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Rheological Behavior of Castor Oil Biodiesel

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Viscosity, the measurement of the internal flow resistance of a liquid, constitutes an intrinsic property of vegetable oils. It is of remarkable influence in the mechanism of atomization of the fuel spray, in other words, in the operation of the injection system. This property is also reflected in the combustion process, whose efficiency depends the maximum power developed by the engine. This work aims at assessing the rheological behavior of castor oil, castor oil biodiesel, and undegraded and degraded biodiesel at different exposure times and temperatures. Castor oil biodiesel presents viscosity higher than diesel oil, but this drawback can be corrected by means of blends of both components at different proportions. The viscosity data indicated that the heat treatment leads to a degradation of the samples accompanied by an increase of the viscosity, probably because of interactions with intermediary compounds. The degraded samples presented a pseudoplastic behavior, once the flow index, **m**, is smaller than 1.

Introduction

The use of vegetable oil in internal combustion engines is not a recent innovation. Rudolf Diesel (1858−1913), creator of the diesel cycle engines, used peanut vegetable oil to demonstrate its invention in Paris in 1900. In 1912, Diesel said, “The use of vegetable oils as engine fuel may seem negligible today. Nevertheless, such oils may become, in the passing years, as important as oil and coal tar presently.” Nowadays, it is known that oil is a finite resource and that its price tends to increase exponentially, as its reserves have being decreasing.[1−6]

Among the possible fuel candidates that can be obtained from biomass and are also potentially able to run a compression-ignition engine, biodiesel was shown to be the most feasible alternative. To utilize a vegetable oil in a common diesel cycle engine, without need of adaptations in the engine, it is necessary to submit such vegetable oil to a chemical reaction, denominated transesterification, with the main purpose of lowering the vegetable oil viscosity to values close to mineral diesel oil. The ester mixture thus obtained is called biodiesel.

Biodiesel is a renewable, biodegradable, and correct environmentally fuel. It is a succedaneum to the mineral diesel oil, and it is constituted of methyl or ethyl esters of fatty acids obtained from the transesterification reaction of any triglyceride with a short-chain alcohol, frequently methanol or ethanol.[7−9]

The previous transformation of the chemical element carbon (C) from its original form of carbon dioxide (CO_2) to the form of biomass (carbohydrates) by means of photosynthesis, and from biomass to biofuel by means of the transesterification process, is undoubtedly the great factor of the environmental sustainability of biodiesel. It should add to this advantage the remarkable reductions of emissions to the environment of noxious pollutants such as sulfur dioxide, aromatic hydrocarbons, carbon monoxide, and particulate materials.[10−14]

The combustibility of a proposed fuel refers to the degree of how easily it undergoes combustion in the equipment, in the wanted form, for the production of the most appropriate mechanical energy. In diesel engines, the combustibility is related to fuel properties, such as viscosity.[15−18] Viscosity is one of the most

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important biodiesel characteristics and should be maintained within preestablished limits, as it exerts a great influence on the fluidodynamic properties of a fuel in what concerns the diesel engine operation, such as fuel circulation and fuel injection.

This work has as an objective to assess the rheological behavior of castor oil, castor oil biodiesel, and undegraded and degraded biodiesel at different exposure times and temperatures.

Experimental Section

Castor oil biodiesel was produced by means of the transesterification reaction, which consists of the step of conversion of the oil into the esters of the fatty acids that constitute the biodiesel. The transesterification reaction products are composed of two phases, separable by decantation. The heavier phase is composed of crude glycerine. The lighter phase is composed of methyl esters. Later, the purification process will take place.

In the thermal degradation study of the castor oil biodiesel, a 350-mL sample was heated at 150 and 210 °C, with a flow of air, in a system similar to one used for distillation. In a continuous heating process, aliquots were taken after different times of heat treatment: 1, 6, 12, 24, 36, and 48 h. The rheological study was carried out before and after the degradation process. In the rheological study, samples of castor oil, castor oil biodiesel, type D diesel oil, and samples degraded at 150 and 210 °C for the periods of 1, 6, 12, 24, 36, and 48 h were investigated. The viscosity values of the samples were determined at 25 °C with the aid of a model LV-DVII Brookfield viscometer.

