RHEOLOGICAL BEHAVIOUR OF VINASSES FROM A MEXICAN BIOETHANOL FACTORY

By

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KEYWORDS: Rheology, Vinasses, Bioethanol, Viscoelastic, Energy Of Activation.

Abstract

THE KNOWLEDGE of the rheological behaviour of vinasses is very important for the operation and design of a sugarcane bioprocess. This study characterised rheological behaviour of residues from a bioethanol process that uses final molasses as the carbohydrate source. For this, we used a rotational rheometer Anton Paar MCR 301, concentric cylinder system, Peltier plate for temperature control and software Rheoplus for date capture. The temperature effect was compensated with an Arrhenius model, which measures the activation energy of vinasses in the range 298–310 K. The results showed an activation energy of 2.496×10^3 Cal/g-mol, a non-Newtonian behaviour with viscoelastic characteristic, *i.e.* at low shear rate range (0–387 L/s) as fluid or viscous (pseudo plastic) flow. After this, there is an inflection point at high shear rate as solid or elastic flow (dilatant), because the vinasses presented a material restructure. This behaviour is due to the complex chemical composition of vinasse from final molasses, which is a by-product of the sugarcane process. To confirm this behaviour, it was compared with the rheological behaviour of vinasse from sugarcane juice as the carbon source that showed a dilatant behaviour, *i.e.* as a fluid flow. These results showed that, depending on the substrate chemical composition (complex/simple), similar rheological behaviour (complex/simple) is obtained.

Introduction

Residues and derivates from the sugarcane industry can be made into by products, with an economic value and avoid any environmental impact. This impact has a direct effect on the people, by particles emission, contaminant gases, solid residues or discharged fluids that affect environmental health, caused fundamentally by technological advances and low environmental education.

Vinasses from bioethanol production are classified as organic residues of main effect pollutants. From each hectolitre of ethanol produced from final molasses, 10 to 15 hectolitres of vinasse are obtained, with a Chemical Oxygen Demand-COD_5 between 60 and 70 g/L and a pH *ca.* 4.0. This vinasse is often discharged into rivers, booties and quays without treatment.

Rheology is a science that studies flow and deformation of material when subject to low external forces and depicts the fluids on a graph of stress strength versus shear rate, denominated rheogram (see Figures 1a and 1b). In contrast to fluid mechanics that studies *how* normal fluids behave, rheology shows how non-Newtonian fluids behave, *i.e.* that do not obey the Newton law, Equation (1) Bird *et al.* (2006):

$$\tau = \mu \cdot \dot{\gamma} \qquad (1)$$

where: τ is a shear stress [Pa]

μ is the dynamic viscosity [Pa·s]

$\dot{\gamma}$ is the shear rate [sec^{-1}]

There are in industry other very complex non-Newtonian fluids such as viscoelastic fluids, located at the interface between solid and fluid behaviour.

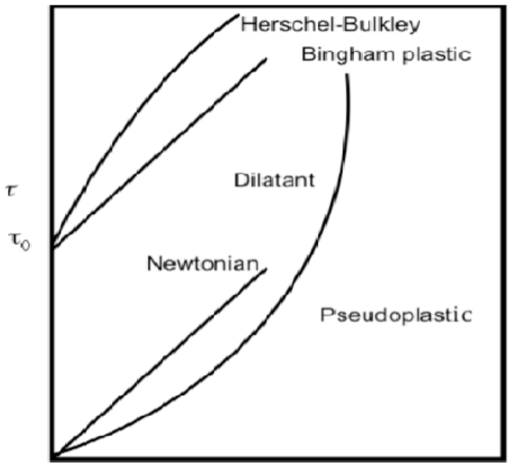

Fig.1a—Rheogram of time independent fluids.

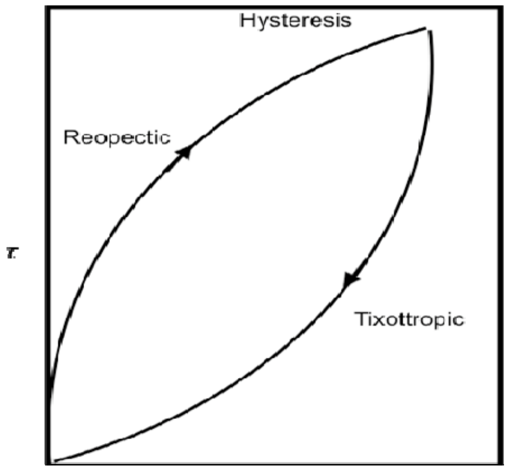

Fig.1b—Rheogram of time dependent fluids.

