A critical approach to viscosity index

Sylvain Verdier [a],[*], Joao A.P. Coutinho [b], Artur M.S. Silva [b], Ole F. Alkilde [a], Jens A. Hansen [a]

[a] *Haldor Topsøe A/S, Nymøllevej 55, 2800 Lyngby, Denmark*
[b] *University of Aveiro, Department of Chemistry, CICECO and QOPNA, 3810-193 Aveiro, Portugal*

ARTICLE INFO

ABSTRACT

The viscosity index (*VI*) is a useful tool for lubricant users and refiners, since it is a measure of the effect of temperature changes on the viscosity of the oil. However, it was found that the viscosity index does not correlate with the flow activation energy E_a, which is the theoretically defined dependence of the viscosity on temperature. In this way, two oils may have the same flow activation energy but a viscosity index varying by up to 120. We therefore believe that the *VI* does not always give a proper representation of the effect of temperature on the kinematic viscosity.

^{13}C NMR spectroscopy was used to identify the molecules with a high *VI*. Twenty different oil samples produced from eight different vacuum gas oils with viscosity indices ranging from −104 to 146 were analyzed and key parameters identified for high *VI* molecules: long alkyl chains, methyl branching in the centre of the molecule, low content of aromatic compounds, no ethyl branching and no tertiary carbons.

A correlation based on four selected peaks was developed, giving a very good prediction of the viscosity index.

1. Introduction

The viscosity index (*VI*) was first proposed by Dean and Davis of Standard Oil in 1929 to represent the effect of temperature on the kinematic viscosity of base stocks and lubricants [1]. Since then, lubricant professionals and refiners have used the viscosity index to quantify how much the temperature influences the viscosity. A high *VI* indicates that the temperature does not influence the viscosity to any large degree and vice versa.

The viscosity index has formed part of many other proposals to determine the viscosity such as the viscosity slope number, the viscosity gradient, the viscosity–gravity constant and the viscosity–temperature number just to name a few [2,3] and survived to present times to become one of the key parameters of determining the lube quality [4] as summarized in Table 1.

The *VI* estimation method is based on two reference groups of oil, each obtained by refining of two crude oils by comparable methods. The H series (derived from Pennsylvania crude oils) represents a low viscosity temperature dependence, whereas the L series (derived from Texas Gulf Coast crude oils) represents a high viscosity temperature dependence. The H series is assigned a *VI* value of 100, and the L series is assigned a *VI* value of 0. If a given oil sample has a *VI* of between 0 and 100 (typical VGO feedstocks), the *VI* is determined by interpolation of the tabulated H and L viscosities. If a given oil sample has a *VI* above 100 (typical hydrocracker

products), the *VI* is determined by extrapolation of the tabulated H viscosities.

Drawbacks and limitations of the viscosity index have been pointed out for decades. Already in 1951, Bondi [5] stated that *"due to their arbitrary nature, viscosity index systems show a few oddities which will eventually lead to their abandonment [...]. The inventors of the viscosity index [...] will probably be the first to recognize that in view of the present status of technology, it has outlived its usefulness and should be replaced by better founded concepts"*. Recently, Lynch [3] reviewed some of these issues and indicated new ones such as the discontinuity of *VI* at low viscosities. Other problems with the *VI* measurements not previously discussed in the open literature are:

- The method has a very poor repeatability and reproducibility. The ASTM test method D 445 (related to the measurement of kinematic viscosity) has a stated repeatability limit of 0.35% and a reproducibility limit of 0.70%. In terms of viscosity index, this would give a repeatability of 0.8 and a reproducibility of 4.5. This gives a very large uncertainty.
- The measurement of *VI* requires that the viscosity is measured at 40 and 100 °C. Nonetheless, it is often not possible to measure the viscosity of waxy samples at 40 °C, since this temperature is often below the cloud and pour points of these samples. A common procedure is to measure the viscosity at 50 or 60 °C and back-calculate to 40 °C using the ASTM or API correlations. However, using this approach will give different *VI* values. The *VI* calculated from viscosities measured at 60 and 100 °C can

Table 1
Classification of different types of lubricants.

Source	Group I Mineral Oil	Group II Mineral Oil	Group III Mineral Oil
Viscosity index	80–120	80–120	⩾120
Saturates (%)	<90	⩾90	⩾90
Sulfur (%)	>0.03	⩽0.03	⩽0.03

be expected to be roughly 5 *VI* points higher than the *VI* calculated from viscosities measured at 50 and 100 °C.

- More fundamentally, as will be shown in the present article, the viscosity index is often not correlated with the dependence of the viscosity on temperature as previously assumed.

Although it has been known for years that the *VI* is outdated, that it has no theoretical background and even some major drawbacks, this parameter is still widely used in the refining and lubricant industry and is as such unavoidable. For this reason an effort was made to understand its relationship with the oil composition in order to be able to maximize its value. The API Project 42 [6] showed that the *VI* decreased as butyl, phenyl and cyclohexyl branches were moved to the middle of a linear paraffin molecule. Lynch [3] proposed a ranking of hydrocarbon families in terms of their influence on the *VI*: *n*-paraffins > isoparaffins with a few branches > multiple-branched isoparaffins = mononaphthenes with long chains attached = monoaromatics with long chains > diaromatics > polyaromatics = polycyclic naphthenes with multiple short chains attached. Miller et al. [7] suggested that minimizing the overall branching while maximizing the branching towards the middle of the lubricant base oil molecules provides fluids with a high *VI* and low pour points. Kobayashi et al. [8] showed in an NMR study of lube base oils prepared by hydrocracking/isomerization of Fisher-Tropsch waxes that the *VI* could be correlated to the average branching number *ABN* and the average carbon number *ACN* as follows: $VI = -0.0008x^2 + 0.7599x - 17.449$, where $x = (ACN)^2/ABN$. Therefore, large molecules with little branching have

a high viscosity index. The location of the branches or the type of branches has not been taken into account in the correlation as the authors assumed that the location or the type of branches did not vary very much in the case of hydrocracking/isomerization of Fischer-Tropsch paraffins. However, viscosity index can also be significantly improved by small quantities of additives such as high-molecular weight polymers and hence it is not only dependent on variation in its chemical composition.