Results and Discussion

The castor oil was converted into biodiesel by the alkaline transesterification reaction. 1% of the potassium hydroxide catalyst was dissolved in methanol, in the mass proportion of 20% of oil, and this mixture was added to the oil. The reaction mass was stirred at room temperature for 30 min. After the decantation processes, the glycerin was removed and the purification process of biodiesel was undertaken with the addition of water, after the biodiesel was dried in a rotary evaporator.

The rheological behavior is one of the important issues in the study of finished products, once rheology is concerned with viscosity, plasticity, elasticity, and the flow of matter. In other words, it is constituted by the changes in the form and in the flow of a material, including all these aforementioned concepts. The real fluids, liquids and gases, present a certain resistance to the flow or deformation, resulting from the viscosity of the material. For gases, the viscosity is related to the transfer of impulse because of the molecular agitation. The viscosity of the liquids is more related to the cohesion forces among the molecules.

Two different fluid behaviors are noticed: Newtonian and non-Newtonian. The study of non-Newtonian fluid is more complicated because the viscosity can depend of time. This leads us to examination of two types of non-Newtonian flow: thixotropic and rheopectic. A thixotropic fluid undergoes a decrease in viscosity with time, while it is subjected to constant shearing. A rheopectic fluid is essentially the opposite of thixotropic behavior in that the fluid's viscosity increases with time as it is sheared at a constant rate.

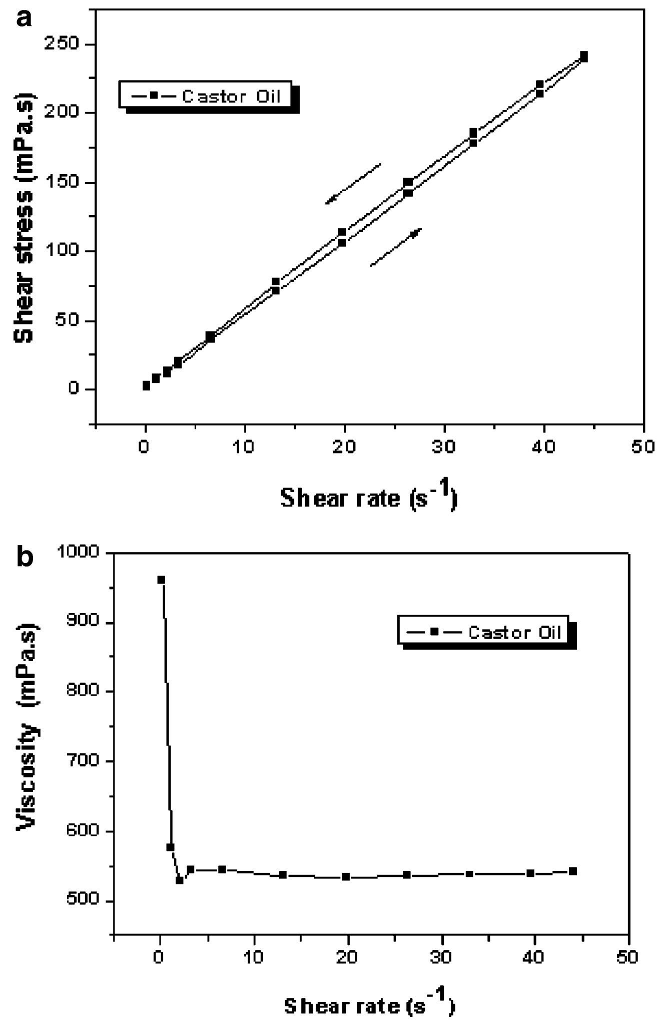

Figure 1. (a) Rheopetic behavior of castor oil. (b) Viscosity vs shear rate for castor oil.

