

CHAPTER II

THEORY

2.1 Lubricating base oil

Nearly all moderns lubricating base oils are obtained from crude oil. These are made from the more viscous portion that remains after removal of gas oil and lighter fractions by distillation of the crude[5]. They have been prepared from crude oils obtained from most parts of the world. Although crude oils from various parts of the world differ widely in properties and appearance, there is relatively little difference in their elemental analysis. Thus, crude oil samples will generally show carbon content ranging from 83 to 87 percent and hydrogen content from 11 to 14 percent. The remainder is composed of elements such as oxygen, nitrogen, sulfur, and various metallic compounds. An elemental analysis, therefore, gives little indication of the extreme range of physical and chemical properties that actually exists, or of the nature of the lubricating base oil that can be produced from a particular crude oil[5-6].

In order to minimize variations and produce products that will provide consistent performance in specific applications, the refiner follows four main stages in the manufacture of finished lubricating base oil from the various available crudes :

- (1) selection and segregation of crudes according to the principal types of hydrocarbons present in them;
- (2) Distillation of the crude to separate it into fractions containing hydrocarbons in the same general boiling range;
- (3) Processing to remove undesirable constituents from the various fractions, or to convert some of these materials to more desirable materials;
- and (4) Blending to the physical characteristics required in the finished products and incorporating chemical agents which improve performance attributes[6].

The manufacture of lubricating base stocks are basically a separation process to make different viscosity grades followed by subtractive processes to remove undesirable components and improve quality to meet the performance requirements. The refining processes commonly used are vacuum distillation, propane deasphalting, furfural extraction, Methyl Ethyl Ketone dewaxing and hydrofinishing. Acid and clay treatment is also sometimes used. The first four items are separation processes. The fifth, hydrofinishing, is a catalytic reaction with hydrogen to decolorize the lubricating base stocks. Figure 2.1 shows a typical flow diagram indicating the five processes in lube oil refining. The aim is to produce lubricating base stocks, which are clear and of good color, stable at high temperatures, cover a range of viscosity and meet other required specifications[5-7].

The using of lubricants is to reduce friction. Over ages many materials have been used as lubricants, superceded by better ones with experience and improvement in technology. Animal fats such as tallow, vegetable oils, simple lubricants of solid or semi-solid fatty nature were used in the early machines. Today, mineral oils derived from crude are the major source of lubricants[5]. They are basically hydrocarbons, organic compounds made up primarily of hydrogen and carbon. Individual molecules may be extremely long with either straight or cyclic members[4]. Most favored are paraffinic crudes.

Paraffinic lubricating base oil is made from crude oils that have relatively high alkane contents. Typical crudes are from the Middle East, North Sea and the Usmid-continent. This is not an exclusive list, nor does it follow that all North Sea crudes, for example, are suitable for production of paraffinic lubricating base oil. The manufacturing process requires aromatic removal by solvent extraction and dewaxing. Paraffinic lubricating base oil is characterized by their good viscosity-temperature characteristics,

i.e. high viscosity index, adequate low-temperature properties and good stability. In oil industry terminology they are frequently referred to as solvent neutrals (SN), where solvent means that the lubricating base oil has been solvent-refined and neutral means that the oil is of neutral pH. An alternative designation is high viscosity index (HVI) lubricating base oil. Most of the lubricating base oils produced in the world are paraffinics and they are available in the full range of viscosities, from light spindle oils to viscous brightstock[7]. Some examples of a range of paraffinic lubricating base oils from typical refinery production are given in Table 2.1.

Table 2.1 : Paraffinic lubricating base oil-typical properties (Arabian crude).

