VISCOSITY, STABILITY AND COMPATIBILITY OF SHALE OIL DISTILLATES

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The temperature dependence of kinematic viscosity for the Estonian kukersite shale oil distillates is described by a fundamental formula known for hydrocarbon blends. A viscosity matrix for distillates has been compiled. The matrix includes the whole kinematic viscosity area, which is practically possible for shale oil distillates. By using the viscosity characterization constants, A and B, it is possible to predict the viscosity of the distillates in a wide temperature range. A program for personal computers has been developed to evaluate the viscosity of shale oil distillate blends. Compatibility of shale oil distillates amongst themselves, with gas oil type hydrocarbon fuels and with heavy petroleum residues has been described.

Compared to conventional petroleum originated fuel oils, the Estonian kukersite shale oil distillates have a lower pour point, a very low vanadium content, good pumpability and a moderate sulfur content. Therefore, shale oil-originated distillate fuel oils are gaining more attention in both Estonia and abroad.

The chemical group composition of petroleum and shale oils is fundamentally different: petroleum originated oils are principally made up of hydrocarbons, whereas kukersite shale oils are for the most part made up of oxygen compounds (ketones, ethers, hydroxybenzene and resorcinol series phenols).

When handling and producing fuel oil blends, the main challenge arises while attempting to predict the resulting stability and kinematic viscosity dependence of both the temperature and blend composition. Still, no systematic research has been done dealing with viscosity properties of shale oil distillates as well as with their compatibility between themselves or when blended with conventional petroleum originated fuel oils.

This study deals with temperature dependence of kinematic viscosity, compatibility and stability for distillates originated from shale oil, which is produced by retorting of the Estonian kukersite oil shale in commercial scale retorts ("gas generators").

Experimental and Results

The temperature dependence of kinematic viscosity for oil shale distillates and their blends having various viscosity was studied. Oil blends were attained by blending distillates produced at the AS *Kiviter* shale oil distillation unit.

The kinematic viscosity of the oils was measured in glass capillary kinematic viscosimeters according to the accepted standard test methods [1, 2]. The compatibility and stability of the oils was evaluated by spot test according to the ASTM standard procedure [3].

It was found that for the Estonian shale oil distillates the temperature dependence of kinematic viscosity is described with great accuracy (correlation coefficient > 0.999) by a fundamental formula known for hydrocarbon blends [4, 5]:

$$\log \log Z = A - B \log T \tag{1}$$

where Z is a function of the kinematic viscosity v (mm^2/s);

T is the temperature (K);

A and B are the viscosity characterization constants, whose values vary from one oil fraction to another.

If the kinematic viscosity exceeds 2.0 mm^2/s, one can approximate that

$$Z = v + 0.7 \ (mm^2/s) \tag{2}$$

When $v > 0.9 \ mm^2/s$, the function Z would accurately be represented by

$$Z = v + 0.7 + C + D \tag{3}$$

where $C = \exp(-1.14883 - 2.65868v)$;

$D = \exp(-0.0038138 - 12.5645v)$.

Equations (1)-(3) hold true in spite of the fact that shale oils are mainly made up of H-bond forming oxygen compounds which often exhibit non-Newtonian properties (the coefficient of viscosity varies with the rate of shear).

Based on their own experiments, the authors have compiled a viscosity matrix for shale oil distillates. The latter includes the whole distillate oils kinematic viscosity area, which is practically possible, beginning with viscosity from 1.8 mm^2/s at 20 °C (from 1.30 mm^2/s at 40 °C) to 240 mm^2/s at 50 °C.

Table 1. **Viscosity Characterization Constants A and B for Shale Oil Distillates**

Base oil No	Nominal viscosity*	A	B	Base oil No	Nominal viscosity*	A	B	Base oil No	Nominal viscosity*	A	B
00	1.30	9.6892	4.0911	11	10.00	12.3393	4.9122	22	60.00	12.1576	4.7447
01	1.50	9.9791	4.1849	12	12.00	12.3166	4.8911	23	70.00	12.1457	4.7336
02	1.75	10.2133	4.2564	13	14.00	12.2989	4.8743	24	80.00	12.1357	4.7244
03	2.00	10.4029	4.3144	14	16.00	12.2806	4.8590	25	100.0	12.1188	4.7091
04	2.50	10.7642	4.4319	15	18.00	12.2745	4.8498	26	120.0	12.1058	4.6973
05	3.00	11.0024	4.5068	16	20.00	12.2570	4.8369	27	140.0	12.0954	4.6877
06	4.00	11.3535	4.6183	17	25.00	12.2341	4.8158	28	160.0	12.0864	4.6795
07	6.00	11.7668	4.7479	18	30.00	12.2175	4.8000	29	180.0	12.0785	4.6724
08	8.00	12.0553	4.8412	19	35.00	22.2061	4.7880	30	200.0	12.0725	4.6666
09	10.00	12.2574	4.9063	20	40.00	12.1922	4.7762	31	220.0	12.0656	4.6607
10	12.00	12.4013	4.9518	21	50.00	12.1717	4.7581	32	240.0	12.0594	4.6555

* For base oils Nos 00-10 the nominal viscosity is given at 40 °C and for base oils Nos 11-32 at 50 °C.