Figure 1a displays the rheological behavior of castor oil which presents a small hysteresis; this is characteristic of rheopetic behavior. Castor oil presents a high viscosity (Figure 1b). The presence of a high content of hydroxyacids in the castor oil is reflected in its colligative properties. In vegetable oil, the viscosity increases with chain lengths of fatty acids of triglyceride and decreases with increases in the unsaturation. So, viscosity is a function of molecules dimension and orientation.[19]

The biodiesel obtained from the castor oil (Figure 2a) presents a lower viscosity than castor oil because of the transesterification process, but it still presents a high viscosity when compared with the type D mineral diesel oil; this drawback can be corrected by means of blends of biodiesel/mineral diesel at different proportions. The mineral diesel oil presented a Newtonian behavior, a linear relationship between shear stress and shear rate, leading to a viscosity independent of the shear stress. The castor oil biodiesel (Figure 2b) presents viscosity higher than mineral diesel oil because of the presence of small amounts of triglyceride.

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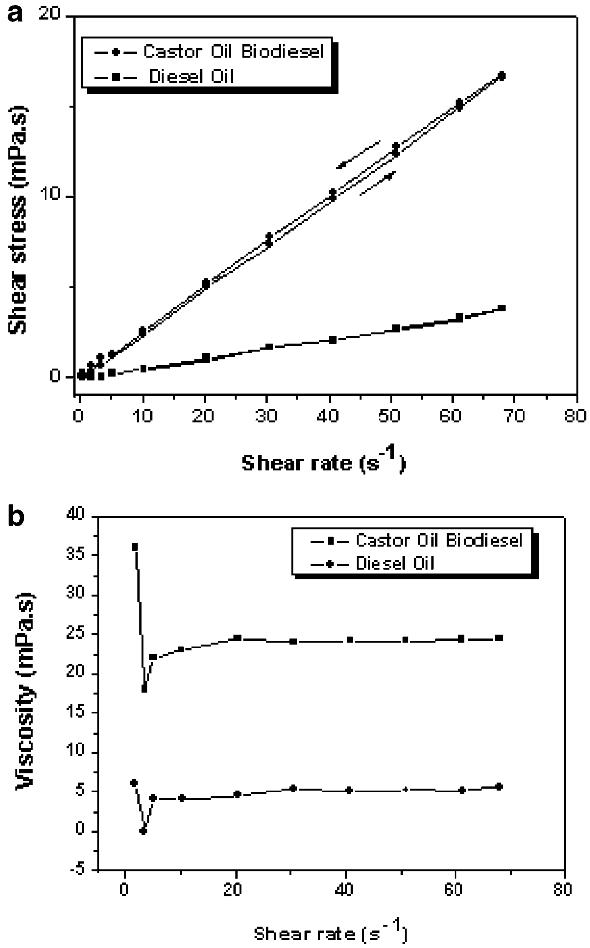

Figure 2. (a) Rheological behavior of the castor oil biodiesel and mineral diesel oil. (b) Viscosity vs shear rate of the castor oil biodiesel and mineral diesel oil.

