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Bioethanol production process rheology

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ABSTRACT

The increase of bioethanol request in Mexico forces to accelerate the construction of new production plants and to implement process improvements. Locally, the main raw material in bioethanol production process is sugar cane molasses. Nevertheless, there are different problems within the process that minimize their production potential. There is a generation of sludge and its embedding at the inner wall of the first distillation column, and its mechanical cleaning causes an attrition and damage on it. This raises greater embeddings and shorter useful life of the column. In order to improve the process efficiency, becomes necessary to study the behavior of raw material and its transformations during the process, through Rheology. Molasses and its transformations are clearly affected by changes in shear rate and temperature. Incrustation, formed in the first distillation column, presented a high consistency index value (K), a strong shear thinning behavior and viscoelastic characteristics. This confirms the high content presence of dextran gum in the incrustation sample. Both results, rheological and physical, concur with the embedding real problems inside the column. Arrhenius model was used to describe the influence of temperature on fermented mash. Activation energy was obtained as well.

1. Introduction

Bioenergy is major stake holder in meeting global future energy needs. Bioenergy could sustainably offer a quarter and a third of global primary energy supply by 2050. Bioenergy is the only renewable source that can replace fossil fuels in all energy markets in the production of heat, electricity and fuels for transport (Naveen et al., 2014).

Biofuels in Mexico, as bioethanol, have been taken more importance in matter of bioenergy obtained by non-fossil sources. It has been established that by 2024 the share of non-fossil sources in electricity generation will be 35% (SENER, 2013). However, the increase in this biofuel request, forces to accelerate the construction of new production plants and to implement process improvements (Marriaga, 2009).

The bioethanol production process from molasses is based on properties that have some microorganisms, as *Saccharomyces cerevisiae*, to metabolize sugars and produce as waste, ethyl alcohol. To carry out this process from sugar cane molasses in an industrial plant, it is necessary to have several operations summarized in three stages: mashes preparation, continuous fermentation and distillation – rectification.

Locally, the main raw material in bioethanol production process is sugar cane molasses. Molasses contain water, inorganic matters, sugar and non-sugar organic substances such as organic acids, lipids and inorganic salts, invert sugar, gums and macromolecules of high molecular weight (Hasan and Nurhan, 2004). Nevertheless, there are different problems within the process that minimize the production potential. There is a generation of sludge and its embedding at the inner wall of the first distillation column. This implies losses due to down time used for scraping and cleaning of the column. Due to column cleaning is mechanical, an attrition and damage is caused, which raise greater embedding and shorter useful life of the column.

In order to improve the process efficiency, becomes necessary to study the behavior of raw material and its transformations during the process, through Rheology. Rheology is well stablished as the science of the deformation and flow of matter: It is the study of the manner in which materials respond to applied stress or strain (Steffe, 1996).

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2. Materials and methods

Samples were collected from a local distillery factory in Orizaba, Veracruz, Mexico. Their description, properties and characteristics are mentioned below.

Molasses: sub product from sugar cane sucrose refinery process and main raw material in distillation process (pH of 5.54, 68.86 g SS_T/L, viscosity of 2.15 Pa s, density of 1.35 g/mL, protein content of 3.68%, reduced sugar content of 220.55 g/L, and 1133.14 g COD_T/L).

Mash: conditioned molasses in order to start fermentation process (pH of 5.18, 9.13 g SS_T/L, viscosity of 0.03 Pa s, density of 1.03 g/mL, protein content of 1.08%, reduced sugar content of 46.77 g/L, and 114.72 g COD_T/L).

Fermented mash: generated mash after fermentation stage, and before distillation process (pH of 5.17, 7.66 g SS_T/L, viscosity of 0.02 Pa s, density of 0.99 g/mL, protein content of 1.05%, reduced sugar content of 26.48 g/L, and 114.32 g COD_T/L).

Incrustation in distillation column: material formed and incrusted in the first distillation column inner walls (pH of 5.02, 43.37 g SS_T/L, viscosity of 0.59 Pa s, density of 1.29 g/mL, protein content of 0.20%, and 485.76 g COD_T/L and dextran content of 235,523.22 ppm).

Impure bioethanol: resulting bioethanol from first distillation column (pH of 4.63, 0.15 g SS_T/L, viscosity of 0.004 Pa s, and density of 0.90 g/mL).

pH was determined by potentiometry, SS_T by technique 2540 Solids/Standard Methods, viscosity by rheometry, density by pycnometry, protein content by Kjeldahl method, reduced sugar content by Fehling method, COD_T by technique 5220 D Chemical Oxygen Demand/Standard Methods and dextran content by HPLC.

