VISCOUS-FLOW MECHANISM OF #6 FUEL OIL – PALM OLEIN MIXTURES

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Abstract

The viscosities of mixtures of #6 fuel oil and palm olein at 60 °C do not obey Kendall-Monroe equation. Molecular considerations predict deviation from ideal-mixture behaviour for this kind of "binary" material. It is proposed that the observed positive deviations are mainly due to looser molecular packing in the mixtures than in the "pure" components. Thus, mixing results in a lesser degree of hindrance for the viscous-flow process. The empirical fit of fluidity as a function of olein mass fraction (x) is ln $[\Phi_{mix}/\Phi_{olein}]$ = - (2,72±0,05) + (5,6±0,3) x - (2,9±0,3) x^2; r^2 = 0,992, p < 0,01.

Resumen

Las viscosidades a 60 °C de mezclas de aceite bunker C y oleína de palma no muestran conformidad con la ecuación de Kendall-Monroe. Consideraciones moleculares predicen la desviación del comportamiento de mezcla ideal, para este caso de material "binario". Se propone que las desviaciones positivas de la fluidez se deben a un menor grado de empacamiento molecular de los dos componentes "puros" de las mezclas, resultando así en una menor resistencia al flujo. El ajuste empírico de la fluidez como función de la fracción ponderal de oleína (x) es ln $[\Phi_{mix}/\Phi_{olein}]$ = - (2,72±0,05) + (5,6±0,3) x - (2,9±0,3) x^2; r^2 = 0,992, p < 0,01.

I   INTRODUCTION

It is widely accepted that climate change is an urgent problem that requires globally concerted actions. Atmospheric CO_2 accounts for 63 % of the gaseous radiative forcing responsible for anthropogenic climate change [1]. From the so-called Keeling curve, we have calculated that atmospheric CO_2 has been increasing at an annual rate of 0,4 % during the last five decades. This growth is mainly due to two sources of this greenhouse gas: a) emissions from fossil-fuel

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combustion and industrial processes (23 Gt CO_2 per year) and b) production due to land-use change, mainly land clearing (5,5 Gt CO_2 per year). The first source has been growing rapidly over recent years, and the latter remaining nearly steady [1].
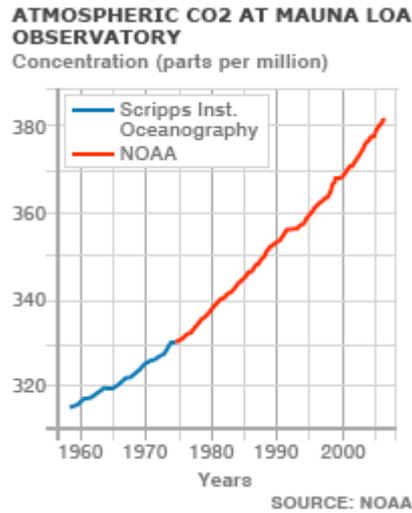

FIGURE 1. Keeling curve. The proportional rate of CO_2 enrichment is 0,40 % y^{-1} during the last five decades [2].

Different actions make possible the lessening of enviromental impacts due to CO_2 accumulation in the atmosphere. One is the improvement in the use of thermal energy and also the partial substitution of fossil fuels used in industrial activities such as cement production, and the operation of thermoelectrical units or boilers. These fuel materials should be derived from renewable sources, such as the case of vegetable oils or animal fats.

It was brought to our attention the possibility of using mixtures of palm olein and #6 fuel oil (bunker C) as fuel for the operation of thermoelectrical generators. Three aspects must be considered in assessing the feasibility of the proposal.

The first is the calorific value of this vegetable oil, which is 38 MJ/kg. This quantity is similar to the observed value of 40 MJ/kg for #6 fuel oil. The second aspect to be considered is price and availability of palm olein, situations that need be analysed in specific scenarios. The third aspect is the resulting viscosities of #6 fuel oil-olein mixtures. If viscosities are higher than values expected from linear dependence of the logarithm of viscosity with composition (*vide infra*), higher energy costs would be involved in the pumping of the fuel mixture due to friction loss.

Binary liquid ideal mixtures of x_i mole-fraction composition obey Kendall-Monroe equation [3]:

$$\ln \Phi_{mix} = x_1 \ln \Phi_1 + x_2 \ln \Phi_2 \qquad (1)$$

where Φ refers to fluidity. The ideal-mixture condition is approached when the molecules of the components are similar in polarity, shape and size [4]. This condition assures *microscopic laminar flow* due to independence of the sliding process of the molecular layers, from the chemical identity of the constituents.

