the same level of sediments of 0.4% in the atmospheric tower bottom (ATB) product was investigated. A relation of vacuum residual feedstock properties to the conversion that is achievable in the EBVRHC at sediments of about 0.4% in the H-Oil ATB product was found. However, the properties of the obtained vacuum tower bottom (VTB) products were not discussed there. The current study aims at investigating the relations between properties of 28 H-Oil VTB products obtained in the LUKOIL Neftohim Burgas (LNB) ebullated bed vacuum residue (EBVR) H-Oil hydrocracking unit and juxtaposes these H-Oil VTB properties relations to those of the vacuum residual oils extracted from 15 crude oils and 3 imported atmospheric residues, whose blends were processed in the LNB EBVR H-Oil hydrocracking unit.

The aim of this work is to investigate the relations of properties of the straight run vacuum residual oils and those of the obtained thereof unconverted vacuum residual oils in the LNB EBVR H-Oil hydrocracking unit and define the similarity and the dissimilarity between them in terms of their further usage.

2. Experimental

The studied straight run vacuum residual oils (SRVROs) were obtained by TBP distillation of crude oils and atmospheric residual oils (AROs) which have been processed in the LNB refinery. The atmospheric part of the TBP distillation was performed in accordance with ASTM D-2892, while the vacuum part of the TBP distillation was carried out in accordance with ASTM D-5236. The SRVROs were the fractions of the crudes or atmospheric residual oils which boil above 540°C.

The secondary H-Oil vacuum residual oils were obtained at the LNB H-Oil vacuum residue hydrocracking during processing SRVROs which were produced from blends of crudes and AROs under study. The methods used to measure the vacuum residue properties are explained in our recent work [2]. The density of the vacuum residual oils and their C_5- and C_7-asphaltenes were measured indirectly from the densities of a series of solutions of asphaltenes and vacuum residues in toluene at different concentrations as described in [2]. Solutions of asphaltene in toluene at concentrations up to an asphaltene mass fraction of 3% were prepared. Solutions of vacuum residues in toluene at concentrations up to a vacuum residue mass fraction of 6% were prepared.

The density of the SRVROs was also measured by pycnometer according to ASTM D 941. Properties of crudes and AROs and the obtained thereof SRVROs are presented in Table 1. Table 1 includes more than one set of data for some crude oils. They are related to different cargoes of the same crude and are indicators for some variability in some properties of the same crude. Table 2 summarizes the properties of the 28 H-Oil vacuum tower bottom products under study. The data about vacuum residue densities reported in Tables 1 and 2 are obtained by dilution with toluene.

3. Results and discussion

In order to find a statistically meaningful correlations between the different studying properties, an intercriteria analysis (ICrA) was performed. More about the application of ICrA for crude and oil fractions is discussed in [3]. The correlations between the studied properties are called: 'positive consonance', 'negative consonance' or 'dissonance' [3]. The values of positive consonance with μ = 0.75÷1.00 means 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. Table 3 presents data of ICrA matrix of the statistically meaningful relations of properties of the studied crudes and derived thereof vacuum residual oils.

It is evident from the data in Table 3 that the crude density strongly correlates with the vacuum residual oil content (μ = 0.98), weakly correlates with the vacuum residue viscosity (μ = 0.80), and moderately correlates with vacuum residue penetration (μ = 0.90). The crude sulphur content moderately correlates with the vacuum residual oil properties: density (μ = 0.93); Conradson carbon content (CCR) (μ = 0.92); saturates content (μ = 0.10); C_7-asphaltene content (μ = 0.90); C_5-asphaltene content (μ = 0.88); density of C_5-deasphalted oil (DAO C_5 d_{15}) (μ = 0.92); density of C_7-deasphalted oil (DAO C_5 d_{15}) (μ = 0.88); density of C_5-

asphaltenes (d_{15} C_5 asp.) (μ = 0.85); viscosity (μ = 0.87); softening point (SP) (μ = 0.89); and penetration (μ = 0.06). The crude sulphur content strongly correlates with the vacuum residue sulphur content (μ = 0.98). These findings are in line with the conclusions of Swafford, and McCarthy [4] according to which the sulphur content correlates with the aromaticity. The higher the crude sulphur content the higher the vacuum residue density, and Conradson carbon content (which are known to correlate with the aromaticity [5]), and the lower the saturate content. It is interesting to note here that the vacuum gas oil (VGO) property density moderately correlates with the vacuum residual (VR) oil properties density (μ = 0.93); CCR (μ = 0.86); sulphur (μ = 0.94); saturate content (μ = 0.12); DAO C_5 d_{15} (μ = 0.91); DAO C_7 d_{15}) (μ = 0.87); d_{15} C_5 asp. (μ = 0.89); d_{15} C_7 asp. (μ = 0.80); SP (μ = 0.86); and penetration (μ = 0.07). These correlations of the VGO density with the vacuum residue properties density and Conradson carbon content suggest a feasible similarity of the aromatic structures in the VGO with those of the VR. Having in mind that the VGO is easier to characterize than the VR one may suppose that the conclusions of analyzing the VGO from a crude oil might be transferred to those of the VR from the same crude.

The VR density strongly correlates with the VR CCR (μ = 0.97) that supports the conclusion, that the correlation between these two properties can be used to verify the correctness of their measurements, stated in our recent work [5]. It should be noted here that densities of the SRVROs were measured not only by dilution with toluene but also by the use of pycnometer (ASTM D 941). The measured by pycnometer densities were found to not correlate with many of the VR properties that correlate with the density measured by dilution with toluene, and the reason is that the SRVRO density measured by dilution with toluene does not statistically meaningful correlate with the SRVRO density measured by pycnometer as depicted in Figure 1 (R<0.75).

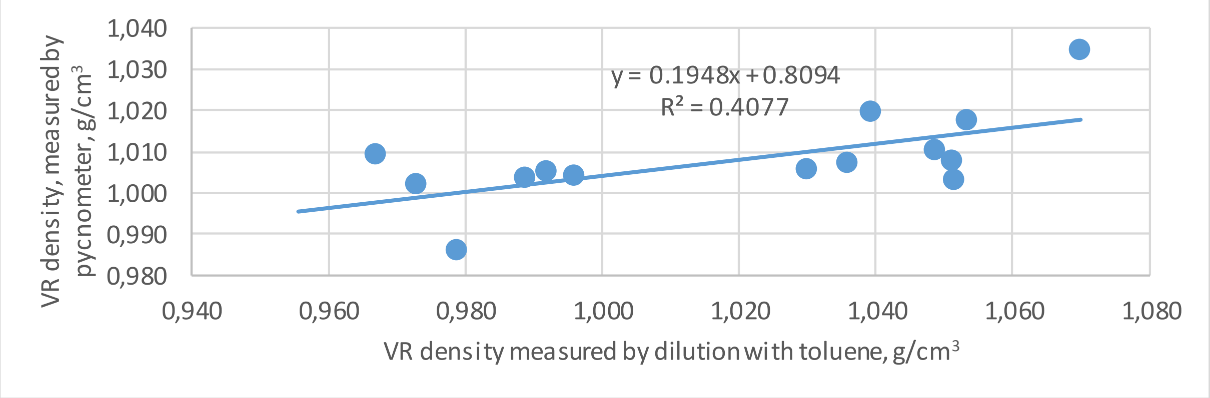

Figure 1. Relation of vacuum residue density measured by pycnometer to that measured by dilution with toluene