Table 3. **Compatibility of Shale Oil Distillates by ASTM D 4740 Spot Test**

Shale oil distillate	Light "diesel oil" fraction	Light gas oil fraction	Heavy gas oil fraction	Commercial shale oil originated fuel oil
Light "diesel oil" fraction		No 1	No 2	No 1
Light gas oil fraction	No 1		No 1	No 1
Heavy gas oil fraction	No 2	No 1		No 2
Commercial shale oil originated fuel oil	No 1	No 1	No 2	No 1-2

Table 2. **Viscosity of Shale Oil Distillates at 20−80 °C**

Base oil No	Viscosity, mm^2/s						
	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C
00	1.78	1.51	**1.30**	1.14	1.01	0.91	0.83
01	2.12	1.77	**1.50**	1.30	1.14	1.01	0.91
02	2.58	2.10	**1.75**	1.49	1.29	1.14	1.01
03	3.05	2.44	**2.00**	1.68	1.44	1.25	1.11
04	4.05	3.13	**2.50**	2.05	1.72	1.47	1.28
05	5.12	3.85	**3.00**	2.41	1.99	1.68	1.44
06	7.46	5.34	**4.00**	3.11	2.50	2.06	1.73
07	12.81	8.50	**6.00**	4.45	3.43	2.73	2.23
08	18.94	11.87	**8.00**	5.71	4.27	3.31	2.65
09	25.76	15.40	**10.00**	6.93	5.05	3.84	3.02
10	33.19	19.07	**12.00**	8.11	5.79	4.33	3.36
11	45.15	24.94	15.20	**10.00**	7.00	5.14	3.93
12	59.25	31.57	18.68	**12.00**	8.23	5.95	4.49
13	74.62	38.55	22.24	**14.00**	9.44	6.73	5.02
14	91.19	45.85	25.88	**16.00**	10.63	7.49	5.53
15	108.9	53.45	29.58	**18.00**	11.81	8.22	6.01
16	127.6	61.32	33.35	**20.00**	12.96	8.94	6.49
17	178.9	82.09	42.99	**25.00**	15.80	10.67	7.61
18	235.9	104.2	52.92	**30.00**	18.56	12.32	8.66
19	298.1	127.6	63.10	**35.00**	21.27	13.91	9.65
20	365.2	152.0	73.49	**40.00**	23.94	15.45	10.61
21	512.9	203 8	94.82	**50.00**	29.14	18.41	12.41
22	677.2	259.1	116.8	**60.00**	34.22	21.23	14.10
23	856.5	317.4	139.3	**70.00**	39.20	23.95	15.70
24	1050	378.3	162.3	**80.00**	44.09	26.58	17.23
25	1476	507.6	209.5	**100.0**	53.66	31.63	20.13
26	1948	645.4	258.1	**120.0**	62.99	36.46	22.84
27	2465	790.7	307.9	**140.0**	72.13	41.10	25.42
28	3021	942.8	358.7	**160.0**	81.11	45.60	27.88
29	3615	1101	410.5	**180.0**	89.96	49.97	30.25
30	4245	1265	463.1	**200.0**	98.68	54.23	32.53
31	4907	1434	516.4	**220.0**	107.3	58.40	34.75
32	5601	1608	570.5	**240.0**	115.8	62.49	36.91

The matrix contains 33 base oils (from No 00 to No 32) whose viscosity characterization constants *A* and *B* are presented in Table 1.

Constant *B* characterizes how drastically the viscosity of the oil decreases in relation to rise in temperature. The greater the value is for *B*, the more the viscosity depends on the temperature.

Constant *B* of oil shale distillate fractions is, as a rule, greater than that of petroleum originated distillate oils having the same viscosity at a standard temperature (40 or 50 °C). It is remarkable that, in contrast to

petroleum originated oils, the value of *B* for oil shale distillates does not increase monotonously upon transition from one base oil to another. *B* attains its maximum value in the case of base oil No 10, when at 40 °C the viscosity is only 12 mm^2/s. The authors attribute this fact to the circumstance that the concentration of resorcinol alkyl derivatives, a specific group component of kukersite shale oil, has also a maximum value in distillate fractions, the B of which is the greatest.

By using constants *A* and *B* from Table 1, it is possible to predict the viscosity of the shale oil distillates in a wide temperature range (Table 2).