In an NMR study of unconventional catalytically hydrogenated base stocks with a low aromatic content, Sarpal et al. [9] discussed the importance of isoparaffins. The authors suggested that there was no direct correlation between the number of different carbons (*n*-paraffins, isoparaffins, cycloparaffins) and the *VI*. In a subsequent work [10], the same authors showed how the carbon type composition as well as the distribution of branched structures affected the *VI*. Their results are summarized in Fig. 1, which is a re-plot of their data to highlight the effect of the various hydrocarbon families on the viscosity index.

Their results showed, in agreement with the data from the authors mentioned above, that n-paraffins and isoparaffins increased the *VI*, whereas cycloparaffins contributed to a decrease in the *VI*. It also seemed as if methyl branching had a favourable impact on the *VI*, whereas the number of branching sites should be as low as possible, i.e. tertiary carbons have a negative effect on the *VI*. As is evident from the discussion in the articles by Sarpal et al. [9,10], neither the interpretation of the ¹³C NMR spectra nor that of the results reported are straightforward, and these should therefore be considered as being qualitative.

The purpose of the study carried out at Topsøe was to develop an alternative and robust method for the determination of viscosity indices. It was shown that despite the definition of the viscosity index being a measure of the variation in kinematic viscosity due to changes in the temperature of a petroleum product, it was not possible to obtain a meaningful correlation between the *VI* and the flow activation energy, which once more showed how poorly founded the viscosity index concept is. Based on the preceding studies [3,6–10] on the molecular structure dependence of the
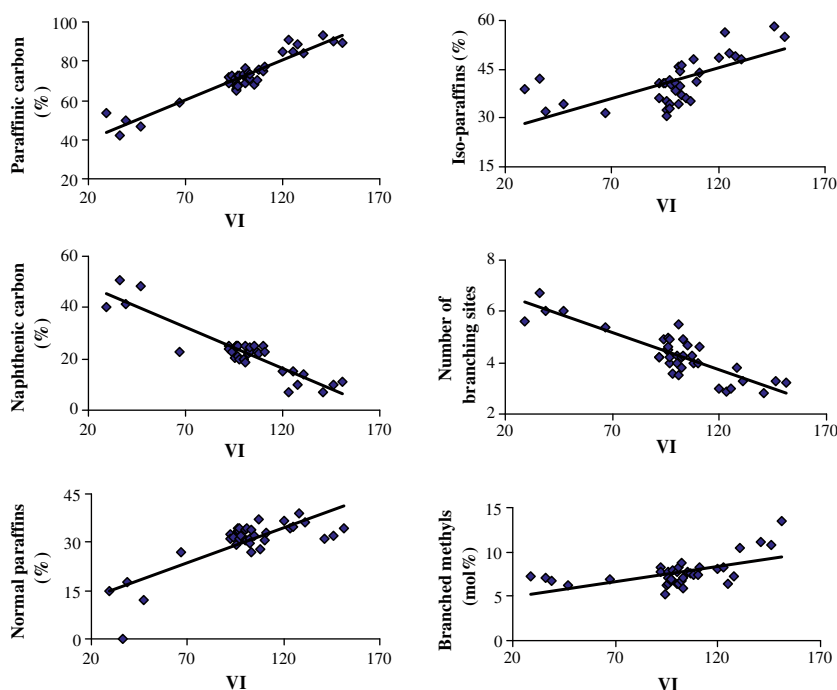
Fig. 1. Influence of different carbon types and branching indices on the viscosity index (data from [10]).

Table 2
Standards used for the measurement of physical properties.

Property measured	Standard method
Nitrogen	ASTM D-4629
Sulphur	ASTM D-5453
Hydrogen	ASTM D-4808
Specific gravity	ASTM D-4052
Flash point	ASTM D-93
Cloud point	ASTM D-5773
Pour point	ASTM D-5949
Kinematic viscosity	ASTM D-7042
Viscosity index	ASTM D-2270
Aromatics	IP-391
Carbon residue	ASTM D-4350
Simulated distillation	ASTM D-2887

viscosity indices, a ^{13}C NMR study of 20 oil samples with different characteristics was carried out, and it was shown that it was possible to develop a good correlation for the VI, and that NMR could be used as an adequate technique to estimate the VI and to under-

stand the relationship between the oil composition and the viscosity index of the oil in question.

2. Experimental

2.1. Measurement of physical properties

The different physical properties of the oil samples were measured at the Topsøe Research Laboratories according to ASTM standards (except for the total aromatic content determined by the IP method). The details of the different methods are given in Table 2. The reproducibilities and repeatabilities are described in the different ASTM standards.

2.2. ^{13}C NMR spectroscopy

The NMR analyses were performed at the Department of Chemistry of the University of Aveiro in Portugal. Quantitative ^{13}C NMR spectra were recorded on a Bruker Advance 300 spectrometer

Table 3
Properties of the 20 hydrotreated/hydrocracked oil samples (HT: hydrotreated; HC: hydrocracked; VGO: vacuum gas oil).