The SRVRO density measured by dilution with toluene strongly correlates with the SRVRO properties DAO C_7 d_{15} (μ = 0.95) and d_{15} C_5 asp. (μ = 0.95). It moderately correlates with the SRVRO properties sulphur (μ = 0.93); saturate content (μ = 0.06); DAO C_5 d_{15} (μ = 0.91); softening point (μ = 0.87); and penetration (μ = 0.07). The density weakly correlates with the content of C_7-asphaltenes (μ = 0.81); content of C_5-asphaltenes (μ = 0.84); d_{15} C_7 asp. (μ = 0.77); viscosity (μ = 0.79).

The SRVRO Conradson carbon content moderately correlates with the SRVRO properties sulphur content (μ = 0.90); saturate content (μ = 0.07); the content of C_7-asphaltenes (μ = 0.87); the content of C_5-asphaltenes (μ = 0.88); DAO C_7 d_{15} (μ = 0.90); d_{15} C_5 asp. (μ = 0.91); DAO C_7 d_{15} (μ = 0.90); viscosity (μ = 0.93); softening point (μ = 0.93); and penetration (μ = 0.07). It weakly correlates with DAO C_7 d_{15} (μ = 0.84).

Considering that the VR sulphur content strongly correlates with the crude oil sulphur content (μ = 0.98) the properties of VR that correlate with the sulphur content have been already discussed above.

Table 1. Physical and chemical properties of the crude oils and derived thereof vacuum residual oils (SRVROs)

	Urals1	Urals2	AM	AH	AH2	VD	BL	BL2	BH	KK	IH	KEB	EB	KH	NAR	IRB	KH2	KH3	CPC1	CPC2	LSCO1	LSCO2	VAR	TAR
d_{15} °C, g/cm^3	0.877	0.875	0.8721	0.889	0.892	0.8321	0.878		0.905	0.873	0.882	0.876	0.891	0.858		0.9794	0.8754	0.878	0.795	0.805	0.854	0.8469		0.959
Sulphur, %	1.53	1.39	2.48	2.91	2.97	1.97	2.85		3.86	2.65	2.27	2.64	1.76	0.81		2.71	0.65	0.40	0.55	0.63	0.57	0.59	0.91	2.16
IBP- 110 °C , wt.%	6.5	6.2	8.9	6.9	6.9	14.8	8.4		6.7	9.4	8.5	8.5	5.7	16.3			5.3	5.8	17.8	16.5	8.6	9.9		
110-180 °C , wt.%	8.6	8.7	10.8	9.1	8.9	15.7	10.5		9.0	11.8	10.1	10.3	9.1	10.9			7.6	6.0	19.5	16.8	11.4	10.7		
180-240°C, wt.%	8.7	9.4	9.1	7.5	8.1	11.0	7.7		7.8	8.5	7.9	8.8	8.9	2.3			7.7	5.8	12.7	13.1	9.1	10.2		
240-360°C, wt.%	21.0	20.8	20.4	18.7	19.9	21.4	18.9		17.7	20.2	19.6	19.9	19.0	11.8	3.4	14.5	20.6	19.0	24.1	23.2	23.1	24.6		
360-540°C, wt.%	29.0	29.0	24.6	24.8	24.5	21.6	25.2		24.0	24.4	24.8	23.9	30.2	34.2	46.7	25.5	30.8	39.1	18.1	20.0	28.1	25.6		
> 540 °C, wt.%	25.2	24.9	25.2	32.0	30.5	14.6	28.3		33.8	24.6	28.1	27.7	26.2	23.7	50.0	60.0	27.1	23.4	6.8	9.3	18.7	17.4		
VGO d_{15}, g/cm^3	0.910		0.923	0.926		0.934	0.927		0.944	0.925	0.927	0.924	0.913	0.895			0.897	0.900	0.890	0.897	0.904	0.913		0.916
VR d_{15} °C, g /cm^3	0.996	0.995	1.030	1.040	1.047	1.052	1.051	1.045	1.070	1.053	1.049	1.036	1.049	0.989	1.001	1.0421	0.9730	0.967	0.956	0.981	0.992	0.993	0.979	1.007
VR CCR, wt.%	17.5		20.7	23.6		21.4	23.8		28.9	25.2	23.9	23.3	25.5	17.1		23.5	13.6	10.9	9.2	16.0	14.0	14.9	13.5	18.8
VR sulphur, %	3.0	2.9	5.4	5.8		6.0	5.9		7.1	5.9	5.2	5.7	3.3	1.7	2.9		1.48	0.94	1.32	2.10	1.58	1.59	1.2	
Saturates, wt.%	25.6	22.4	11.8	12.4	12.0	11.7	12.3	15.0	12.3	15.2	17.0	15.0	12.0	33.0	28.7	16.9	36.9	44.5	44.4				30.4	22.4
Aromatics, wt.%	52.5	66.5	68.3	61.9	62.2	73.5	64.8	65.0	54.1	55.4	52.6	64.2	57.9	50.2	50.9	57.6	44.9	42.7	46.2	40.8		42.9	53.2	55.5
Resins, wt.%	7.8	4.9	5.3	4.4	6.1	6.4	4.9	6.2	5.8	5.0	5.0	4.2	12.6	5.7	6.7	5.9	5.8	9.8	3.8	10.3		4.5	8.1	10.0
C_7-asph., wt.%	14.1	6.3	14.6	21.3	19.9	8.5	18.0	13.8	27.7	24.3	25.4	16.6	17.5	11.1	13.7	19.6	12.3	3.0	5.6	3.4	7.8	5.6	8.3	12.1
C_5-asph., wt.%	17.6	13.9	25.5	32.9	29.5	19.5	27.7	22.5	37.0	33.1	36.2	25.7	27.3	17.8	21.3	30.2	24.5	8.7	11.9	11.0	15.5	13.1	16.3	22.1
DAO C_5 d_{15}, g/cm^3	0.969		0.991	0.983		1.024	1.005		1.014	0.997	0.981	0.997		0.965		0.992			0.942		0.970		0.957	0.975
DAO C_7 d_{15}, g/cm^3	0.977	0.985	1.007	1.011	1.031	1.037	1.023		1.027	1.013	1.004	1.008	1.024	0.979		1.010			0.949		0.978		0.965	0.987
C_5-asph. d_{15}, g/cm^3	1.147		1.166	1.177		1.182	1.195		1.180	1.191	1.194	1.168		1.116		1.179			1.070		1.135		1.111	1.135
C_7-asph. d_{15}, g/cm^3	1.132	1.172	1.191	1.158	1.204	1.244	1.204		1.201	1.204	1.209	1.207	1.193	1.075		1.200			1.074		1.199		1.161	1.174
Kin. vis.at 80°C, mm^2/s of the blend 70%VR/ 30 %FCC HCO	220.9		338.3	374.6		219.3	368.9		731.9	514.1	528.6	392.3		117.1							116.9			
Sofening point,°C	40.1	42.4	44.7	51.2		43.7	50.3		68.6	58.1	61.9	47.8		27.8		54.0	31.5							
Penetration	182.0		104.0			79.0					20.0	67.0		300.0										
V, ppm	255		143.0	115		21	42	77	187	139	202	81	80.0		226	127		105	120		116	79	40	115
Ni, ppm	79		40.0	48		17	12	21	48	49	63	24	74.0		27	63		12	35		46	32	8	20