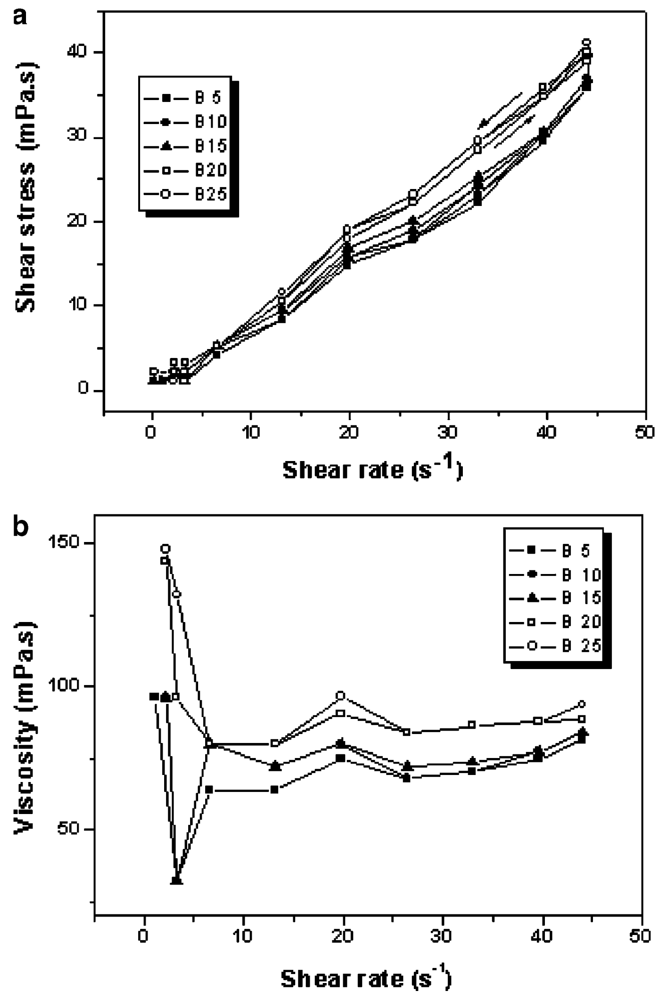

Figure 3. (a) Rheological behavior of the biodiesel/mineral diesel oil blends. (b) Viscosity of the biodiesel/mineral diesel oil blends.

The blends of castor oil biodiesel/mineral diesel oil in the proportions of 5, 10, 15, 20, and 25% (v/v) of biodiesel presented rheopexy (Figure 3a). Rheopexy occurs when there is an increase of the viscosity with the time of shear. This phenomenon is generally reversible, returning the fluid to its initial viscosity some time after ceasing the shear. This behavior indicates the formation of a three-dimensional network among the molecules, which is broken during the shear. The viscosity of blends increases with a higher amount of biodiesel in the blend (Figure 3b).

Regarding the degraded samples at 150° C for the periods of 1, 6, 12, 24, 36, and 48 h (Figure 4), it was observed that the samples degraded for an exposure time from 1 to 12 h presented the same rheological behavior. On the other hand, the samples submitted to a higher exposure time presented rheopexy, indicating that a higher degradation was necessary to modify the rheological properties of the samples.

In relation to the degraded samples at 210° C for the exposure times of 1, 6, 12, and 24 h (Figure 5), it was observed that the samples submitted to heat treatments from 1 to 12 h presented the same rheological behavior. The sample exposed for 24 h presented an abrupt change of behavior.

In the samples degraded for 36 and 48 h, it was not possible to measure the viscosity due to the formation of a gum, mainly in the case of 48 h of exposure. The

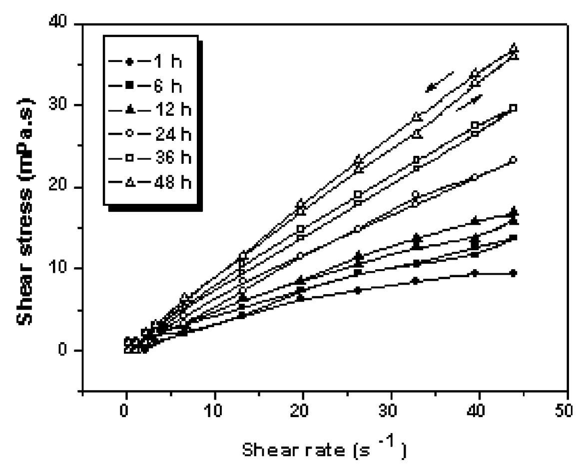

Figure 4. Castor oil biodiesel degraded at 150 °C for different degradation times.

high molecular weight products formed during the oxidation process of the biodiesel lead to the deleterious increase in the viscosity and to the formation of insoluble materials that were deposited in the vessel where the degradation was carried out.