The knowledge of the rheological behaviour of vinasses is very important to project, operate and design sugarcane bioprocesses, such as energy requirements during mixing and transport, friction losses in pipelines and accessories, and in other aspects of engineering. The rheological research gradually also finds applications in the following: kinetic reactions, chemical structures and components, concentration and distribution of molecular mass, Cantú-Lozano (1990).

Methodology

The vinasse samples were collected from two bioethanol factories, a Mexican and a Brazilian. The rheological characterisation was realised in an Anton Paar ™ rheometer model MCR301 with a Peltier plate for control of temperature (Figure 2). A concentric cylinder and parallel plates geometry and Rheoplus software for data capture were used with vinasse samples of 30 mL.

Fig. 2—Rheometer Anton Paar MCR 301.

Rheological behavior of Mexican vinasse samples was characterised by Herschel-Bulkley model Equation (2) Morel *et al*. (2008)

$$\tau = \tau_0 + K\dot{\gamma}^n \qquad (2)$$

where: τ is a shear stress [Pa]

τ_o is a yield stress [Pa]

K is the consistence index [Pa·s^n]

n is the rheological index [–]

$\dot{\gamma}$ is the shear rate [sec^{-1}]

The activation energy (Ea) was calculated using the Arrhenius model equation (3), which correlates the apparent viscosity (η_a) with temperature. In this case, vinasse samples were rotated in the rheometer at 200 rpm within a temperature range of 298–310 K.

$$\eta_a = \eta_0 \cdot e^{\frac{E_a}{RT}} \qquad (3)$$

where: η_0 is initial viscosity [Pa·s]

Ea is flow activation energy [Cal·g-mol^{-1}]

R is ideal gases constant [Cal·g-mol^{-1}·K^{-1}]

T is absolute temperature [K]

Results

Rheological characterisation

Figure 3 shows the rheogram of behaviour of shear stress versus shear rate of a diluted Mexican vinasse sample and Table 1 shows the parameters of the Herschel Bulkley model from Mexican vinasse, performed with software Rheoplus, the values of: yield stress τ_0 and consistency index, K_{HB}, decreases with temperature increases. The flow behaviour index, *n*, approaches Newtonian behaviour*, i.e*. n=1.0.

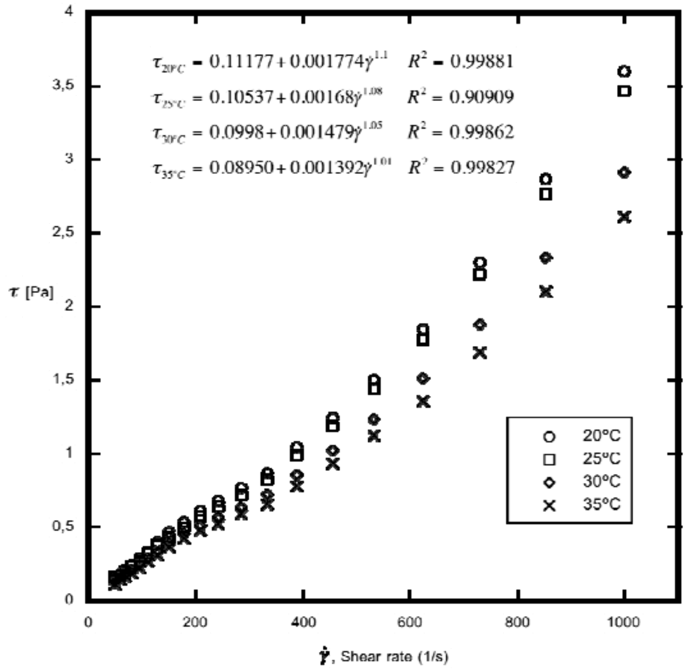

Fig. 3—Rheogram of Mexican vinasse diluted, performed with Herschel Bulkley model as function of temperature.

Table 1—Parameters of Herschel Bulkley from Mexican vinasse.

τ_0 [Pa]	K_{HB} [Pa·sec^n] x10^3	N[–]	T [K]	R^2
0.11177	1.774	1.1	293.15	0.99881
0.10537	1.68	1.08	298.15	0.90909
0.0998	1.479	1.05	303.15	0.99862
0.08950	1.392	1.01	308.15	0.99827

Viscosity comparison

In Figure 4, we present comparisons of experimental data of viscosity apparent behaviour of a concentrated sample of Mexican vinasse that uses final molasses as a carbohydrate source with a concentrated sample of Brazilian vinasse that uses sugar juice as a carbohydrate source.

The Mexican vinasse presents non-Newtonian behaviour with viscoelastic characteristics at low shear rate (0–387 sec^{-1}), as pseudoplastic and, after an inflection point (387–2200 sec^{-1}), at high shear rate as dilatant flow with tendencies of solid behaviour.