Table 2. Physical and chemical properties of the H-Oil VTBs under study

Nr.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Conversion,wt.%	75	69	70.4	74.9	64.6	64.2	58.5	67.5	73.0	67.3	61.3	62.0	55.3	72.3	67.4	65.8	64.9	72.5	75.3	81.2	70.7	74.3	72.7	75.7	67.0	68.9	64.7	67.3
ATB HFT, wt.%	0.23	0.41	0.38	0.36	0.44	0.38	0.46	0.42	0.16	0.53	0.42	0.65	0.32	0.38	0.42	0.50	0.49	0.30	0.10	0.36	0.39	0.20	0.370	0.290	0.410	0.640	2.290	0.440
d$_{15}$,g/cm^3	1.005	1.010	1.020	1.020	1.024	1.014	1.001	1.025	1.035	1.028	1.008	1.015	0.985	1.026	1.019	1.012	1.017	1.033	1.041	1.055	1.029	1.058	1.036	1.049	1.008	1.022	0.995	1.009
CCR,wt.%	21.8	22.6	23.4	24.1	23.6	22.1	19.1	23.6	24.0	23.1	22.5	22.5	17.9	24.7	23.3	22.4	23.3	25.5	25.5	28.2	24.4	28.8	25.7	27.6	22.2	22.4		
VIS (70%VTB/30% HCO) at 80°C, mm^2/s	90.7	106.7	112.8	103.1	103.7	117.2	89.2	116.4	114.7	103.3	89.6	106.6	78.4	89.6	96.5	90.2	74.2	107	111.7	113.9								
Soft. point, °C	37.8	38.4	37.5	38.1	41.3	37.9	27.6	41.0	36.0		40.7	37.4	26.7	39.4	33.5	33.5	28.0	40.85	44.6	50.9	55.8	56.3	44.7	51.1				
H, wt.%	10.8	10.7	10.6	10.4	10.5	10.9	11.2	10.4	10.6	10.2	10.6	10.7	11.7					10.4	10.6			9.6					11.21	
C, wt.%	88.2	88.0	88.2	88.4	88.7	87.2	87.2	87.8	87.7	87.2	87.3	88.0	87.4					87.7	88.2			87.7					88.13	
N, wt.%	0.4	0.4	0.5	0.5	0.5	0.6	0.5	0.5	0.6	0.7	0.5	0.5	0.5					0.66	0.6			0.7					0.48	
S, wt.%	1.22	1.44	1.66	1.40	1.42	1.39	1.50	1.58	1.52	1.61	1.62	1.49	1.07	1.56	1.53	1.55	1.53	1.61	1.40	1.61	1.38	1.69	1.78	1.59	1.47	1.58	1.17	1.30
H/C	1.46	1.46	1.44	1.41	1.42	1.49	1.53	1.43	1.45	1.41	1.45	1.46	1.60					1.42	1.44			1.31						
S/N	3.4	3.3	3.7	2.9	2.9	2.5	3.1	3.4	2.6	2.3	3.4	3.3	2.1															
Saturates, wt.%	29.1	29.5		26.0		23.1		23.2		20.0		21.7	34.5					23.5	22.6		19.4		23.1	21.4			26.1	25.6
Aromatics, wt.%	50.1	49.9		53.1		55.6		53.2		40.9		48.7	44.2					51.3	51.4		53.5		47.4	50.3			51.6	56.4
Resins, wt.%	10.7	13.8		6.5		5.9		7.2		24.4		18.9	5.6					6.7	7.5		5.7		5.4	10.0			10.3	5.8
C$_7$- asphaltenes, wt.%	10.1	6.8	15.4	14.5	16.1	15.3	10.8	16.4	14.5	14.7	18.2	10.7	15.7	17.7	16.4	10.2	15.4	17.2	18.5	20.0	21.3	22.8	21.4	18.3	14.6	16.4	12.0	12.2
C$_5$-asphaltenes,wt.%	21.0	26.4	26.0	27.0	23.6	24.9	25.5	26.0	28.5	28.6	28.9	27.7	24.5	27.4	25.4	26.3	24.4	25.8	28.5	23.1	26.0	27.5	24.2	29.8	21.9	24.0		
C$_7$-asph.d$_{15}$, g/cm^3	1.262	1.219	1.272	1.249	1.231	1.273	1.222	1.266	1.272	1.304	1.198	1.198	1.157	1.249	1.208	1.258	1.249	1.240	1.289		1.265	1.327	1.249	1.240	1.268	1.267	1.266	1.216
C$_5$-asph. d$_{15}$, g/cm^3	1.198	1.209	1.214	1.268	1.222	1.185	1.162	1.177	1.203	1.191	1.189	1.165	1.138	1.197	1.202	1.185	1.209	1.224	1.242	1.250	1.226	1.283	1.238	1.230	1.217	1.221		
DAO C$_7$ d$_{15}$, g/cm^3	0.983	0.997	0.985	0.989	0.992	0.978	0.979	0.988	1.004	0.992	0.974	0.997	0.959	0.988	0.989	0.990	0.983	0.998	0.997		0.979	0.998	0.989	1.014	0.974	0.984	0.967	0.986
DAO C$_5$ d$_{15}$, g/cm^3	0.964	0.954	0.966	0.951	0.975	0.968	0.955	0.980	0.981	0.974	0.949	0.967	0.944	0.973	0.969	0.962	0.967	0.980	0.978	1.008	0.974	0.992	0.984	0.988	0.962	0.971		
<540ºC	13.33	13.21	13.21	13.67	10.77	11.43	12.14	12.33	13.44	13.75	13.00	13.00	13.33	15.59	16.56	17.06	19.00											

Table 3. Intercriteria matrix of properties of crude oils and derived thereof vacuum residual oils (the figures in bold mean statistically meaningful correlation)