The proposal can be stated that non-linear dependency of ln Φ_{mix} on x is expected when either positive or negative deviations from ideal behaviour occurs. Experimental observation supports the proposal [3]. For example, C_6H_6-EtOH mixtures show positive deviations from Raoult's law, and this suggests the same mathematical result on equation (1), a result borne out by experiment. The opposite is observed for Cl_3CH-Et_2O mixtures.

We present the rheological behaviour of mixtures of #6 fuel oil and palm olein and the compatibilty of the mixtures.

II   MATERIALS AND METHODS

Materials. Palm olein was obtained as a gift from Palma Tica® (Costa Rica) and the #6 fuel oil sample used in this study was from the state-owned petroleum company Recope (Costa Rica). All mixtures of mass fraction x were prepared gravimetrically.

Viscometric measurements and compatibility. A Saybolt Furol viscometer was used, according to procedure ASTM-D88. The measurements were done at 60,0 °C. The compatibility test was carried out as indicated by ASTM-D2781.

Data treatment. The 1/(kinematic viscosity) – composition data were subjected to Anova analysis in the Kendall-Monroe equation form $\ln(1/kinematic\,viscosity)_{mix} = \sum_0 a_j x^j$ for linear and quadratic fits, by using polynomial-regression analysis with the *Excel* package.

III   RESULTS AND DISCUSION

Macroscopic properties. Table 1 gives the kinematic viscosities of the mixtures studied. The measurements were carried out at 60,0 °C.

TABLE 1
KINEMATIC VISCOSITIY OF MIXTURES OF #6 FUEL OIL AND PALM OLEIN AT 60,0 °C.

Mass fraction of palm olein	Kinematic viscosity / SSF
0,000	290,1
0,051	191,1
0,100	152,0
0,199	90,6
0,301	65,0
0,399	41,4
0,500	36,6
1,000	17,5

Figure 1 shows the correlation of ln [Φ_{mix}/Φ_{olein}] *vs.* x is nonlinear. Anova analysis shows that both linear and quadratic terms are statistically significant to at least $p < 0,01$, $r^2 = 0,992$.

In analogy to Kendall-Monroe equation, the following empirical relationship results:

$$\ln [\Phi_{mix}/\Phi_{olein}] = - (2,72\pm0,05) + (5,6\pm0,3)\, x - (2,9\pm0,3)\, x^2 \qquad (2)$$

Though 1/(kinematic viscosity) = density/absolute viscosity = density × absolute fluididty, it is clear that density changes with x much less than absolute fluididty does, as seen from the density values for the two components at 60,0 °C: 0,89 g/cm^3 for palm olein and 0,97 g/cm^3 for #6 fuel oil. Thus, $[\partial \ln(1/\text{kinematic viscosity})_{\text{mix}}/\partial x]_T \approx [\partial \ln \Phi_{\text{mix}}/\partial x]_T$. This means that one can use the inverse of the kinematic viscosity in place of exact Φ_{mix} values for the analysis of the results of this work.

The observed positive deviation from equation (1) indicates that no additional energy expenditure should be expected in the pumping of these mixtures than what is required for fuel oil alone, a favourable mechanical feature of the system.

It is important to determine the composition at which one has the greatest difference between the real system and the situation predicted by the Kendall-Monroe equation.
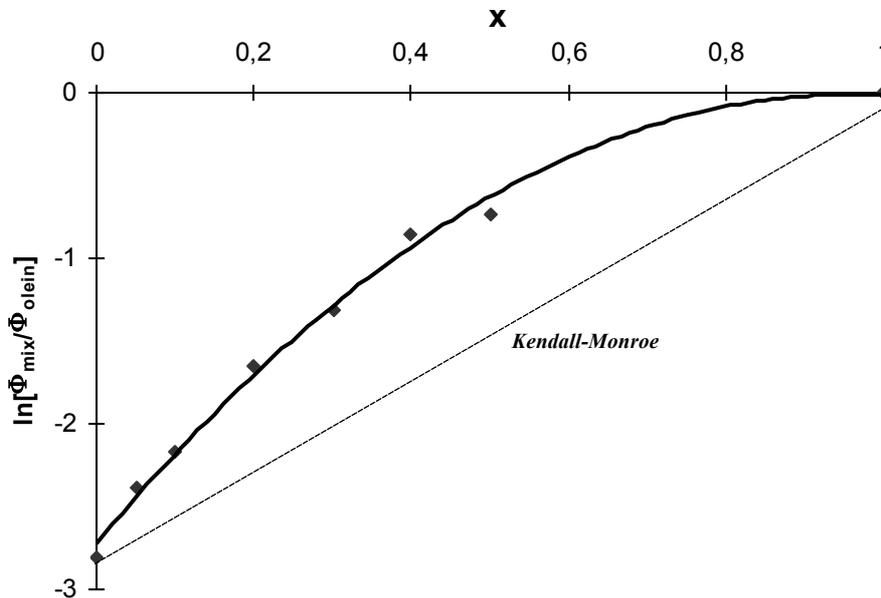

FIGURE 2. Effect of composition on the fluidity of binary mixtures of #6 fuel oil and palm olein at 60,0 °C.