The Brazilian vinasse presents a dilatant behaviour. These results showed that, depending on substrate chemical composition (complex/simple), similar rheological behaviour (complex/simple) is obtained.

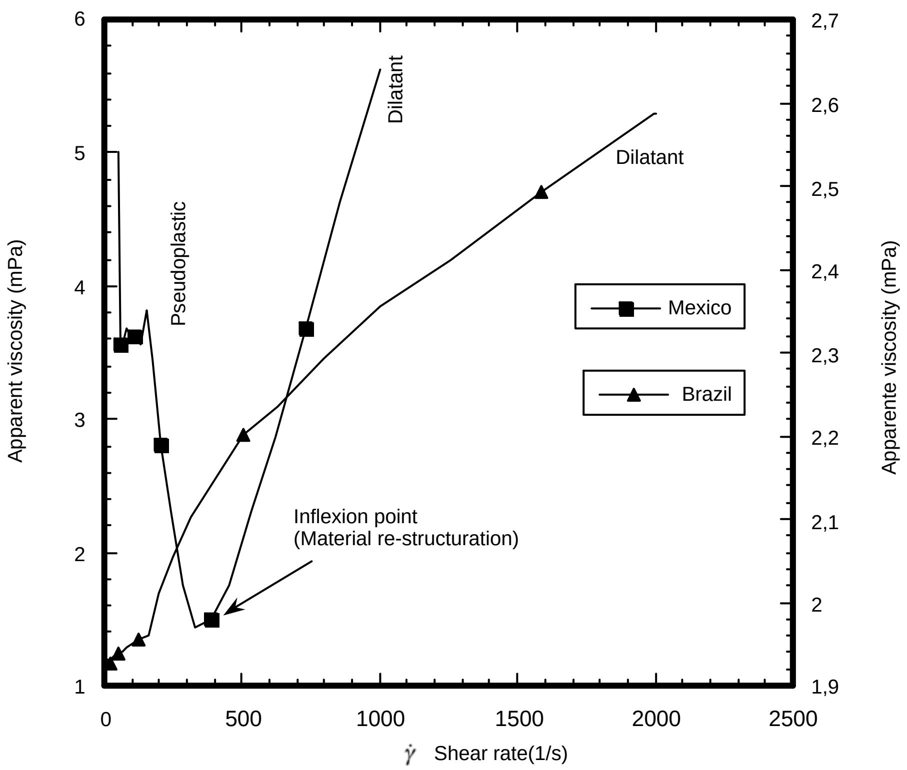

Fig. 4—Comparison of apparent viscosities of two concentrated samples, Mexican and Brazilian vinasses

Effect of temperature

The effect of temperature was investigated with the Arrhenius model, Eq. (3),. Figure 5 shows its linearisation with logarithm of viscosity against temperature reciprocal absolute. Equation (4) and Table 2 present the parameters of the Arrhenius model.

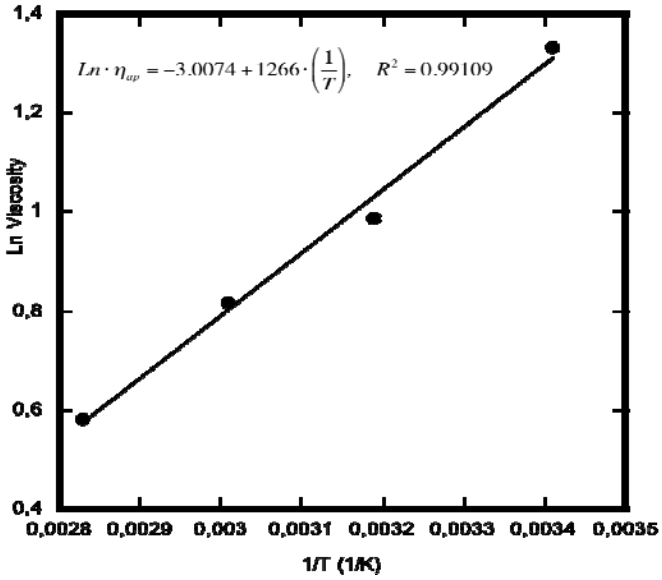

Fig. 5—Linearisation of Arrhenius model.

$$Ln\,\eta_{ap} = -3.0074 + 1266\left(\frac{1}{T}\right), \quad R^2 = 0.99109 \qquad (4)$$

Table 2—Parameters of Arrhenius model for Mexican vinasse.