	Crude d 15	*Crude Sul*	*VGO d15*	*VR d 15*	*VR CCR*	*VR Sul*	*Sat*	*C7-asp*	*C5-asp*	*DAO C5 d15*	*DAO C7 d15*	*d15-C5 asp*	*d15-C7asp*	*C5 ins.-C7 sol*	*VIS*	*SP*	*Pen.*
Crude d_{15}	1																
> 540 °C	**0.98**	0.63															
VR d_{15}	0.62	**0.93**	**0.93**	1.00													
VR CCR	0.61	**0.92**	**0.86**	**0.97**	1.00												
VR Sul	0.58	**0.98**	**0.94**	**0.93**	**0.90**	1.00											
Sat.	0.47	**0.10**	**0.12**	**0.06**	**0.07**	**0.11**	1.00										
Aro	0.49	0.71	0.70	0.67	0.62	0.70	-0.80										
C_7-asp	0.60	**0.90**	0.73	**0.81**	**0.87**	**0.78**	-0.69	1.00									
C_5-asp	0.62	0.88	0.75	**0.84**	**0.88**	**0.81**	-0.73	**0.98**	1.00								
DAO C_5 d_{15}	0.64	**0.92**	**0.91**	**0.91**	**0.84**	**0.90**	**-0.89**	0.52	0.61	1.00							
DAO C_7 d_{15}	0.64	**0.88**	**0.87**	**0.95**	**0.90**	**0.87**	**-0.93**	0.63	0.72	**0.97**	1.00						
d_{15}-C_5 asp	0.68	**0.85**	**0.89**	**0.95**	**0.91**	**0.89**	**-0.94**	**0.76**	**0.82**	**0.85**	**0.91**	1.00					
d_{15}-C_7asp	0.57	0.64	**0.80**	**0.77**	0.65	0.67	**-0.87**	0.41	0.52	**0.81**	0.77	**0.81**	1.00				
VIS	**0.80**	**0.87**	**0.75**	**0.79**	**0.93**	0.73	-0.55	**0.92**	**0.92**	0.41	0.47	0.65	0.51	0.25	1.00		
SP	0.40	**0.89**	**0.86**	**0.87**	**0.93**	0.83	-0.73	**0.84**	**0.82**	0.47	0.59	**0.80**	0.64	0.15	**0.97**	1.00	
Pen.	**0.10**	**0.06**	**0.07**	**0.07**	**0.93**	**0.08**	**0.87**	0.45	-0.74	0.39	0.31	**0.02**	**0.07**	**0.13**	**-0.85**	**-0.92**	1.00

**Note:* The marked in bold figures concern statistically meaningful correlation*

The VR saturate content moderately correlates with the VR properties: DAO C_5 d_{15} (μ = 0.89); DAO C_7 d_{15} (μ = 0.93); d_{15} C_5 asp. (μ = 0.94); d_{15} C_7 asp. (μ = 0.87); and penetration (μ = 0.87). It weakly correlates with the VR aromatics content (μ = 0.80). It is interesting to note here the correlation of the VR saturate content with the VR C_5 asphaltene density, which suggests that the higher the VR saturate content, the lower the asphaltene aromaticity is. One could also suppose that the lower density higher saturates content SRVROs may have aromatic and resin fractions which are richer in hydrogen and has lower aromaticity similar to their asphaltene fractions than the lower density, the lower saturate content SRVROs. In order to verify this assumption, two SRVROs not included in the data of Table 1 were separated in SARA fractions and their element compositions were determined. The data for these two SRVROs are summarized in Table 4.

Table 4. SARA analysis data and element composition of SARA fractions of a lower and a higher density SRVRO

SARA, wt.%		*C, %m/m*	*H, %m/m*	*N, %m/m*	*S, %m/m*	d_{15}
A higher density (d_{15}=1.0511) SRVRO						
Sat.	15.0	84.9	13.9	0.1	3.7	0.895
Aro.	65.0	83.1	9.9	0.3	8.3	1.059
Res.	6.2	81.0	9.75	1.11	6.9	1.068
Asp. (C_7)	13.8	81.5	7.4	0.87	10.4	1.202
Whole VR			10.1	0.36	7.2	1.051
A lower density (d_{15}=0.9580) SRVRO						
Sat.	48.5	86.3	13.9	< 0.01	0.1	0.895
Aro.	39.3	86.7	10.8	0.59	1.4	1.017
Res.	9.5	83.6	10.5	1.26	1.6	1.031
Asp. (C_7)	2.7	85.1	8.2	1.13	2.9	1.153
Whole VR			12.2	0.38	0.82	0.958

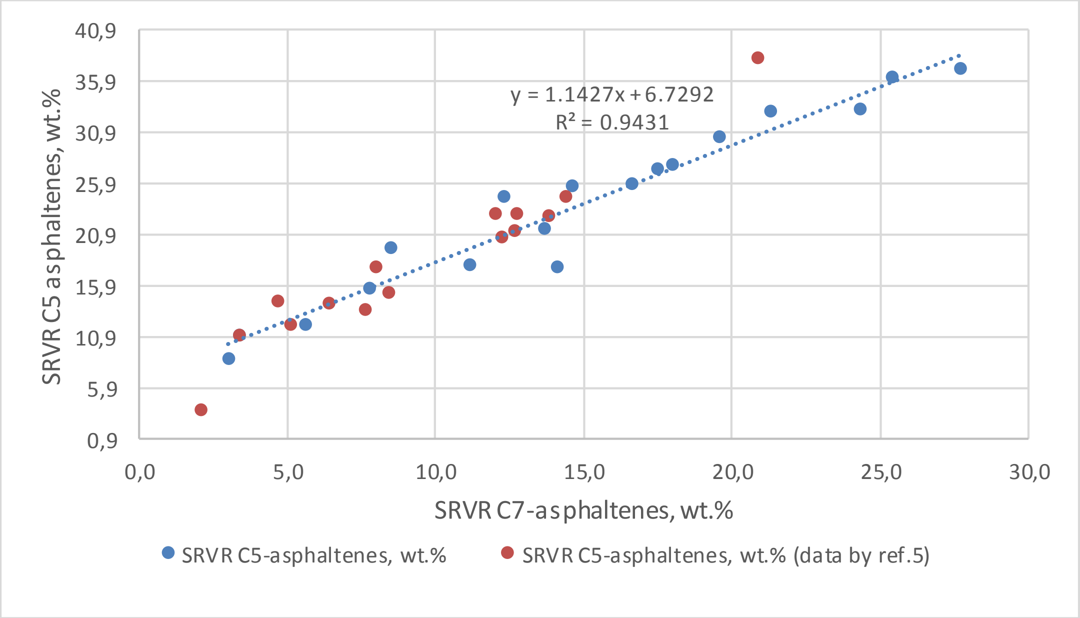

Figure 2. Relation of C_7 to C_5 asphaltenes in SRVROs originating from different crudes

It is evident from the data in Table 4 that indeed the lower density, the lower saturate content SRVRO has aromatic, resin and C_7 asphaltene fractions which have a lower hydrogen content and lower density than the same SARA fractions of the higher density, lower saturate content SRVRO.