$y_{\text{Kendall}} = \ln \Phi_{\text{bunker}} + \ln (\Phi_{\text{olein}}/\Phi_{\text{bunker}})\, x$

$y_{\text{real}} = -5{,}58 + 5{,}6\, x - 2{,}9\, x^2$

$d(y_{\text{real}} - y_{\text{Kendall}})/dx = 5{,}6 - 5{,}8\, x - \ln (\Phi_{\text{olein}}/\Phi_{\text{bunker}})$

$d(y_{\text{real}} - y_{\text{Kendall}})/dx = 0$

$x_{\text{max}} = 0{,}48$

The above straightforward exercise shows the best mixture to contain ~ 50 % (m/m) of olein, in order to have the maximum fluididty relative to Kendall-Monroe rheology.

An additional aspect to be considered is that of compatibility of the two components. If the components are compatible, there is assurance that no phase separation will occur after mixing. ASTM-2781 procedure shows good compatibility (degree 1 – 2) for all mixtures studied.

Microscopic considerations. The thermal coefficient of cubic expansion of a particular material, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$, is an inverse function of intermolecular forces and of how well molecules are packed in supramolecular lattices [5]:

$$\alpha = \frac{7\, C_p}{72\, \lambda\, \Delta_{vap}H} \tag{3}$$

where λ is related to the packing of molecules in the liquid. The α values of palm olein [(7,0±0,2) × 10^{-4} K^{-1}] and of #6 fuel oil [(6,90 ±0,09) × 10^{-4} K^{-1}] are identical [6].

The petro-material is mainly made up of long-chain hydrocarbons from C_{20} to C_{70}. Palm olein triacylglyceride molecules (TAG) are smaller objects than those in fuel oil. It is clear that intermolecular attractive forces in the latter material must be somehow greater than those between TAG, because the C_n are long coiled molecules with large molecular surfaces, whilst TAG have almost cylindrical compact shapes, as shown by the space filling model below [obtained from the internet site www.3dchem.com/molecules.asp?ID=320#].

Figure 3. Space filling model for triacylglycerols.

The qualitative idea agrees with the difference in $\Delta_{vap}H° = 163±4$ kJ/mol (190 kJ/kg) for TAG in general [7] and values in the range 101,8 kJ/mol and 192,6 kJ/mol for C_{20} - C_{38} [8]. A value of apparent $\Delta_{vap}H° = 220$ kJ/kg is reported for #6 fuel oil [9].

We give the following interpretation to the findings discussed in this work. The magnitude of intermolecular forces does not seem to play the main role in this case.

Packing arrangement influences many properties of liquids such as density, viscosity and diffusivity [10]. The supramolecular configuration in both "pure" components is similar, as can be expected from the α values. The λ parameters are calculated from equation 3 with the aid from C_p values reported in the literature: 1,9 kJ K^{-1}/kg for #6 fuel oil [9] and 1,96 kJ K^{-1}/kg for palm oil [11]. The resulting values are $\lambda_{fuel\,oil} = 1,2$ and $\lambda_{olein} = 1,4$.

The difference in molecular sizes and shapes between the molecular objects in TAG and in #6 fuel oil results in greater amount of excluded volume in the mixtures. This means looser intermolecular packing in the mixtures than in the *pure* components. Though intermolecular forces are somehow greater in #6 fuel oil, the looser lattice in the mixtures renders a lesser degree of hindrance to the viscous-flow process, relative to the situations of the two "pure" components.

The observed compatibility of the mixtures can be understood in terms of the similar dielectric constants and Hildebrand solubility parameters ($\delta_H \approx \sqrt{\frac{\Delta_{vap}H}{V_m}}$) [12] of these two materials.

The mean dielectric constant of vegetable oils is 3,1 and a value of 2,6 is accepted for #6 fuel oil. From the $\Delta_{vap}H$ and densities indicated above, one calculates $\delta_H = 13,0$ $MPa^{1/2}$ for palm olein and $\delta_H = 14,6$ $MPa^{1/2}$ for #6 fuel oil.

Conclusion. The fluidity of mixtures of #6 fuel oil and palm olein shows positive deviations from the Kendall-Monroe equation at 60,0 °C. The most fluidal mixture contains 48% of palm olein (m/m). This observation indicates that use of this type of mixtures as fuel means no extra energy requirement for pumping the fuel mixture from storage reservoirs to combustion chambers. Mixtures with up to 48 % olein (m/m) are compatible, according to test ASTM-2781.

This rheology feature is thought to be the result of looser packing of molecules in the mixtures than in the "pure" components.

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