Grade	Spindle	150 SN	500 SN	Brightstock
Density at 20°C (gm/l)	0.85	0.87	0.89	0.91
Viscosity at 40°C (cSt)	12.7	27.3	95.5	550
Viscosity at 100°C (cSt)	3.1	5.0	10.8	33
Viscosity index	100	103	97	92
Pour point (°C)	-15	-12	-9	-9
Sulphur content (%wt)	0.4	0.9	1.1	1.5

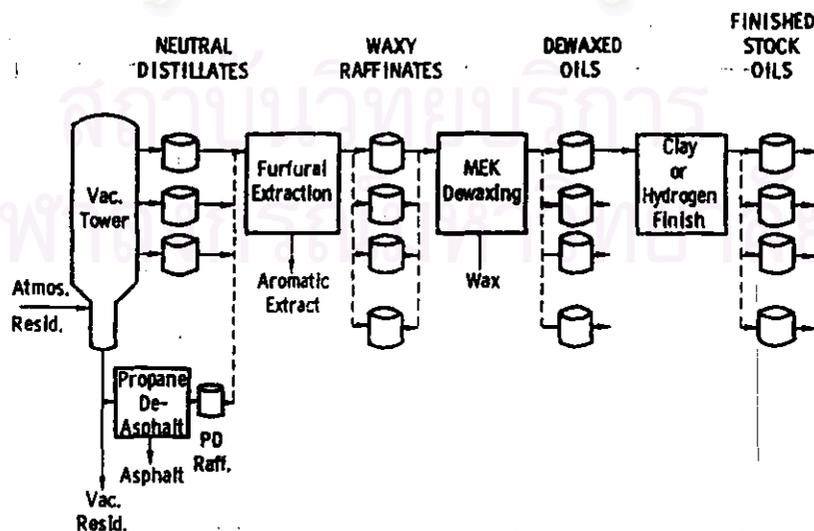
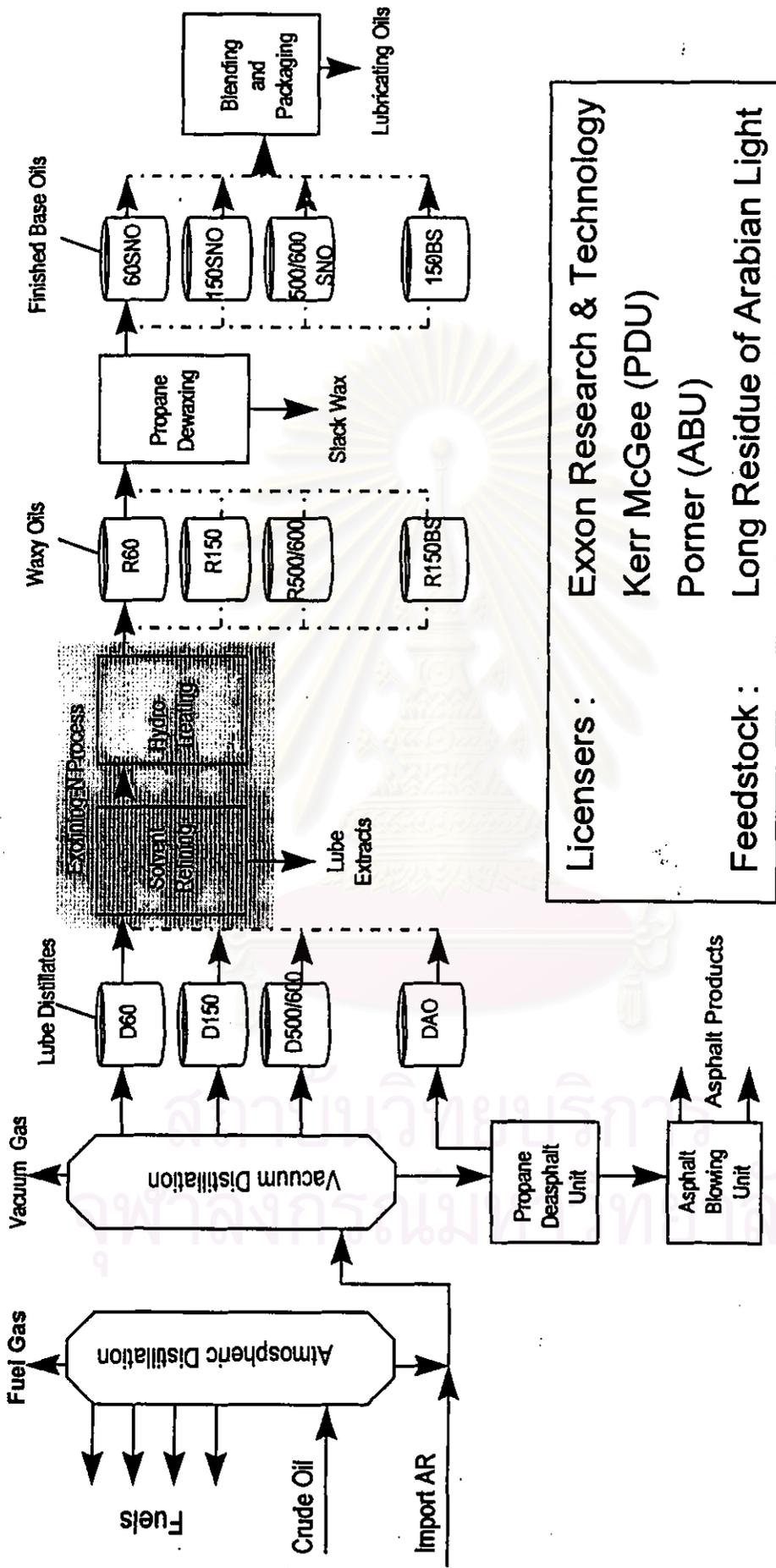