The VR C_7 asphaltene content strongly correlates with the C_5 asphaltene content ($\mu = 0.98$), moderately correlates with the VR viscosity ($\mu = 0.92$) and weakly correlates with the VR softening point ($\mu = 0.84$) and the C_5 asphaltene density ($\mu = 0.76$). Figure 2 exemplifies the relation of C_7 to C_5 asphaltenes in SRVROs originating from different crudes. The data in blue squares are from this work, while that in red diamonds are taken from ref. 5. This data indicates that when information of C_5 or C_7 asphaltene content for an SRVR is available, the content of the other asphaltenes can be predicted by the equation shown in Figure 2.

Table 5 presents data of ICrA matrix of the statistically meaningful relations of properties of the studied 28 H-Oil VTB products.

Table 5. Intercriteria matrix of properties of VTBs (the figures in bold mean statistically meaningful correlation)

	Conv	*VTB D15*	*VTB CCR*	*VTB VIS*	*SP*	*H*	*H/C*	*Sat*
Conv	1.00							
d_{15}	**0.78**	1.00						
CCR	**0.82**	**0.96**	1.00					
SP	0.66	**0.80**	**0.82**	0.68	1.00			
H	0.34	**0.10**	**0.07**	0.37	**0.08**	1.00		
Sul	0.35	0.64	0.59	0.32	0.37	**0.23**		
H/C	0.30	**0.12**	**0.06**	0.38	**0.08**	**0.99**	1.00	
Sat	0.38	**0.23**	0.30	**0.23**	**0.19**	**0.75**	0.74	1.00
C_7-asp d_{15}	0.59	0.59	0.56	0.49	0.55	0.32	0.26	0.38
C_5-asp d_{15}	**0.79**	**0.75**	**0.81**	0.38	0.70	**0.22**	**0.19**	0.64
DAO C_7 d_{15}	0.65	**0.79**	**0.73**	0.58	0.46	0.27	0.28	0.47
DAO C_5 d_{15}	0.69	**0.91**	**0.84**	0.55	0.69	0.28	0.29	**0.22**

**Note: The marked in bold figures concern statistically meaningful correlation*

The data in Table 5 indicates that the SRVRO conversion in the EBVRHC weakly correlates with the VTB properties density ($\mu = 0.78$); Conradson carbon content ($\mu = 0.82$); and the density of C_5 asphaltenes ($\mu = 0.79$). Therefore with increasing of VR conversion in the EBVRHC aromaticity of the VTB product increases most probably as a result of denuding of the alkyl chains attached to the aromatic cores of the VR aromatic molecules.

Similar to the SRVROs, the properties density and CCR content strongly correlate ($\mu = 0.96$). However, as evident from Figure 3, the relation of CCR to density in H-Oil VTBs is a bit different than that of the SRVROs. Figure 3 also includes data from ref.5 with red diamonds which are based on SRVROs (77% of the data), H-Oil VTBs (17% of the data) and visbreaker vacuum residual oils (6% of the data). From this data, one may conclude that the relation established in ref. 5 is very close to that for the SRVROs since the data in ref.5 is mainly based on SRVROs (77% of the data) and that the relation of the properties VR CCR and density may vary for the straight run VROs and the secondary VROs. However, this relation is always strong.

The H-Oil VTB properties density and CCR as evident from Table 5 moderately correlate with hydrogen content ($\mu = 0.10$; and $\mu = 0.07$ respectively) and H/C atomic ratio ($\mu = 0.12$; and $\mu = 0.06$ respectively). As shown in Figures 4 and 5 the relation of the H-Oil VTB properties density and CCR lie on the curve established in ref.5 and therefore can be calculated from the relations for these properties determined in ref.5.

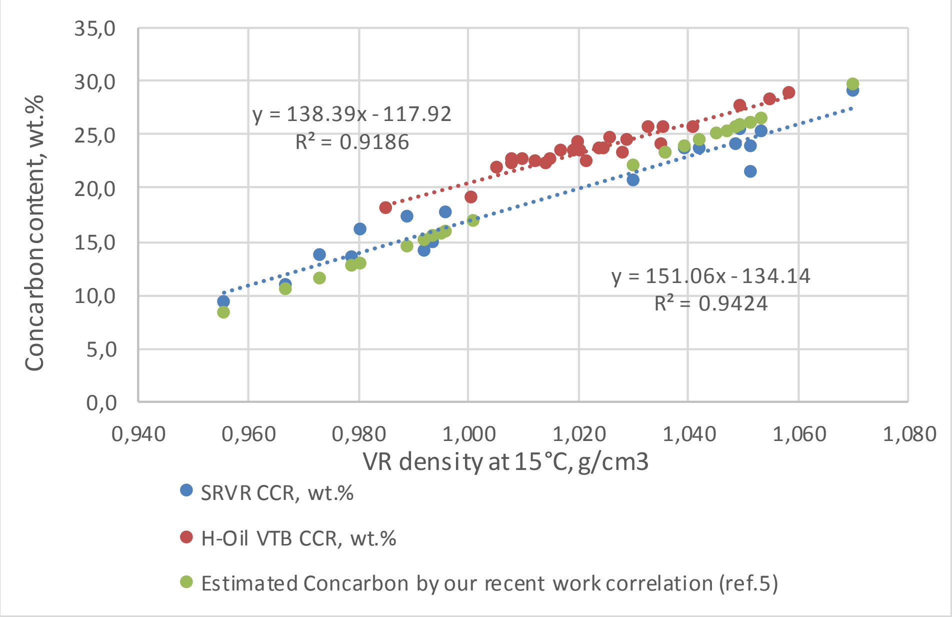

Figure 3. Relation of density to Conradson carbon content for SRVROs and H-Oil VTB products

Similar to the SRVROs, the H-Oil VTB density correlates with the density of C_5-asphaltenes and with the C_5-deasphalted oil (DAO). Figures 6 and 7 illustrate the relations of VR density to the C_5-asphalene density and the C_5-DAO density for SRVROs and H-Oil VTBs. This data shows that the increase of VR density is associated with an increase of C_5-asphalene density and the C_5-DAO density. However, the curve of H-Oil VTB C_5-asphalene density lies above that of the SRVOs, while the curve of the C_5-DAO density of H-Oil VTB lies below that of the SRVOs. These findings are in line with the lower colloidal stability of the secondary H-Oil VTB in which a higher aromatic, higher density asphaltenes are surrounded by a lower aromatic, lower density DAO.