Sample	Kinematic viscosity at 60 °C (mm²/s)	Kinematic viscosity at 100 °C (mm²/s)	Specific gravity	Aromatics (wt%)	Cloud point (°C)	N (wt ppm)	S (wt ppm)	Feed	Type of treatment[a]	VI
1	20.52	6.63	0.8661	6.19	−14	<0.5	39.0	A	HT + HC	92
2	7.11	3.09	0.8627	18.17	18	<0.5	2.6	B	HT + HC	97
3	9.70	3.89	0.8490	3.23	2	–	–	C	HT + HC	101
4	17.37	5.97	0.873	23.70	41	25.0	65.0	D	HT + HC	102
5	18.00	6.21	0.8613	5.34	19	0.5	96.0	A	HT + HC	105
6	18.83	6.61	0.8682	14.98	53	0.5	33.0	A	HT + HC	120
7	6.45	2.96	0.8346	4.93	–	<0.5	3.8	B	HT + HC	121
8	12.31	4.95	0.8382	1.83	51	<0.5	<0.5	A	HT + HC	142
9	10.38	4.37	0.8350	3.90	43	<0.5	5.2	B	HT + HC	145
10	12.19	4.95	0.838	1.44	50	<0.5	10.0	A	HT + HC	146
11	30.80	9.00	0.9252	39.42	46	886.0	23303.0	A	VGO	91
12	141.20	19.00	0.9628	50.16	–	5038.0	8200.0	E	VGO	−104
13	23.30	7.10	0.925	44.50	32	1171.0	25480.0	F	VGO	78
14	2.30	1.30	–	65.53	−31	230.0	112.8	G	HT	–
15	92.30	19.40	0.9271	55.79	45	1217.0	3612.0	G	HT	71
16	1.61	1.00	0.8616	49.24	−17	0.3	12.8	H	HT	–
17	70.80	12.80	0.9427	49.22	−49	3212.0	1124.0	E	HT	−38
18	10.40	4.20	0.8668	18.17	43	16.0	–	A	HT	119
19	11.80	4.60	0.8622	–	48	3.0	–	A	HT	116
20	11.6	4.5	0.8712	17.96	39	27	–	A	HT	117

[a] The hydrotreating catalysts are NiMo/alumina and the hydrocracking catalysts are NiW/alumina + zeolite.

Table 4
Properties of the eight different feeds.

Sample name	A	B	C	D	E	F	G	H
Type of feed	VGO	VGO	VGO	VGO	VGO	VGO	Doped VGO	VGO
Sulphur (wt%)	2.33	1.27	0.86	1.26	0.82	2.55	3.50	1.47
Nitrogen (wt ppm)	886	854	732	1005	5038	1171	2359	607
Hydrogen (wt%)	12.27	12.57	12.95	12.58	11.45	11.96	11.12	11.12
Specific Gravity	0.9252	0.9026	0.8788	0.9028	0.9628	0.925	0.9669	0.8974
Flash point (°C)	190	190	130	180	190	160	220	40
Pour point (°C)	43	30	30	29	<−62	28	36	−20
VI	91	87	–	91	−104	78	–	–
Aromatics	39.42	37.33	24.66	36.44	50.16	44.5	50.58	53.22
Carbon residue (wt%)	0.44	0.01	–	0.1	0.212	0.645	4.137	–
Simulated distillation								
IBP (°C)	295.5	241.5	167.1	257	312.6	220.6	235.6	88.2
10 wt% (°C)	390.5	364	297.9	361	379	324.6	373.8	192.2
30 wt% (°C)	433	396.5	355.3	400	418.2	385	446.2	228.8
50 wt% (°C)	461	418	388.4	421	443.4	427.4	508.2	266
70 wt% (°C)	489.5	439	417.3	443.5	472	472.8	565.8	301.6
90 wt% (°C)	527	466.5	458.7	482.5	514.6	538.4	640.4	344
95 wt% (°C)	543.5	478	481.3	501.5	534	577.2	677	358.4
FBP (°C)	580	508.5	521.6	554.5	582.2	667.8	726.6	393

operating at 75.47 MHz. Oil samples were diluted by 50% in CDCl3, and the spectra were recorded at 293 K with TMS as internal reference. The inverse gated decoupling sequence, which allows a quantitative analysis and comparison of signal intensities, was used as follows: 90° pulse angle (4.5 µs); 819 ms acquisition time; 12 s relaxation delay; 32 K data points and 3400 scans.

2.3. Oil samples

In the study carried out at Topsøe, 20 different oil samples were analyzed. Samples Nos. 1–10 were hydrotreated and hydrocracked vacuum gas oil (VGO), samples Nos. 11–13 were VGO feed, and samples Nos. 14–20 were hydrotreated VGO feed. The properties of these different oil samples are given in Table 3. All samples were produced using different catalysts developed by Topsøe. A total of eight different feeds were used to produce these samples. The properties of these feeds are given in Table 4. The *VI* was not determined for samples 14 and 16, as their kinematic viscosities at 100 °C were below 2 cSt.

3. Results and discussion

3.1. Viscosity index and the temperature dependence of viscosity

For non-associated fluids (e.g. lube oils, which are a mixture of different hydrocarbons), the temperature dependence of the viscosity can be described by an Arrhenius-type law. It was first proposed by De Guzman [11], and it is often known as the Andrade equation [12]:

$$\ln \eta = A + \frac{B}{T} \tag{1}$$

This equation successfully describes the viscosity of many fluids at freezing to boiling point even if it does not take the effect of pressure into account [13].

Initially, it was an empirical equation, the theoretical background of which was first developed by Eyring and later recalculated by Weymann [14]. The theory can be explained as follows: a shearing force applied across two layers of molecules produces a flow when a single molecule squeezes past its neighbour and drops into a vacant equilibrium position (a hole) at a distance of λ from its original position. This passage of one molecule past the force fields of its neighbours can be described as a jump over a potential energy barrier. On the basis of Eyring's theory, the dynamic viscosity η can be expressed as:

$$\eta = \frac{N_A h}{V_m} e^{\Delta G_0/RT} = \frac{N_A \cdot h \cdot e^{-\Delta S_0/R}}{V_m} \times e^{\Delta H_0/RT} \tag{2}$$

where N_A is Avogadro's number, h is the Planck constant, V_m is the molar volume of the liquid, R is the ideal gas constant, T is the absolute temperature, and ΔG_0 is the Gibbs energy of activation.