Figure 2.1 : Lube processing



Licensers : Exxon Research & Technology
 Kerr McGee (PDU)
 Pomer (ABU)

Feedstock : Long Residue of Arabian Light



May 1999

Figure 2.2 : Lubricating base oil production flow scheme

2.2 Viscosity

Viscosity is a measurement of the internal friction within a liquid; the way the molecules interact to resist motion[2,4,6,7]. It is a vital property of a lubricant because it influences the ability of the oil to form a lubricating film or to minimize friction and reduce wear.

Newton defined the absolute or dynamic viscosity of a liquid as the ratio between the shear stress applied and the rate of shear that results. Imagine two plates of equal area A , which are separated by a liquid film of thickness D , as shown in Figure 2.3. The shear stress is the force (F) applied to the top plate (causing it to move relative to the bottom plate) divided by the area (A) of the plate. Shear rate is the velocity (V) of the top plate divided by the separation distance (D).

The unit of absolute viscosity is the pascal second (Pa.s), although the centipoise (cP) is often used as an alternative unit ($1 \text{ Pa.s} = 10^3 \text{ cP}$). Absolute viscosity is usually measured with rotary viscometers in which a rotor spins in a container of the fluid and the resistance to rotation (torque) is measured.

Another method of defining viscosity is to measure the rate of flow of the liquid through a capillary under the influence of the constant force of gravity. This is the kinematic viscosity and is defined as follows:

$$\text{Kinematic viscosity} = \frac{\text{Absolute viscosity}}{\text{Liquid density}}$$

The unit of kinematic viscosity is m^2/s , but for practical reasons it is more common to use the centistoke (cSt) ($1 \text{ cSt} = 10^{-6} \text{ m}^2/\text{s}$).

There are other, empirical, scales in use, such as SUS (Saybolt Universal Seconds) or the Redwood scales, and conversion tables are available. Lubricating base oil grades are sometimes referred to by their SUS viscosities.

Kinematic viscosity is routinely measured with ease and great precision in capillary viscometers suspended in constant temperature baths. Standard methods are ASTM D-445 and a number of standard temperatures are used. Measurement of the kinematic viscosity at more than one temperature allows the viscosity / temperature relationship to be determined.

Absolute viscosity is an important measurement for the lubricating properties of oils used in gears and bearings. However, it cannot be measured with the same degree of simplicity and precision as kinematic viscosity[4,7].