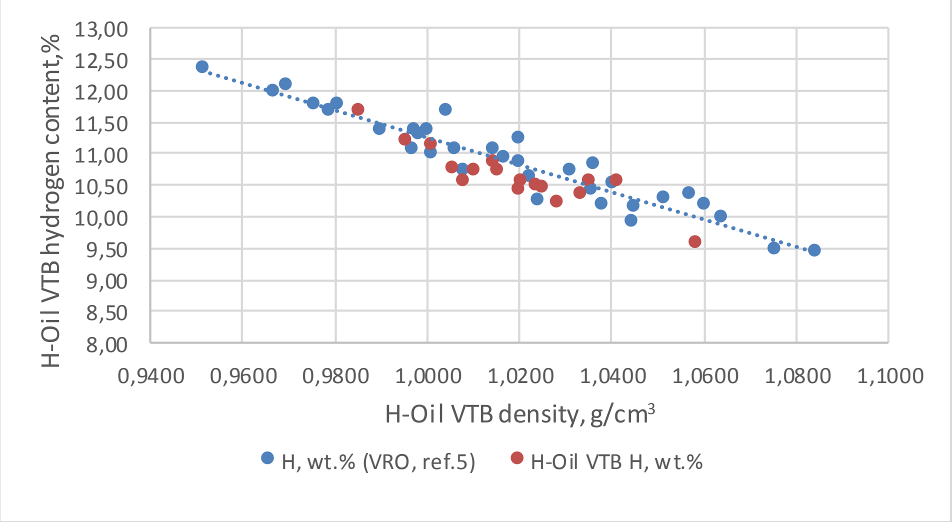

Figure 4. Relation of H-Oil VTB density to H-Oil VTB hydrogen content

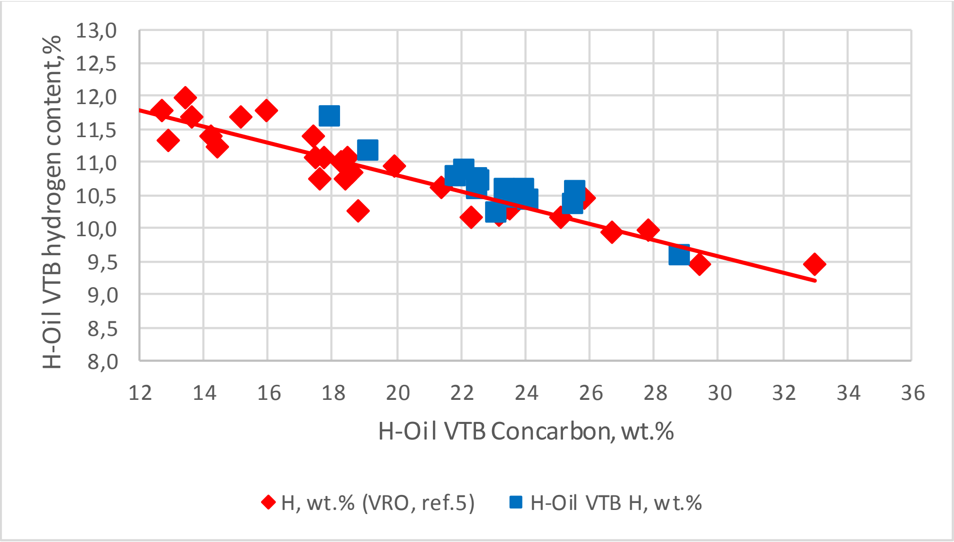

Figure 5. Relation of H-Oil VTB Conradson carbon content to H-Oil VTB hydrogen content

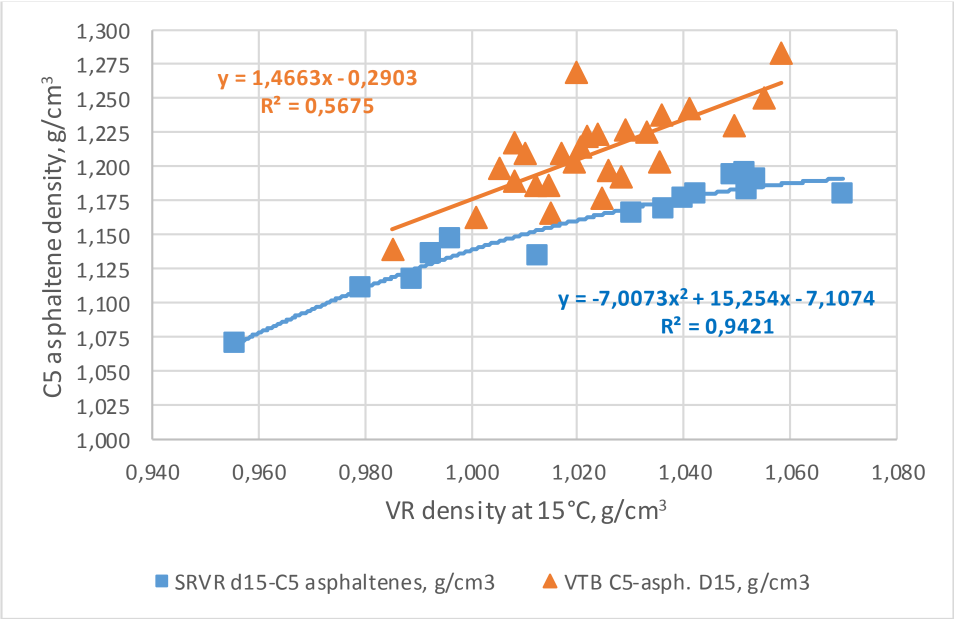

Figure 6. Relation of VR density to C_5-asphaltene density for SRVROs and for H-Oil VTBs

Figure 8 shows the relation of VR density to saturate content of SRVROs and H-Oil VTBs. This data indicates that the VR saturate content in both primary and secondary VROs can be estimated from a second order polynomial of the VR density. However, the H-Oil VTBs have a higher saturate content at the same value of the density of the VRO. The relations shown in Figure 8 can be used as a tool for verifying the correctness of the SARA analysis. If the measured saturate content deviates from the established dependence on density, it would mean or incorrect measurement of SARA or density, or appearance of a new phenomenon not accounted for in this relation. It must be pointed out that this second order polynomial dependence of VR saturates on density has been tested on 97 SRVROs measured in different laboratories and proved its validity [6]. This study shows that the second order polynomial also fits the dependence of the H-Oil VTB saturates on density.