The increase of viscosity of degraded biodiesel at 150 and 210 °C (Figure 6) suggests that high molecular weight compounds were formed during the degradation, by means of oxidation and polymerization processes. At

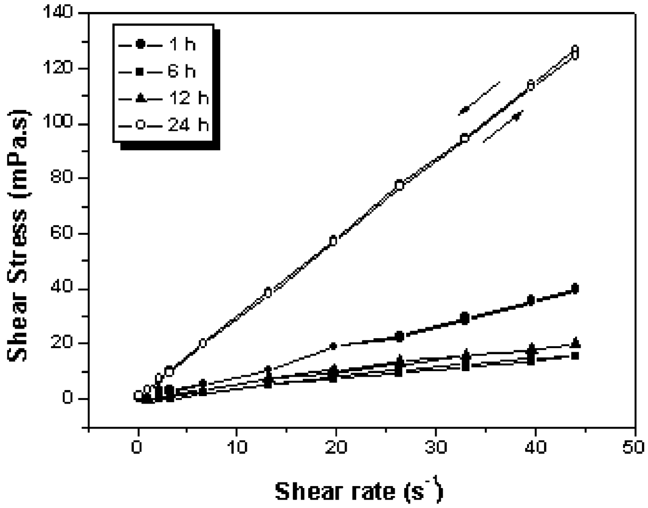

Figure 5. Castor oil biodiesel degraded at 210 °C for different degradation times.

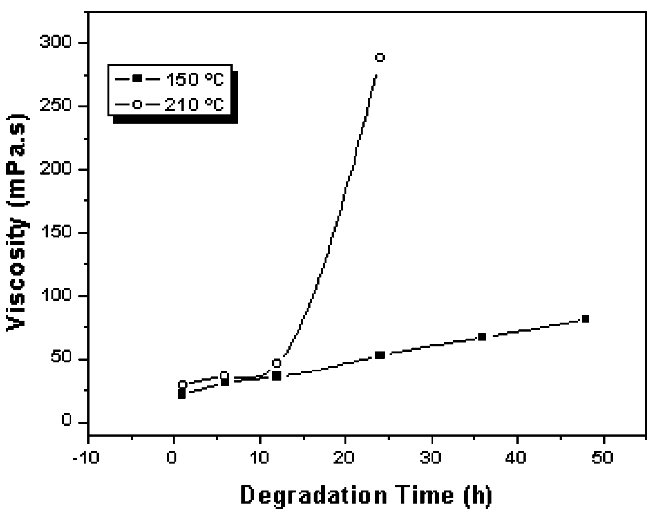

Figure 6. Viscosity of castor oil biodiesel degraded at 150 and 210 °C.

210 °C occurred the formation of higher amount of gum in lower degradation times.

The flow index (**m**) was determined in the degraded samples to characterize the deviation of Newtonian behavior. The systems can be classified according to the type of flow as pseudoplastic (**m** < 1), Newtonian (**m** = 1), and dilatant (**m** > 1). The rheological behavior of the samples degraded can be described according to the following equation:

Table 1. Flow Index as a Function of the Degradation Temperature and Time

degradation time/h	m 150 °C	m 210 °C
1	0.4988	0.3510
6	0.3391	0.2858
12	0.2858	0.2051
24	0.1613	0.1867
36	0.0942	
48	0.0462	

$$\sigma = \eta\gamma^{m} \tag{1}$$

in which σ is the shear stress, γ is the shear rate, η is the viscosity; and m is the adimensional flow index, which characterizes the deviation to the Newtonian behavior.

The values of the flow index (**m**) were smaller than 1 for all the samples degraded at 150 and 210 °C, indicating that they displayed a pseudoplastic behavior (Table 1). The pseudoplastic behavior is characterized by the decrease of the flow resistance of the material with the increase of the shear rate.

Conclusions

Castor oil biodiesel presents a high viscosity when compared with mineral diesel oil, but this drawback can be corrected by means of blends of both components at different proportions. The blends of castor oil biodiesel/mineral diesel oil at the proportions of 5, 10, 15, 20, and 25% of biodiesel presented rheopexy. The viscosity of blends increases with a higher amount of biodiesel in the blend.

On the basis of the increase of the biodiesel viscosity, it can be suggested that high molecular weight compounds were formed during the processes of oxidative degradation and polymerization. The degraded samples presented pseudoplastic behavior, once the flow index, **m**, is smaller than 1.

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