2.1. Rheological characterization

Rheological properties were assessed using an Anton Paar Physica MCR301 rheometer, and Rheoplus/32 V2.81 software for data capture and analysis. According to the sample, different Peltier systems and geometries were used. For molasses and incrustation, it was used plate Peltier (P-PTD200/TG-SN80091455) and 50 mm of diameter and 2° angle cone geometry (CP50-2/TG-SN6659), and 25 mm of diameter and 2° angle cone geometry (CP25-2/TG-SN6614), respectively. For both mashes it was used cylinder Peltier (C-PTD200-SN80123149) and stirrer geometry (ST22-4V-40-SN10120), and for impure bioethanol cylinder Peltier (C-PTD200-SN80123149) and cylinder geometry (CC27/T200/AL-SN9337). Every experiment was made with replica.

2.1.1. Steady state

In order to determine each steady state sample behavior, different rotational tests were made varying temperature (T) according to industrial operation conditions, and varying shear rate ($\dot{\gamma}$) from 0 to 1000 s^{-1}. As response variables were defined viscosity (η) and shear stress (τ_0). The tests mentioned before, were developed for molasses at 25 °C and 35 °C, mash at 25 °C, fermented mash at 25 °C and 90 °C, incrustation in distillation column at 25 °C, and impure bioethanol at 25 °C and 90 °C. Geometry type and Peltier system at rotational tests were explained above. Fitted constitutive rheological models for the shear rate- shear stress relation and for the dependence of the obtained rheological parameters on temperature were obtained by Rheoplus/32 V2.81 software. The equations reliability was evaluated by determination coefficient (R^2) and the "Student test".

2.1.2. Dynamic state

Viscoelastic properties of the incrustation in the linear viscoelastic region (LVE) were analyzed. The LVE region can be considered as a measure of gel strength. In amplitude test, stronger gels have a more extensive LVE region in comparison with weak gels (Naji-Tabasi and Razavi, 2016). The shear storage modulus (G′) and the shear loss modulus (G″) are both functions of frequency: G′ may be interpreted as the component of the stress in face with the strain (elastic behavior), G″ may be interpreted as the component of the stress 90° out of face with the strain (viscous behavior).

There were made oscillatory tests to the incrustation sample only: amplitude and frequency sweeps were carried out. Oscillatory sweeps were performed at a temperature of 25 °C (T) and varying amplitude (γ) as well as frequency (ω). Frequency was maintained at 10 s^{-1} for amplitude sweep from 0.1 to 1000%, meanwhile, amplitude was maintained at 10% for frequency sweep from 0.1 to 100 s^{-1}. It was obtained the storage modulus (G′), and the loss modulus (G″).

2.1.3. Temperature effect

The temperature influence on the apparent viscosity can be expressed in terms of an Arrhenius type equation (1) involving the absolute temperature (T), the universal gas constant (R), and the activation energy for viscosity (E_a).

$$\eta_\alpha = \eta_0 e^{\frac{E_a}{RT}} \quad (1)$$

Values of E_a and η_0 are determined from experimental data. Higher E_a values indicate a more rapid change in viscosity with respect to temperature (Steffe, 1996). E_a represents the energy barrier that must be overcome before the elementary flow process can occur (Astolfi-Filho et al., 2011). This parameter refers to the amount of energy that the fluid has to absorb so that its molecule packings line up.

In order to quantify the temperature effect on the viscosity, a temperature ramp was performed for fermented mash at a constant shear rate of 500 s^{-1} and at temperature range from 25 °C to 90 °C. The resulting equation was evaluated by linear regression analysis obtaining the determination coefficient (R^2).

3. Results and discussion

3.1. Steady state

Rotational flow curves (rheograms) of the different samples are shown in Figs. 1 and 2.

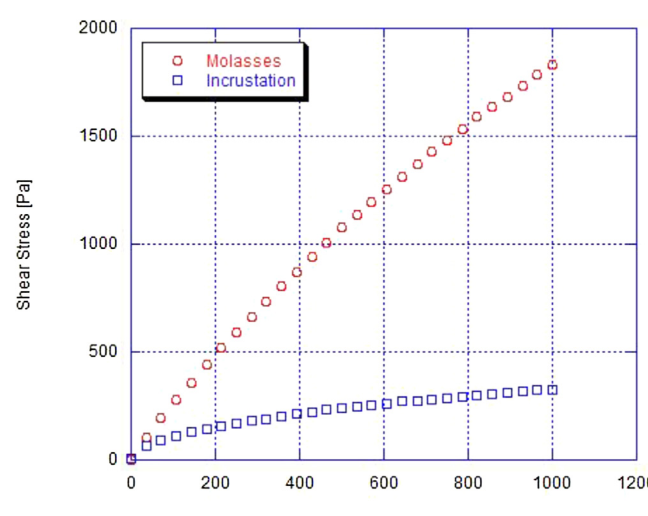

Fig. 1. Molasses and incrustation samples behavior at 25 °C.