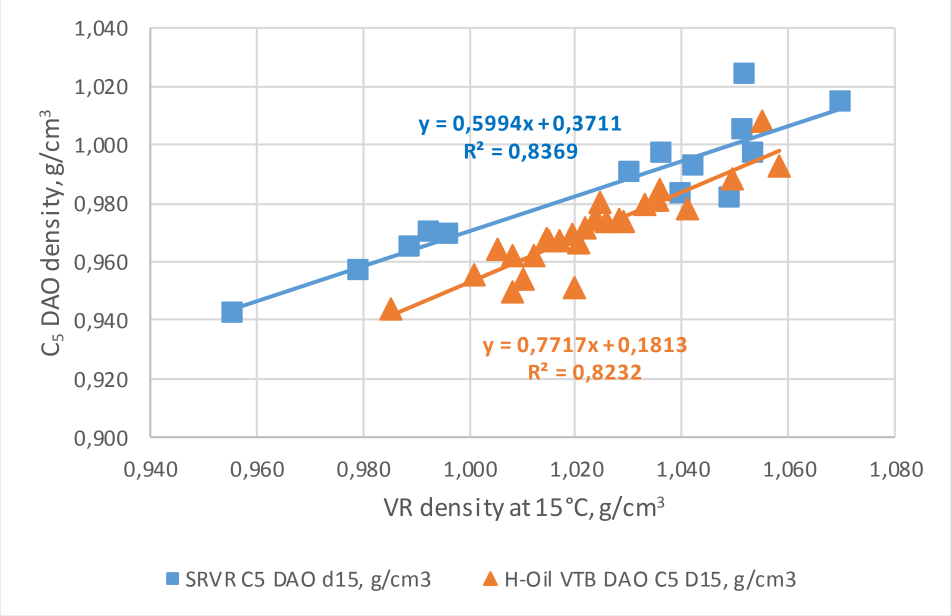

Figure 7. Relation of VR density to C5-DAO density for SRVROs and for H-Oil VTBs

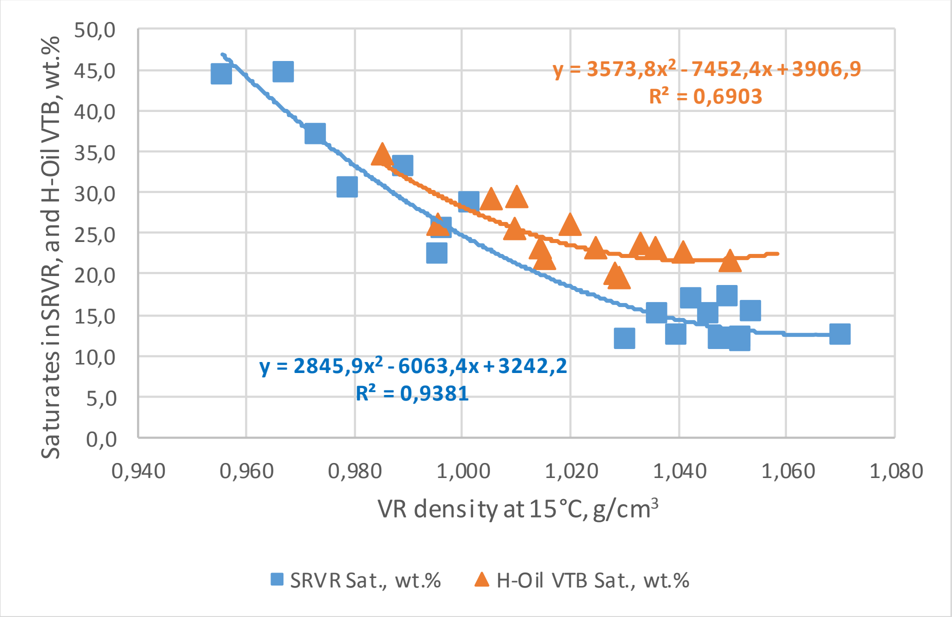

Figure 8. Relation of VR density to saturate content of SRVROs and of H-Oil VTBs

Similar to the SRVROs the VR Conradson carbon content of the H-Oil VTBs correlates with the property softening point. Figure 9 shows this dependence and indicates that at the same CCR, the H-Oil VTBs are harder and have a lower softening point.

Dissimilar to the SRVROs, the H-Oil VTB viscosity does not correlate with the asphaltene content, as shown in Figure 10. Instead, the H-Oil VTB viscosity correlates with the saturate content as presented in Figure 11. This data suggests that the H-Oil VTB viscosity depends on the hydrogenation activity of the catalyst, and it is not influenced by the number of asphaltenes in it in contradiction to the SRVROs. The lower viscosity of the H-Oil VTBs at the same asphaltene content supposes a different size and shape of the asphaltenes in comparison to the SRVRO asphaltenes. It also suggests higher mobility of the asphaltenes in the H-

Oil VTBs which along with the lower aromaticity of the DAO contributes to the easier asphaltene aggregation observed in the H-Oil VTBs.

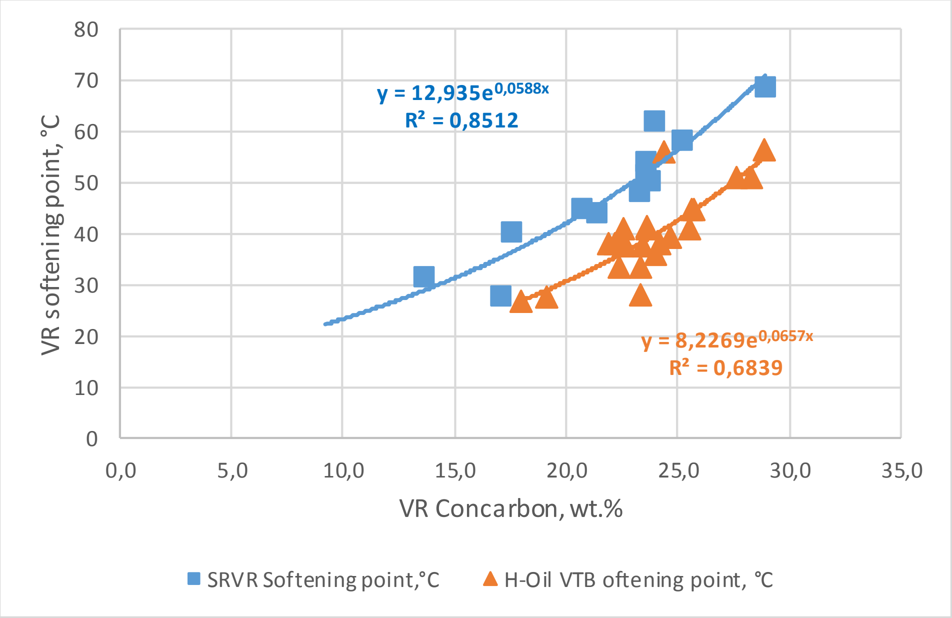

Figure 9. Relation of VR Conradson carbon content to softening point for SRVROs and for H-Oil VTB s

By regression the data for VTB density and 540°C- fraction content in H-Oil VTB and the kinematic viscosity of the blend 70% H-Oil VTB/30% FCC HCO the following equation was developed:

$Kin.Vis = 685.3D15 - 3.866(540°C -) - 543.5$ R=0.84

where: Kin. Vis = kinematic viscosity of the blend 70% H-Oil VTB/30% FCC HCO at 80°C mm^2/s; (properties of the diluent FCC HCO are given in ref.7); D15 = density of H-Oil VTB at 15°C, g/cm$^{3;}$ 540°C = fraction content of the material boiling below 540°C according to high temperature simulation distillation, ASTM D 7169.