The temperature dependence of the viscosity is therefore as follows:

$$\ln(\eta) = \ln(\eta_0) + \frac{E_a}{RT} \tag{3}$$

where η is the dynamic viscosity (in mPa s), T the temperature (in K), R the gas constant, $E_a = \Delta H_0$ the flow activation energy (in kJ/mole) and $\eta_0 = N_A h \cdot e^{-\Delta S_0/R}/V_m$ the pre-exponential viscosity.

Activation energy is derived from Eq. (3) and is calculated as follows:

- Kinematic viscosity is measured at intervals of 10 °C between 50 and 100 °C.
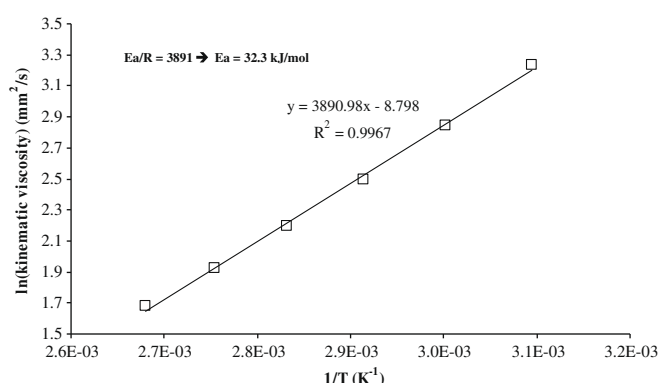- The logarithm of kinematic viscosity is then plotted vs. 1/T.

Fig. 2. Determination of the flow activation energy for sample 1.

- A linear regression is achieved and the slope being equal to E_a/R, the flow activation energy is determined.

Fig. 2 shows how the activation energy of sample 1 has been determined.

The pre-exponential factor depends on the chemical structure of the fluid. Smaller molecules will have a smaller molar volume (increasing η_0) but will also create more disorder, which increases the entropy (decreasing η_0). Therefore, V_m and ΔS_0 have competing effects, and no general trend can be seen with respect to the size of the molecules.

The heat of activation ΔH_0 can be divided into two according to the following theory: the heat of activation for hole formation and the heat of activation for motion. The latter is usually zero or very small in simple liquids but increases with molecular size. Bondi [5] suggested that the heat of activation is essentially a function of molecular flexibility and polarizability.

The flow activation energy has long been used in the oil industry, especially to study the interactions in heavy oils [15–19], but to the authors' knowledge it was never applied specifically to lube oils.

The extension of the flow activation energy concept to include the kinematic viscosity used in the definition of *VI* is straightforward. The kinematic and dynamic viscosities are related as follows:

$$v = \frac{\eta}{\rho} \tag{4}$$

where v is the kinematic viscosity, and ρ is the density.

The temperature dependence of the density is a function of the isobaric thermal expansivity α_p:

$$\rho = \rho_0 \cdot \exp\lfloor -\alpha_p \cdot T \rfloor \tag{5}$$

Hence,

$$v = \frac{\eta_0 \cdot \exp(E_a/RT)}{\rho_0 \cdot \exp[-\alpha_p \cdot T]} = \frac{\eta_0}{\rho_0} \cdot \exp(E_a/RT + \alpha_p T)$$
$$= v_0 \cdot \exp(E_a/RT + \alpha_p T) \tag{6}$$

α_p can be considered as a constant for the fluids being investigated. Furthermore, $\alpha_p T$ is around 0.1, whereas $\frac{E}{RT}$ is around 10. Therefore, the temperature dependence of both viscosities may be assumed to be proportional to each other. This was investigated for the 20 samples included in this study, and *VI* as shown in Fig. 3, the flow activation energies were very similar (absolute average deviation: 3% and maximum deviation: 7.4% for the lowest activation energy). Therefore, the activation energy calculated from kinematic viscosities can be approximated to the one calculated from dynamic viscosities.

Given the definition of, it would be fair to assume that the flow activation energy and the *VI* could be correlated. If this was the
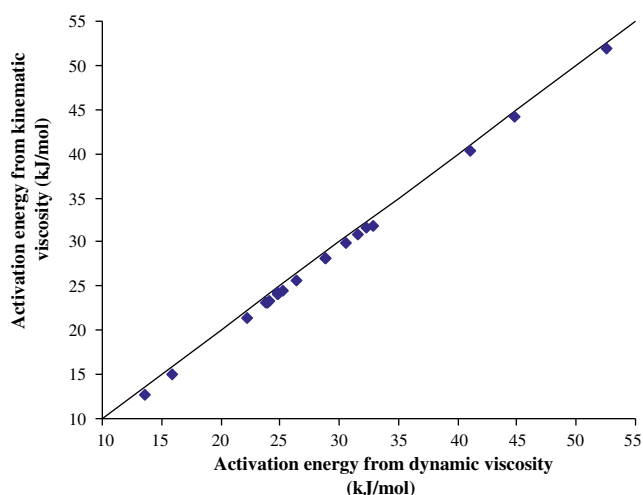
Fig. 3. Activation energies calculated from both kinematic and dynamic viscosities from the 20 samples being investigated

case, this combination would give the *VI* the theoretical background it lacks. It was attempted to find such a relationship between the two parameters as shown in Fig. 4, but we surprisingly established that no such relationship existed between the *VI* and the flow activation energy. Oils with the same flow activation energy in fact had *VI* values varying from 96 to 145. This proves that the *VI* is not always a measure of the temperature dependence of the viscosity. While the *VI* was fairly proportional to E_a for the samples produced from Feed *A*, the viscosity index seemed to be independent of E_a for the samples produced from Feed *B*.

