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Viscoelastic models for Mexican heavy crude oil and comparison with a mixture of heptadecane and eicosane. Part II

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Abstract

The viscoelastic properties of crude oils, at a fixed temperature, can be interpreted in terms of a distribution of relaxation times. A square relaxation spectrum applied to the Maxwell model is in accordance with experimental results obtained for a crude oil specimen from the Cantarell reservoir in south-east Mexico. As a continuation of a previous paper, the Weissenberg number formerly proposed for steady viscosity, is also proposed to scale G' and G'' at different temperatures. Although, the mixture of *n*-heptadecane and *n*-eicosane provided good results in the description of viscous properties of the considered crude oil – as reported in the previous paper – the viscoelastic properties of the mixture of *n*-heptadecane and *n*-eicosane are very poor in comparison to those of crude oil. In general, aging of crude oil causes an increment of $\tan\delta$ quicker with temperature increment. Moreover, two years of aging cause a huge increment of G'. The main objective of this paper is providing a suitable and complete model to describe the viscoelastic properties of the considered crude oil.

Keywords: Crude oil; Rheology of crude oil; Weissenberg number; Storage modulus; Loss modulus

1. Introduction

Crude petroleum is a mixture of several compounds, each with different boiling temperatures that can be separated into a variety of generic fractions by distillation and by fractionation [1,2]. However, petroleum from different sources exhibits different characteristics, and the behavioral characteristics are often difficult to define with a high degree of precision. There is a wide variation of properties of petroleum, with proportions of different constituents varying largely [1–4]. Thus, some crude oils have higher proportions of the lower boiling constituents, whereas others (such as bitumen, also referred to as natural asphalt) have greater proportions of the higher boiling constituents (often called the "asphaltic components" or "residuum"). However, from a meso-structural point of view, crude oils can be classified in the general field of suspensions. Their rheology frequently shows a shear thinning behavior in steady shear strain conditions, as well as normal stresses [5]. This very complex behavior depends partially on a Newtonian contribution of suspending fluid, combined with a non-Newtonian contribution due to the colloidal particles [6]. The Weissenberg number was successfully used to scale viscosities of both crude oil and the convenient alkanes' mixtures, at different temperature levels. This number was developed starting from an Arrhenius factor, determined by means of the effect of temperature onto the viscosity, which became part of the Weissenberg number. A dimensionless frequency, formally equivalent to the Weissenberg number, is used to scale G' and G'', and takes the following form

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$$\omega' = k'\omega, \tag{1}$$

where ω is the frequency and k' is the relaxation time. In this paper it is specifically considered the case of crude oil samples of the Mexican reservoir of Cantarell.

The main objective of this paper is providing a suitable and complete model to describe the viscoelastic properties of the considered crude oil. This objective is achieved through the mentioned Weissenberg number, in order to describe the behavior of G' and G'' at different temperature levels; and through a modified Mawell model with a relaxation spectrum, in order to describe the shape of both G' and G'' curves, at a set temperature.

As a continuation of the previous paper, a mention is dedicated to a blend of *n*-heptadecane (C17) and *n*-eicosane (C20) in order to show that the storage and loss moduli, G' and G'', in this case, are very different in trend and magnitude from those of crude oil, in spite of the similarity that occurs in steady shear flow.

2. Methods, equipments and materials

2.1. Reduced viscoelastic variables

The expression of an Arrhenius factor in order to describe the behavior of viscosity with temperature is present in several theories such as the Adam–Gibbs theory [7,8], in several modified expressions of the WLF equation [9] as well as in phenomenological equations which relate viscosity and temperature [9]. They were first used to explain the viscoelastic properties in the glass transition range for polymers [7–9]; nevertheless, they are still valid 100 °C above the transition temperature. These theories provide a suitable framework to express the presence of an activation energy related to a transformation which involves several molecules or several unit segments either of a oligomer or a polymer. These models are ascribable to the general equation found in the first part of this work:

$$k'(T) = \alpha(T)\exp(\varepsilon/RT) = \dot{\gamma}_{cT}^{-1}, \tag{2}$$

where k' is the relaxation time related to the molecular processes involved, ε is the activation energy involved in these processes, R the gas constant, T the absolute temperature, $\alpha(T)$ is the inverse of the frequency factor, in our case, taken as dependent upon temperature, and $\dot{\gamma}_{cT}$ is the critical shear rate, which is the shear rate corresponding to the onset of the Newtonian plateau after the shear thinning region, in conditions of steady shear flow. The critical shear rate and critical viscosity η_{cT} were determined in our previous work [10]. Their values are reported in Table 1. Therefore, a dimensionless frequency is defined and based on the same relaxation time k', according to Eq. (1).

$$\omega' = k'(T)\omega \tag{3}$$

In a similar way, e.g., G'' is scaled:

$$G''_{\prime} = G''_T \eta_{cT}^{-1} k' = \frac{G''}{\tau_{cT}}, \tag{4}$$

Table 1
Critical shear rates and critical viscosities

$\dot{\gamma}_{cT}$ (s^{-1})	η_{cT} (poise)	T (K)
0.025	1069.1	293
0.059	319.2	303
0.141	127.1	313

where η_{cT} and τ_{cT} are the critical viscosity and shear stress at temperature T, respectively. The critical shear stress is determined by means of the critical shear viscosity and the relaxation time, as shown in Eq. (4). A similar reasoning can be done for G'. There are several methods to obtain master curves of oscillatory functions [11]. In this paper, the described dimensionless variables were chosen because they allowed us to have a direct linkage with the viscous properties, as determined in steady shear flow.

2.2. Distribution of relaxation times: the effect of particle dispersion

The relaxation time λ concerns with those properties which are related either to particles or polymer dispersions. The assumption of one relaxation time will not fit the plots of G' and G''; however, the use of a square shaped distribution of relaxation times can reproduce the main characteristics of G' and G''.

The storage and loss moduli in the Maxwell model are given, for one relaxation time, by:

$$G'(\omega) = \frac{G\omega^2\lambda^2}{1+\omega^2\lambda^2}, \tag{5}$$

$$G''(\omega) = \frac{G\omega\lambda}{1+\omega^2\lambda^2}, \tag{6}$$

where ω is the frequency and G the elastic modulus. As said above, this model implies that we have only one relaxation time λ, but crude oil and several other mixtures or dispersions have several relaxation times or, more generally, a distribution of relaxation times, as the simplified version proposed herewith

$$G'(\omega) = \int_{-\infty}^{\infty} \frac{\omega^2\lambda^2 H(\lambda)}{1+\omega^2\lambda^2}\,\mathrm{d}\ln\lambda, \tag{7}$$

$$G''(\omega) = \int_{-\infty}^{\infty} \frac{\omega\lambda H(\lambda)}{1+\omega^2\lambda^2}\,\mathrm{d}\ln\lambda, \tag{8}$$

where $H(\lambda)$ is the relaxation spectrum. In our case, we choose a square distribution, which implies the limit relaxation time λ_0. In brief, in the range $0 \leqslant \lambda \leqslant \lambda_0$, $H(\lambda)$ is constant and for $\lambda > \lambda_0$ is null. In the case of this relaxation spectrum, the storage and loss moduli turn out to be:

$$G'(\omega) = \frac{G_0}{2}\ln(1+\omega^2\lambda_0^2), \tag{9}$$

$$G''(\omega) = G_0\tan^{-1}(\omega\lambda_0). \tag{10}$$