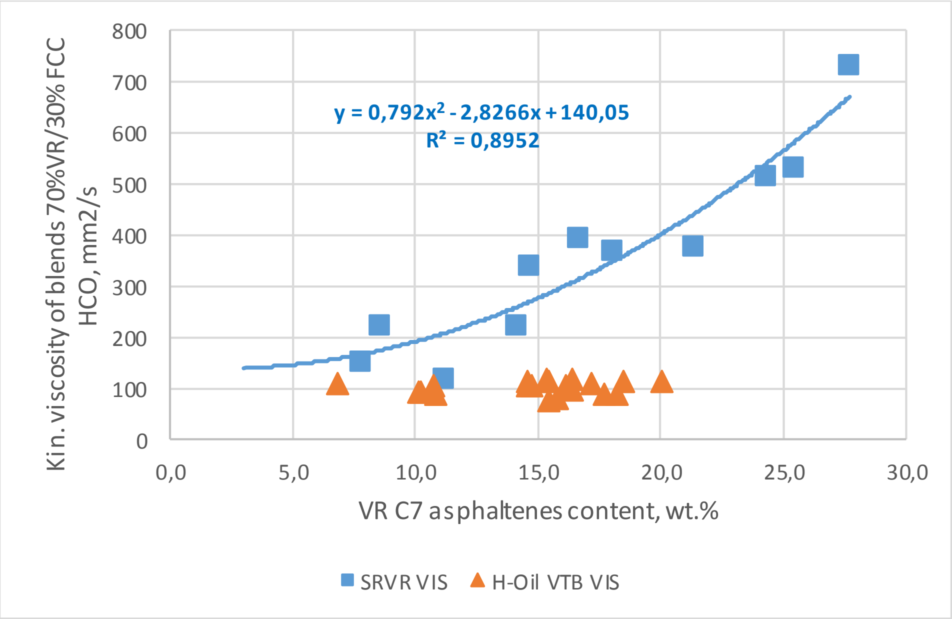

Figure 10. Relation of VR asphaltene content to viscosity for SRVROs and for H-Oil VTBs

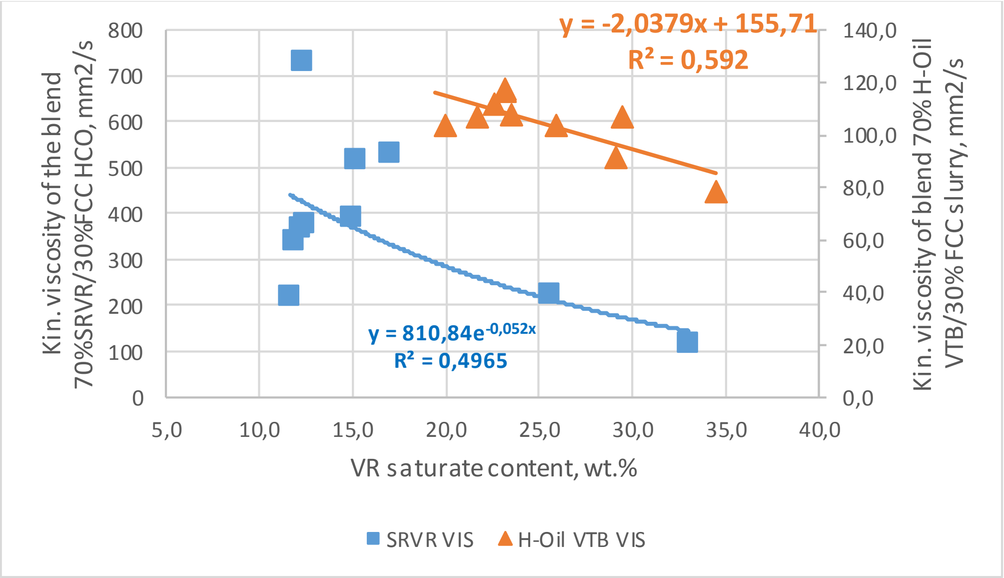

Figure 11. VR saturate content versus VR viscosity for SRVROs and for H-Oil VTBs

The sediment content in the H-Oil residual oils is the main limiting factor that constraints severity and consequently, conversion increase [2]. From the data in Tables 2 and 5, no relation of ATB sediment to any of the VTB properties can be seen. It should be pointed out here that the ATB and VTB sediments correlate (sediments of H-Oil VTB = 1.6 H-Oil ATB) as shown in [7]. In LNB H-Oil hydrocracker ATB sediments are controlled due to the higher reliability of the measurement of the lower viscosity ATB product. That is why ATB sediment content is given in Table 2, where properties of the H-Oil VTBs are presented. It seems that none of the measured properties of the VTBs in this work can explain the phenomenon of sediment formation in the H-Oil vacuum residue hydrocracking. Additional work is needed to puzzle out which properties of the H-Oil residual oils govern the process of sedimentation.

4. Conclusions

24 straight run vacuum residual oils and 28 H-Oil VTBs obtained during processing different blends of the 24 SRVROs in the LNB EBVR H-Oil hydrocracking unit were analyzed for their physical and chemical properties. It was found that in both primary and secondary VROs, the density and the Conradson carbon content strongly correlate. This dependence can be used as a tool to verify the correctness of the measurement of these properties. It was confirmed again that the measurement of the density of the VROs by pycnometer gives unreliable data and dilution with toluene is proposed to correctly measure the VRO density. It was also confirmed that the VRO saturate content can be predicted from data of VRO density and the use of second order polynomial fits for both SRVROs and H-Oil VTBs. However, the H-Oil VTBs have a higher saturate content than the SRVROs at the same density. It was established that the lower density, the higher saturate content VROs have a lower density, a higher hydrogen content of asphaltenes, resins and of aromatics than those of the higher density lower saturate content VROs. The H-Oil VTBs have higher density asphaltenes and lower density maltenes than the SRVROs, which can explain the lower colloidal stability of the H-Oil VTBs. The properties of H-Oil VTB Conradson carbon content and density correlate with the VTB hydrogen content and H/C atomic ratio and these correlations coincide with those already established on the base of data of SRVROs (77% of the data), of H-Oil VTBs (17% of the data) and of visbreaker vacuum residual oils (6% of the data) as shown in ref.5. Therefore the data of density and CCR can be reliably used to correctly estimate hydrogen content and H/C atomic ratio in both SRVROs and H-Oil VTBs.

Dissimilar to the SRVROs the H-Oil VTB viscosity does not correlate with the asphaltene content. Instead, it correlates with the saturate content. Therefore the H-Oil VTB viscosity depends on the hydrogenation activity of the catalyst, and it is not influenced by the number of asphaltenes in it in contradiction to the SRVROs. The viscosity of the H-Oil VTBs is lower than that of the SRVROs, but the softening point of the H-Oil VTBs is higher than that of the SRVROs. While the SRVRO softening point strongly correlates with its viscosity, such a relation does not exist for the H-Oil VTBs, which suggests different rheological properties of the H-Oil VTBs in contrast to these of the SRVROs

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