η_0 [Pa] x10^2	E_a [Cal/g-mol]	R^2
4.942	2496.55	0.99109

Therefore the Arrhenius equation is defined, for these conditions, as follows:

$$\eta_{ap} = 4.942x10^{-2}\,Pa \cdot s \cdot e^{\left(\frac{2496.55\ Cal/g-mol}{RT}\right)} \qquad (5)$$

Conclusions

The examined diluted Mexican vinasse, presents a non-Newtonian behaviour according to Herschel Bulkley model. With temperature increase, it approaches Newtonian behaviour ($\tau_0 \to 0$, n = 1.0 and $K_{HB} \equiv \mu$)

The examined concentrated Mexican vinasse presents a non-Newtonian behaviour with viscoelastic characteristic and high temperature, sensibility and shows a high Activation Energy Flow.

Depending on the chemical composition of the substrate (complex/simple), similar rheological behaviour (complex/simple) is obtained.

In a general way, Rheology of Vinasses is a useful tool to determine differences in: concentration, components and temperature sensibility.

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COMPORTEMENT RHÉOLOGIQUE DES VINASSES D'UNE DISTILLERIE DE BIOÉTHANOL AU MEXIQUE

Par

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MOTS-CLÉS: Rhéologie, Vinasses, Bioéthanol, Viscoélasticité Énergie d'Activation.

Résumé

LA CONNAISSANCE du comportement rhéologique des vinasses est très importante pour le l'utilisation et la conception d'un bioprocessus impliquant la canne à sucre. Cette étude a porté sur le comportement rhéologique des résidus d'un procédé de production de bioéthanol utilisant la mélasse finale comme source de glucides. Pour ce faire, nous avons utilisé un rhéomètre rotatif, Anton Paar MCR 301, un système de cylindre concentrique, une plaque Peltier pour contrôler la température et le logiciel Rheoplus pour l'acquisition des données. L'effet de température a été compensé avec un modèle d'Arrhenius, qui mesure l'énergie d'activation de la vinasse dans une plage de 298–310 K. Les résultats ont démontré une énergie d'activation de $2,496.10^3$ $cal.g^{-1}.mol^{-1}$, un comportement non-Newtonien avec une caractéristique viscoélastique (c'est-à-dire à faible cisaillement**)** de 0–387 $L.s^{-1}$ comme écoulement fluide ou visqueux (pseudo plastique). Après cela, nous distinguons un point d'inflexion à taux élevé de cisaillement comme pour un solide ou un flux élastique dilatant, dû à une restructuration de la vinasse. Ce comportement est dû à la composition chimique complexe de la vinasse produite à partir de la mélasse finale, qui est un sous-produit de l'usinage de la canne. Pour confirmer ce comportement, nous l'avons comparé avec le comportement rhéologique de la vinasse produite à partir de jus de canne comme source de carbone, qui a démontré un comportement dilatant, c'est-à-dire celui d'un écoulement fluide. Ces résultats ont démontré qu'en fonction de la composition chimique du substrat (complexe ou simple), des comportements rhéologiques similaires (complexe ou simple) sont obtenus.

COMPORTAMIENTO REOLÓGICO DE LAS VINAZAS DE UNA FÁBRICA MEXICANA DE BIOETANOL

Por

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PALABRAS CLAVE: Reología, Vinazas, Bioetanol, Viscoelástico, Energía de Activación.

Resumen

EL CONOCIMIENTO del comportamiento reológico de las vinazas es muy importante para la operación y diseño de un bioproceso de la caña de azúcar. Este estudio caracteriza comportamientos reológicos de residuos del proceso de bioetanol que emplea melazas como fuente de carbohidratos. Para esto empleamos un reómetro rotacional Antón Para MCR 301, sistema de cilindros concéntricos, platos Peltier para control de temperatura y software "Rheoplus" para la captura de datos. El efecto de la temperatura se compensó con un modelo de Arrenius, que mide la energía de activación de las vinazas en el rango 298-310 K. los resultados muestran una energía de activación de 2,496x 10^3 Cal/g-mol, un comportamiento no newtoniano, con características viscoelásticas i.e. en un rango bajo de efecto cortante (0- 387L/s) como fluido ó flujo viscoso 9pseudo plástico). Después de esto, hay un punto de inflexión a altos efectos cortantes como sólido ó flujo elástico 9dilatante), porque las vinazas presentan una reestructuración material. Este comportamiento se debe a la compleja composición química de las vinazas de melazas, que son un subproducto del proceso azucarero. Para confirmar este comportamiento, se comparó con el comportamiento reológico de vinazas de jugos de caña como fuente de carbono, que mostró un comportamiento dilatante i.e. como un fluido fluido. Estos resultados muestran que, dependiendo de la composición química del sustrato (complejo/simple) se obtienen similares comportamientos reológicos (complejo/simple).