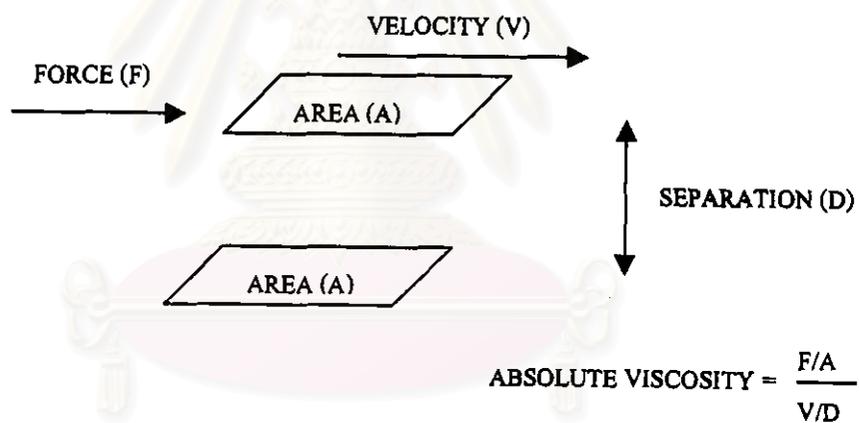


Figure 2.3 : Definition of absolute viscosity

2.3 Literature reviews

Models to predict the kinematic viscosities of mixture of gases, non-polar liquids, pure hydrocarbons and some petroleum products from the kinematic viscosity of the blending components have been proposed by various research groups. Numerous empirical correlation have therefore been developed based on a statistic tool. The kinematic blending equation derived from this work, however, is based on a linear regression analysis.

K.S. Pedersen and others[8] developed a correlation based on the corresponding state principles to predict the viscosity of both gaseous and liquid hydrocarbon ranging from dilute gases to heavy oils. The required input is the critical constants and the molecular weight of each component. Accurate results were obtained for viscosities of crude oils and also shown to give satisfactory results for pure hydrocarbons and binary mixtures.

T. Wakabayashi[9] made to correlate the viscosity of crude oil fraction with specific gravity and molecular weight. The following equation is derived by stepwise multiple regression: $\log \nu = 1.37 (d \log M)^2 + 16.12 (d \log M)^{-2} - 9.06$
The calculated viscosity has an average absolute deviation of 15.9%, and therefore this equation is useful for estimating the transport properties of crude oil.

P. Burg and others[10] had developed the models for prediction of the kinematic viscosity of crude oil from chromatographic data. Multivariate analysis method was applied to results of behavior models for viscosities, which were established and allowed acceptable predictions. It is of great interest for modeling industrial processes.

Method of Grunberg and Nissan[2] : in this procedure, the low-temperature liquid viscosity for mixtures is given as

$$\ln \eta_m = \sum_i x_i \ln y_i + \sum_i \sum_j x_i x_j G_{ij} \quad \dots \text{Eq.(1)}$$

or a binary of 1 and 2,

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad \dots \text{Eq.(2)}$$

since $G_{ii} = 0$, x is the liquid mole fraction and G_{ij} is an interaction parameter which is a function of the components i and j as well as the temperature. When the interaction parameter was regressed from experimental data, nonassociated mixtures and many mixtures containing alcohol, carboxylic acid, and ketone were fitted satisfactorily. The overall root mean square deviation for the mixture tested was 1.6%.

The ASTM D-341[11] method is based on Wright's method[12] with the use of standard viscosity-temperature charts to predict the viscosities of blends of petroleum products. These charts were derived with computer assistance to provide linearity over a greater range on the basis of the most reliable of modern data. The following equation was proposed by Wright :

$$\log \log Z = A - B \log T \quad \dots \text{Eq.(3)}$$

where :

$$Z = (\nu + 0.7 + C - D + E - F + G - H),$$

$$\log = \text{logarithm to base 10,}$$

$$\nu = \text{kinematic viscosity, cSt}$$

$$T = \text{temperature, K or } ^\circ\text{R,}$$

$$A \text{ and } B = \text{constants,}$$

$$C = \exp(-1.14883 - 2.65868 \nu),$$

$$D = \exp(-0.0038138 - 12.5645 \nu),$$

$$E = \exp(5.46491 - 37.6289 \nu),$$

$$F = \exp(13.0458 - 74.6851 \nu),$$

$$G = \exp(37.4619 - 192.643 \nu), \text{ and}$$

$$H = \exp(80.4945 - 400.468 \nu).$$

The terms C through H are exponentials on the natural base e since this simplifies computer programming. Eq(3) uses logarithms to the base 10 for general convenience when used in short form. The limits of applicability are listed below:

$$Z = (\nu + 0.7) \quad 2 \times 10^7 \text{ to } 2.00 \text{ cSt}$$

$$Z = (\nu + 0.7 + C) \quad 2 \times 10^7 \text{ to } 1.65 \text{ cSt}$$

$$Z = (\nu + 0.7 + C - D) \quad 2 \times 10^7 \text{ to } 0.90 \text{ cSt}$$

$$Z = (\nu + 0.7 + C - D + E) \quad 2 \times 10^7 \text{ to } 0.30 \text{ cSt}$$

$$Z = (\nu + 0.7 + C - D + E - F + G) \quad 2 \times 10^7 \text{ to } 0.24 \text{ cSt}$$

$$Z = (\nu + 0.7 + C - D + E - F + G - H) \quad 2 \times 10^7 \text{ to } 0.21 \text{ cSt}$$

The complete design equation for the chart as given is not useful for inter-calculations of kinematic viscosity and temperature over the full chart kinematic viscosity range. More convenient equations[13] which agree closely with the chart scale are given below. These are necessary when calculations involve kinematic viscosities smaller than 2.0 cSt.

$$\log \log Z = A - B \log T$$

$$Z = \nu + 0.7 + \exp(-1.47 - 1.84 \nu - 0.51 \nu^2) \quad \dots \text{Eq.(4)}$$

$$\nu = [Z - 0.7] - \exp(-0.7487 - 3.295[Z - 0.7] + 0.6119[Z - 0.7]^2 - 0.3193[Z - 0.7]^3) \quad \dots \text{Eq.(5)}$$

where :

$$\log = \text{logarithm to base 10,}$$

$$\nu = \text{kinematic viscosity, cSt}$$

$$T = \text{temperature, K or } ^\circ\text{R,}$$

$$A \text{ and } B = \text{constants}$$

In addition, ASTM D-341 method has described two methods for oil blending calculations: (1) a plotting technique on ASTM viscosity temperature charts and (2) calculation formula. In either case, the required data are the kinematic viscosities of each component oil at 40 and 100°C and the desired kinematic viscosity of the oil blend at one of these temperatures.

(1) Plot the known data for each component on an ASTM viscosity-temperature chart and carefully draw straight lines through the points. The lines should extend beyond the blend kinematic viscosity required. Locate, or draw, the desired blend kinematic viscosity horizontal line on the chart through both of the component oil lines. Lay a centimetre scale along this line and carefully measure the distance between the lines for the two oils where they cross the line of the desired blend kinematic viscosity. Without moving the scale, on the same horizontal kinematic viscosity line read the distance from the low viscosity oil line to the temperature desired. Dividing the latter by the first measurement between the two oils gives the volume fraction needed for the high viscosity oil. Figure 2.4 shows the oil blending calculation from viscosity-temperature chart.

(2) The required blend may also be calculated using a calculator or computer.

The relationships are at 40°C:

$$\text{volume fraction high viscosity oil} = \left[\frac{(E-A)(C-D)}{(E-F)(A-C)} + 1 \right]^{-1} \quad \dots \text{Eq.(6)}$$

at 100°C:

$$\text{volume fraction high viscosity oil} = \left[\frac{(F-B)(C-D)}{(E-F)(B-D)} + 1 \right]^{-1} \quad \dots \text{Eq.(7)}$$

where:

- $A = \log \log Z_{B(40)}$
- $B = \log \log Z_{B(100)}$
- $C = \log \log Z_{L(40)}$
- $D = \log \log Z_{L(100)}$
- $E = \log \log Z_{H(40)}$
- $F = \log \log Z_{H(100)}$
- $Z = (cSt + 0.70)$

- Subscripts:
- $B =$ blend
 - $L =$ low viscosity oil
 - $H =$ high viscosity oil
 - $(40) = 40^\circ C$
 - $(100) = 100^\circ C$