To check the validity of the previous results, the same approach was extended to include the feeds and products listed in an in-house Topsøe database. However, the activation energy of these was calculated based on two viscosities (measured at 60 and 100 °C) and not on six viscosities as was the case for samples Nos. 1–20 (measured at intervals of 10 °C between 50 and 100 °C). This introduced deviations of only up to 10% in E_a. Two commercial synthetic lubricants were also studied. The results are given in Fig. 5. This figure shows how large the deviations in *VI* can be between two oils with equal activation energies, i.e. between two oils with the same viscosity–temperature behaviour. For e.g. $E_a = 26$ kJ/mole, the viscosity index varied between 64 (for a VGO) and 185 (for the two commercial lubricants). This means that the viscosity of the commercial lubricants has the same dependence on temperature as the viscosity of a VGO, which has a *VI* of 64. It is quite possible that the *VI* correlates with other lube
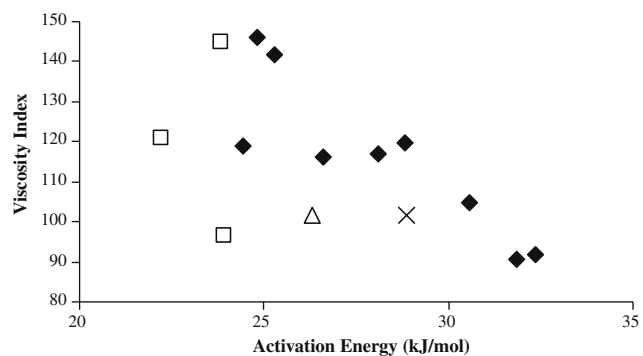

Fig. 4. Activation energy and viscosity index for the products of feeds *A–D* (♦, feed *A*; □, feed *B*; △, feed *D*; ×, feed *D*).
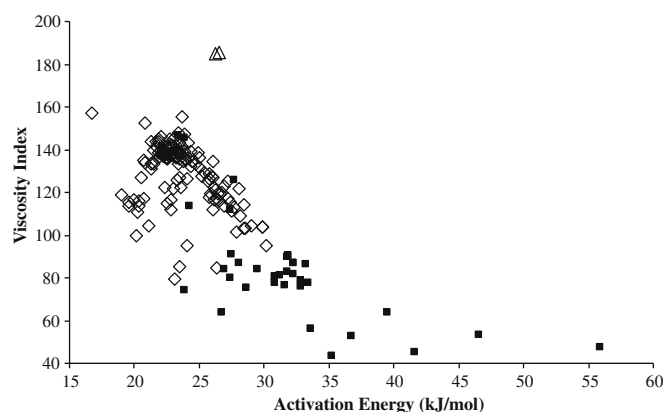

Fig. 5. Activation energy and viscosity index listed in the Topsøe database (■; feeds; ◇, products; △, commercial lubes).

properties such as pumpability, oxidation stability and volatility [3], but the *VI* is definitely not always a measure of the temperature dependence of viscosity as given by the original definition [1].

3.2. Viscosity index and molecular structure

Although it was clearly demonstrated in the previous section that the *VI* is not always a measure of the temperature dependence of the viscosity, it is nonetheless still a key parameter for lubricant manufacturers and users. To optimize its value during production, it was decided at Topsøe to investigate the dependence of the *VI* on the molecular structure of hydrocarbons. 20 samples of hydrotreated and hydrocracked oils were thus studied by ^{13}C NMR spectroscopy.

Fig. 6 shows a typical NMR spectrum with the main peaks observed for these types of oils. The aromatics peaks were observed at δ 117–150 ppm as shown in Fig. 7.

The 20 spectra were analyzed, and the peaks were numbered as shown in Fig. 6. The peak identification followed the work by Sperber et al. [20] with the exception of peak 10, where the assignment proposed by Sarpal et al. [9,10] was adopted (see Table 5). Peak identification is also shown in Fig. 8, where a model molecule is drawn, and where each peak is allocated to its carbon atom. This is only a simple model as lube oils produced from VGO contain naphthenes, naphtheno-aromatics and aromatics.

The study was carried out taking the most important peaks observed in all the measured spectra into account, which are those numbered 2, 3, 7, 10, 15, 17, 18, 19 and 23. Peak 3 corresponds to terminal CH_3 groups of a long (Cn > 6) alkyl chain and was therefore used to normalize the integration areas of the spectra also because there was no interference from neighbouring peaks. The results of the integration of the spectra of samples Nos. 1–20 for the peaks studied are shown in Table 6 along with the viscosity index.

The influence of each peak on the viscosity index is also shown in Table 6. A linear regression was performed for each peak as shown in Fig. 9, and the slope of the *VI* vs. peak area was calculated along with the respective correlation coefficient R^2.