With the exception of the upper right hand corner of the table which is sectioned off by a dotted dividing line, the viscosities in Table 2 have been calculated using Equation (2) for function *Z*. In the area above the dividing line, where *Z* < 2, function *Z* is to be expressed by Equation (3). For the area in the lower left hand corner of the table, separated by a dotted line, experimental data does not exist and therefore, the values for viscosity have been attained by extrapolating on Equations (1) and (2) without experimental verification.

Shale oil distillates are compatible amongst themselves; blends in whatever ratio are stable in a wide temperature range (Table 3).

Fuel oil blends that are produced by blending shale distillate oils and heavy petroleum originated residues, as a rule, are also stable at every ratio. In comparison, compatibility of heavy shale oils, both residual and distillate, with petroleum originated gas oils is poor (Table 4).

It is remarkable that shale oil distillate blends exhibit Newtonian properties when their light component's kinematic viscosity at 50 °C is

Table 4. **Stability of Fuel Oil Blends Produced by Blending Shale Oil Distillates with Petroleum Originated Oils by ASTM D 4740 Spot Test**

Shale oil distillate	Petroleum originated oil[1]			
	1	2	3	4
Light "diesel oil" fraction	No 2	No 1	< 50 vol %: No 3—4 50—90 vol %: No 2—3 > 90 vol %: No 1	No 1
Light gas oil fraction	No 1[2]	No 1	< 40 vol %:No 4 40-50 vol %: No 2-3 > 50 vol %: No1	No 1
Heavy gas oil fraction	No 2	No 2	< 10 vol %:No 4 > 10 vol %: No1	No 2
Commercial shale oil originated fuel oil	No 2	No 1	< 40 vol %:No 4 40—50 vol %: No 2—3 > 50 vol %: No1	No 1

[1] Petroleum originated oils are as follows:
    1 - Conventional heavy residual fuel oil M-40 (stability: No 2).
    2 - Residual pyrolyse oil (stability: No 1).
    3 - Conventional gas oil and diesel fuel oil (stability: No 1).
    4 - Commercial PTU oil (stability: No 1-2).
[2] At temperatures < 50 °C the blend is capable of settling into two layers.

greater than 10 mm^2/s and heavy component's viscosity at the same temperature does not exceed 240 mm^2/s. Therefore, viscosity of these blends may be evaluated using methods known for hydrocarbon blends [6]. A program for personal computers, similar to that described by Huggins [7] has been developed. It can also calculate the proportion of components in a blend to meet the specified viscosity.

It is important to note that methods for evaluation of hydrocarbon blend viscosity are not applicable when shale distillate oils are blended with petroleum-originated oils, both distillate and residual. The same is true for blends of shale distillate oils amongst themselves where the light component viscosity at 50 °C is less than 10 mm^2/s. This can be attributed to the fact that shale oil distillates, which have such a low viscosity, are also made up of hydrocarbons. The authors have in prospect to discuss the evaluation of resulting viscosity for such blends in a special paper.

Conclusions

1. The temperature dependence of kinematic viscosity for the Estonian kukersite shale oil distillates can be described with great accuracy by a fundamental formula known for hydrocarbon blends. The equation holds true in spite of the fact that shale oils are mainly made up of H-bonding oxygen compounds which often exhibit non-Newtonian properties.
2. A viscosity matrix for distillates is compiled. By using the viscosity characterization constants for matrix base oils, it is possible to predict the viscosity of the distillates in a wide temperature range. A program for personal computers has been developed to evaluate the viscosity of shale oil distillate blends.
3. Shale oil distillates are compatible amongst themselves. Fuel oil blends that are produced by blending shale oil distillates and heavy petroleum residues are also stable at every ratio. Heavy shale oils and gas oil type hydrocarbon fuels are poorly compatible.

REFERENCES

1. ASTM D 445. Standard test method for kinematic viscosity of transparent and opaque liquids (and the calculation of dynamic viscosity). - 1997 Annual Book of ASTM Standards. V. 05.01. Petroleum products and lubricants (I).
2. ISO 3104. Petroleum products. - Transparent and opaque liquids. Determination of kinematic viscosity and calculation of dynamic viscosity.

3. ASTM D 4740. Standard test method for stability and compatibility of residual fuels by spot test. - 1997 Annual Book of ASTM Standards. V. 05.03. Petroleum products and lubricants (III).

4. *Wright W. A.* An improved viscosity-temperature chart for hydrocarbons // Journal of Materials, 1969. V. 4, No. 1. P. 19-27.

5. *Manning R. E.* Computational aids for kinematic viscosity conversions from 100 and 210 °F to 40 and 100 °C // Journal of Testing and Evaluation (JTEVA), 1974. V. 2, No. 6. P. 522-528.

6. ASTM D 341. Standard viscosity-temperature charts for liquid petroleum products. - 1997 Annual Book of ASTM Standards. V. 05.01. Petroleum products and lubricants (I).

7. *Huggins P.* Program evaluates component and blend viscosities // Oil and Gas Journal, 1985. V. 83, No. 43. P. 122-129.