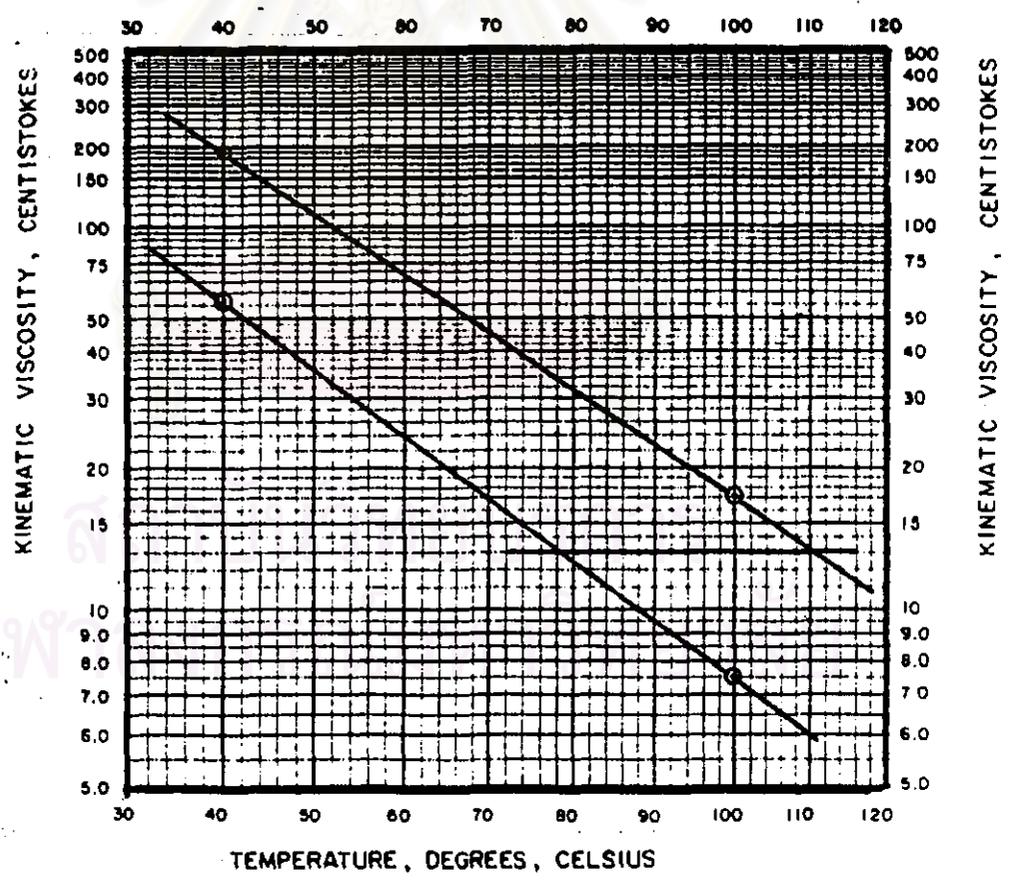


Figure 2.4 : Oil blending calculations

P. Huggins[14] had published the program in BASIC that is based on the concept of blending at constant viscosity employing ASTM D-341 viscosity charts. This program can be evaluated by blending volume fractions of given oils to meet a specified kinematic viscosity at a given temperature, or the viscosity of blends.

J.M. Al-Besharah and others[1] developed the correlation to predict the kinematic viscosity of crude oil blends at constant pressure and temperature, using mixing rules and an excess viscosity function, as follows :

$$(\ln \nu)_{mix} = \sum_i x_i \ln \nu_i + \nu^E \quad \dots \text{Eq.(8)}$$

where :

- x_i = weight fraction of component i
- ν_i = kinematic viscosity of component i
- ν_{mix} = kinematic viscosity of the mixture
- ν^E = excess viscosity function

The term $\sum_i x_i \ln \nu_i$ represents the ideal behavior of the mixture and ν^E represents the non-ideal behavior of the mixture. For ternary mixtures, the latter is represented as follows:

$$\nu^E = a_{12}x_1x_2 + a_{23}x_2x_3 + a_{13}x_1x_3 + a_{123}x_1x_2x_3 \quad \dots \text{Eq.(9)}$$

where a_{ij} is the interaction parameter between components i and j .

Very good predictions were obtained for the viscosities of crude oils; the deviation was in most cases less than 6%. The problem is when applying Eq.(9) to ternary mixtures of lubricating base oil, it is necessary to evaluate the interaction parameters.