We were able to rule out the influence of three hydrocarbon structures on the *VI* right away as their correlation coefficient (R^2) with was quite low (i.e. below 0.3). These structures are related to peak 15 (methylene groups on β positions relative to a tertiary carbon with a methyl side chain on the tertiary carbon), peak 18 (methylene groups in a straight chain in position 3 from the chain end) and peak 23 (methylene groups on α positions relative to a tertiary carbon with a methyl side chain on the tertiary carbon). Amongst the peaks evaluated, just three peaks seemed to
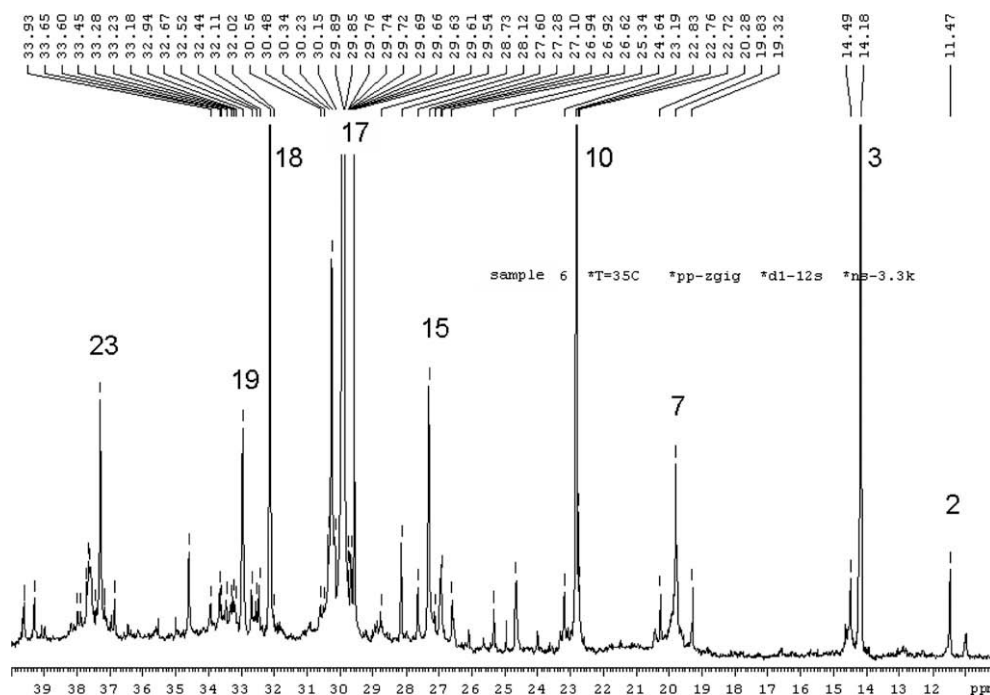
Fig. 6. Aliphatic region of the ^{13}C NMR spectrum (δ, ppm) of sample 6 as an example of the oil studied with peak indexation.
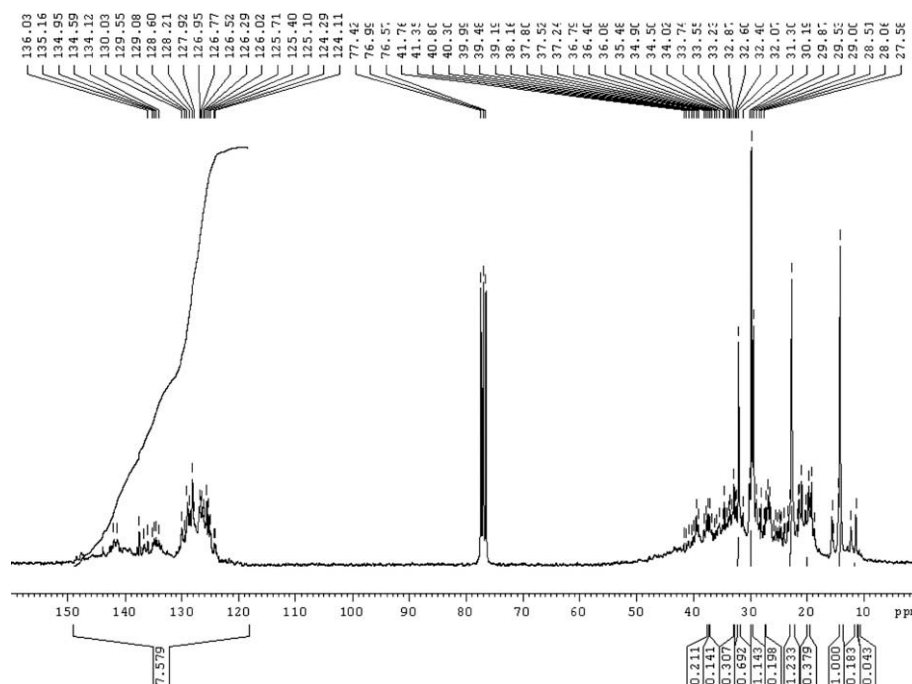

Fig. 7. ^{13}C NMR spectrum (δ, ppm) of sample 14.

have a positive influence on the *VI*, which were peaks 15, 17 and 18, all resulting from methylene groups far enough from a tertiary carbon not to share the detrimental effect of branching on the *VI*. This confirmed that the presence of methylenes in non-branched alkyl chains contributed to an increase of the *VI*, while branching and aromaticity negatively affected the *VI*. As can be seen from Table 6, peak 2 (methyl group at the end of an ethyl branch), peak 7 (methyl branching more than four carbons away from a terminal carbon), peak 10 (methyl branching in carbon β), peak 19 (tertiary carbon related to methyl branching and the aromatic region), all

had a negative influence on the *VI*. In terms of a negative influence on the *VI*, the peaks can be ranked as follows: peak 2 > peak 19 > peak 10 = peak 7 >>> aromatic compounds. Therefore, in order to obtain a high viscosity index, it is convenient to have many non-branched alkyl chains in the hydrocarbon alkyl chains. As concerns the structures, which have a negative impact on the *VI*, it seems to be preferable to have a low aromatic content rather than branching. As concerns branching, methyl branching seemed to have the least detrimental effect on the *VI*, and the position of the methyl branches did not seem to be important. Longer branches

Table 5
Peak identification.

Peak number	^{13}C NMR chemical shift (δ, ppm)	Signification	Structure (from [20] except for peak 10)
2	11.5	Methyl group at end of ethyl branch	1B2
3	14.2	Methyl group at end of alkyl chain (bound to primary carbon)	S1
7	19.9	Methyl branching more than 4 carbons away from terminal CH_3	1B1
10	22.8	Methyl branching in carbon β	S-2 [9,10]
15	27.3	Methylene groups in β carbon away from methyl branch	$\beta\delta^+$-B1
17	30	Methylene groups in straight chain	δ-CH_2
18	32.2	Methylene groups in straight chain	γ-CH_2
19	33.1	Tertiary carbon from a methyl branch	CHB1
23	37.4	Methylene groups in α carbon away from methyl branch	$\alpha\delta^+$-B1
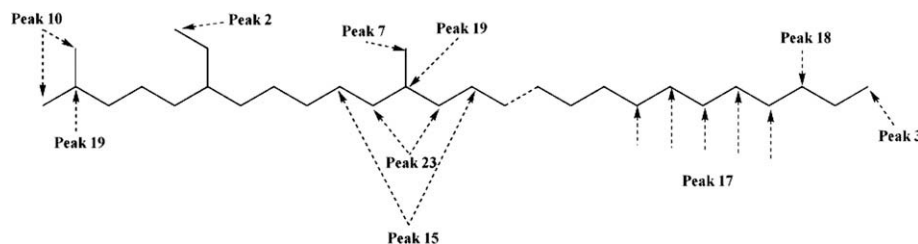
Fig. 8. Peak identification of a model molecule (adapted from Sperber et al. [20]).

Table 6
Normalized areas (Ai/A3) for the peaks of the ^{13}C NMR spectra.

Sample	Peaks (ppm)		11.5	14.2	19.9	22.8	27.3	30.0	32.2	33.1	37.4	117 – 149
	VI	E_a (kJ/mole)	2	3	7	10	15	17	18	19	23	Aromatic
1	92	31.6	0.228	1	1.070	1.327	0.776	2.361	0.792	0.600	0.740	–
2	97	23.2	0.155	1	0.726	1.465		3.904	1.084	0.616	0.613	1.471
3	101	25.6	0.210	1	0.941	1.248	0.695	2.289	0.703	0.507	0.725	–
4	102	28.2	0.132	1	0.934	1.430	0.521	5.750	1.089	0.669	–	1.705
5	105	29.8	0.225	1	0.874	1.224	0.827	3.202	0.766	0.581	0.717	–
6	120	28.1	0.142	1	0.719	1.153	0.475	5.958	0.844	0.470	0.416	0.617
7	121	21.4	0.133	1	0.590	1.212	0.573	4.497	0.947	0.432	0.539	–
8	142	24.5	0.102	1	0.462	0.865	0.559	5.031	0.725	0.326	0.465	–
9	145	23.1	0.107	1	0.401	0.906	0.474	5.779	0.782	0.347	0.386	–
10	146	24.0	0.112	1	0.403	0.883	0.607	5.592	0.753	0.350	0.513	–
11	91	31.8	0.164	1	0.800	1.303	0.551	4.526	0.848	0.425	0.531	5.934
12	−104	51.9	0.351	1	1.435	1.654	0.472	1.209	0.681	0.625	0.954	9.841
13	78	30.8	0.131	1	0.749	1.321	1.381	4.007	0.711	0.374	0.336	6.88
14	–	–	0.183	1	0.379	1.233	0.198	1.143	0.692	0.307	0.141	7.579
15	71	40.3	0.118	1	0.899	1.44	0.619	4.739	0.686	0.561	0.408	6.78
16	–	–	0.193	1	0.238	1.339	0.244	1.456	0.681	0.28	0.153	5.191
17	−38	44.1	0.368	1	1.35	1.484	0.28	1.316	0.69	0.771	0.218	7.978
18	119	23.3	0.206	1	0.699	1.324	0.582	4.616	0.913	0.537	0.539	1.289
19	116	24.3	0.158	1	0.658	1.352	0.556	4.262	0.673	0.399	0.359	1.212
20	117	24.1	0.166	1	0.805	1.316	0.654	4.367	0.896	0.544	0.495	3.01
Slope VI vs. peak area			−696	–	−198	−216	54	33	154	−313	−100	−18
Correlation coefficient R^2			0.714	–	0.779	0.528	0.037	0.586	0.101	0.385	0.077	0.690
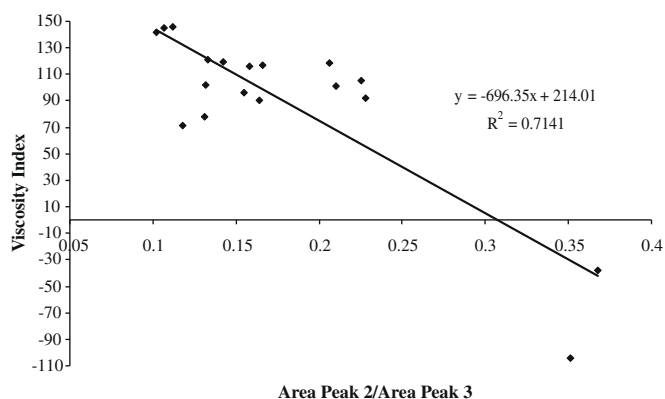
Fig. 9. Viscosity index vs. peak 2/peak 3 (♦, samples 1–20).

should be avoided as these influences the viscosity index to the highest degree. This is in good agreement with results obtained previously [3,6], which showed that the phenyl, cyclohexyl and n-butyl branches reduced the viscosity index.

3.3. Correlating viscosity indexes with ^{13}C NMR data

A principal component analysis applied to the data presented in Table 6 followed by an analysis of variance indicated that the structures affecting the VI the most were those represented by peaks 2, 7, 10 as well as the components of the aromatic region. This is in good agreement with the discussion of the influence of branching on the VI given above. Applying multivariate regression to the ^{13}C NMR data and viscosity indexes, it was found that a good correlation could be obtained between the VI and the relative areas of ethyl branching (A_2), methyl branching (A_7 and A_{10}) and the aro-
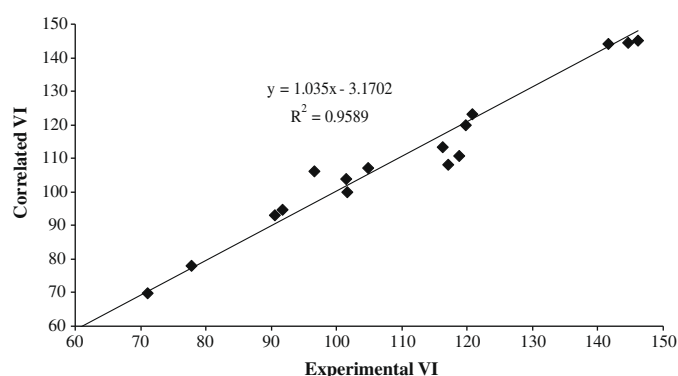
Fig. 10. Deviation between the experimental and the correlated viscosity indices.

matic region (A_{aro}). It was interesting to observe that the influence of the different types of branching was statistically identical, and that the aromatic content had a high non-linear impact on the *VI*. Small aromatic contents had a negligible impact on the *VI*, but as the aromatic content increased, the influence on the *VI* increased dramatically. The proposed correlation for the *VI* with the ^{13}C NMR spectra is thus:

$$VI = 203.0 - 41.32\left(\frac{A_2}{A_3} + \frac{A_7}{A_3} + \frac{A_{10}}{A_3}\right) - 2.206 \cdot 10^{-3}\left(\frac{A_{aro}}{A_3}\right)^5 \qquad (7)$$

This correlation presents an average deviation of 3.0 *VI* points for the oils studied, and a comparison of the experimental and correlated data are presented in Fig. 10.

4. Conclusion

The first part of the present study aimed at investigating the validity of the viscosity index as a measure of the influence of temperature on viscosity. A comparison with the well-defined flow activation energy E_a (which is the slope of ln(viscosity) vs. $1/T$) showed that the *VI* did not correlate with E_a. Two oils with equivalent activation energies, i.e. the viscosities of which have the same temperature response, may have a difference in *VI* of 120. Therefore, the flow activation energy should be preferred over viscosity index as a measure of the influence of temperature on viscosity.

The second part of the present study was dedicated to ^{13}C NMR spectroscopy studies of 20 oil samples (3 VGOs, 7 hydrotreated

VGOs and 10 hydrotreated and hydrocracked VGOs). Of the 24 identified peaks, seven were found to correlate with the viscosity index and flow activation energy. Several common features of molecules having a high VI were found: long alkyl chains, low aromatic content, no ethyl branching and no tertiary carbons.

References

[1] Dean EW, Davis GBH. Viscosity variations of oils with temperature. Chem Met Eng 1929;36:618–9.
[2] McCluer WB, Fenske MR. A method for evaluating the viscosity–temperature characteristics of oils. Ind Eng Chem Anal Ed 1934;6:389–92.
[3] Lynch TR. Process chemistry of lubricant base stocks. Boca Raton: CRC Press; 2007.
[4] Bechtel Corporation. Introduction to lube and wax processing. In: AIChE 2003 Spring Meeting, 2003. 30-3-2003.
[5] Bondi A. Physical chemistry of lubricating oils. New-York: Reinhold Publishing Corporation; 1951.
[6] Dixon JA. Properties of hydrocarbons of high molecular weight. API 42, Amer. Pet. Inst., Res. Project 42, Washington, DC, 1966.
[7] Miller SJ, O'Rear DJ, Rosenbaum JM. Processes for producing lubricant base oils with optimized branching. United States Patent 7018525, Issued on 28 March 2006.
[8] Kobayashi M, Saitoh M, Ishida K, Yachi H. Viscosity properties and molecular structure of lube base oil prepared from Fischer-Tropsch waxes. J Jpn Petrol Inst 2005;48:365–72.
[9] Sarpal AS, Kapur GS, Chopra A, Jain SK, Srivastava SP, Bhatnagar AK. Hydrocarbon characterization of hydrocracked base stocks by one- and two-dimensional NMR spectroscopy. Fuel 1996;75:483–90.
[10] Sarpal AS, Kapur GS, Mukherjee S, Jain SK. Characterization by ^{13}C NMR spectroscopy of base oils produced by different processes. Fuel 1997;76:931–7.
[11] De Guzman JJ. Anales Soc Espan Fia y Quim 1913;11:353.
[12] Andrade ENDC. Phil Mag 1934;17:497–511.
[13] Mehrotra AK, Monnery WD, Svrcek WY. A review of practical calculation methods for the viscosity of liquid hydrocarbons and their mixtures. Fluid Phase Equilib 1996;117:344–55.
[14] Weymann HD. On the hole theory of viscosity, compressibility, and expansivity of liquids. Kolloid-Z u Z Polymere 1962;181:131–7.
[15] Rønningsen HP, Bjørndal B, Baltzer Hansen A, Batsberg Pedersen W. Wax precipitation from North Sea crude oils: 1. Crystallization and dissolution temperatures, and Newtonian and non-Newtonian flow properties. Energy Fuel 1991;5:895–908.
[16] Evdokimov IN, Eliseev NY, Eliseev DY. Thermophysical properties and phase-behaviour of asphaltene-containing petroleum fluids. Fluid Phase Equilib 2003;212:269–78.
[17] Martinez-Boza F, Partal P, Conde B, Gallegos C. Steady-state flow behaviour of synthetic binders. Fuel 2001;80:357–65.
[18] Guo DH, Jiang L. Rheological behaviour of a new kind of fuel-residual oil, coal and water triplex synfuel. Fuel 1998;77:1697–700.
[19] Merezhko Y, Nesterov AN, Syunyaev ZI. Structuring and flow energy functions for heavy fuel oil. Chem Technol Fuels Oils 1990;26:198–201.
[20] Sperber O, Kaminsky W, Geisser A. Structure analysis of paraffin waxes by ^{13}C-NMR spectroscopy. Petrol Sci Technol 2005;23:47–54.