



Guidelines for the rheological characterization of biodiesel



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HIGHLIGHTS

- A methodology for the rheological characterization of biodiesel is presented.
- The rheology of biodiesel depends on the shear and thermal histories.
- Biodiesel is viscoplastic below the crystallization temperature.
- Thermal cycle tests are useful to define the testing conditions.

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ABSTRACT

The rheological characterization of biodiesel at low temperatures is discussed. Gelling typically occurs in this range, and consequently the mechanical behavior becomes viscoplastic. We illustrate that the rheology of the gelled biodiesel is a strong function of the shear and thermal histories, and due to this dependence the testing conditions must be determined prior to the execution of a rheological measurement. We describe in detail how to determine these conditions by means of the thermal cycle test. Finally we present flow curves for different temperatures, to further illustrate the impact of gelling on the biodiesel rheology. We also discuss an important source of specious data that seems to be often overlooked in the literature.

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1. Introduction

Biodiesel is an environmentally friendly alternative fuel to conventional diesel oil. A source of clean and renewable energy, biodiesel has many advantages over petroleum diesel fuels, including its biodegradability, low exhaust emissions, low toxicity, superior lubricity, high flash point and negligible sulfur content [1–7]. It is obtained from the transesterification process of fatty acids (vegetable oil, animal fat, and other oil-based materials) with short-chain alcohols such as methanol or ethanol. In the transesterification process, the viscosity of the source material is reduced by approximately one order of magnitude [8]. Typical feedstocks that can be used to produce biodiesel include soybean, rapeseed, sunflower, cottonseed, corn, palm, among others. Different feedstocks give rise to different properties, due to the different fatty acid compositions [8–10].

Viscosity is one of the most critical specifications in biodiesel standards, and for this reason has been extensively studied [11–14]. High viscosities may cause poor engine starting and performance [5,15–17]. Moreover, crystallization at low temperatures and consequent gelation gives rise to a dramatic increase in viscosity, which may lead to plugging of filters and lines [1,8,10,18,19]. This consists of one of the main disadvantages of the commercial use of biodiesel as a fuel, especially at moderate and cold climate regions. To circumvent these problems, biodiesel is typically blended with other diesel fuels for cold climate operation.

Rheology has been recently used as a tool to measure the viscosity of different types of biodiesel and biodiesel blends [16,18,20–27]. Typically the authors obtain flow curves and temperature ramps to investigate temperature and blend concentration effects on viscosity.

Despite the conclusion often found in this literature that the biodiesel and blends studied are shear thinning (i.e. the steady-state viscosity decreases as the shear rate is increased), a plain Newtonian behavior is actually expected for these fluids above and even at room temperature, because crystallization—which

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occurs at much lower temperatures—is the only factor that can induce a non-Newtonian behavior. In this paper we demonstrate that a flawed conclusion of shear-thinning behavior can originate from improper interpretation of rheological results.

We also present a methodology to perform the rheological characterization of biodiesel fuels under the guidelines of a recently proposed protocol for waxy crude oils [28]. These crudes present a rheological behavior at low temperatures that is in many aspects similar to the biodiesel behavior. We draw attention to the importance of establishing appropriate testing conditions to obtain repetitive and meaningful data, discuss sources of possible measurement error, and show the importance of correctly treating and analyzing the results. In particular, we highlight and illustrate that the rheology of biodiesel is a strong function of the shear and thermal histories, and hence repeatability is only possible if these pre-test variables are carefully controlled.

2. Experimental

A soybean biodiesel provided by Vanguarda Agro was used in this research. The bottles containing the fluid were stored at room temperature. The rheometric experiments described in this paper were carried out in an ARES-G2 rheometer by TA Instruments (USA), which is a strain-controlled rheometer. Its Peltier system (APS) provided the temperature control during the experiments. The following geometries were used when searching for the appropriate testing conditions:

- Smooth parallel plates, 50 mm diameter, with gaps varying between 0.25 and 3 mm.
- Cone and plate, 50 mm diameter, 0.04 rad angle and truncation of 47 μm .
- Couette with recessed end, 34 mm cup diameter, and 30 mm bob diameter.
- DIN Couette, 30 mm cup diameter, and 27.7 mm bob diameter.

After this preliminary investigation involving all the geometries above, the DIN Couette geometry was chosen and used throughout, as will be discussed later.

The results presented in this paper correspond to an average of at least three runs, except in (i) Fig. 6, where we wish to show the results of a test consisting of submitting a sample to three cycles in a row; (ii) Fig. 7, where the idea is to compare the results of three consecutive runs with different samples; and (iii) Fig. 11, where we illustrate the deviation between the results of two identical runs due to torques below the rheometer sensitivity.

Before placing the sample in the rheometer, the biodiesel is homogenized by vigorously hand-shaking the bottle. Then a sample is collected from the bottle and loaded into the rheometer with a syringe. The sample is placed between the plates or in the cup at 25 °C. Then, the rheometer temperature is raised to the initial temperature T_i , which is maintained for 15 min until equilibrium conditions are established.

2.1. The role of the thermal cycle tests

As adumbrated in the introduction, below the crystallization temperature the biodiesel rheological properties are a strong function of the thermal and shear histories, because the size and shape of the crystals—which govern the mechanical behavior—are themselves strong functions of the cooling and shear rates that the biodiesel sample undergoes before the beginning of the actual rheological measurements. Hence any rheological test of biodiesel below the crystallization temperature must be preceded by a well controlled imposition of such histories [28].

One possibility is to impose, prior to each rheological measurement, constant simultaneous cooling rate \dot{T}_h and shear rate $\dot{\gamma}_h$, where the subscript h stands for “history.” It is worth noting, however, that the histories defined by constant \dot{T}_h and $\dot{\gamma}_h$ may not be representative to the process of interest. In this case other histories should be imposed. In this paper we discuss the cases for which constant \dot{T}_h and $\dot{\gamma}_h$ mimic satisfactorily the process of interest.

Other details of the shear and thermal histories to be imposed must be defined with basis on the biodiesel characteristics and on the sought-for application. The initial temperature T_i of the cooling process should be neither too high—to avoid composition changes—nor too low, to ensure the dissolution of crystals and homogeneity. The final temperature T_f is the temperature at which the rheological measurements are desired.

In addition, to obtain good-quality rheological data it is important to select a suitable geometry with which to perform the rheological tests.

Thermal cycle tests are exploratory tests performed in a rotational rheometer that consist of a cooling ramp immediately followed by a heating ramp. The output is the viscosity as a function of temperature. These exploratory tests are used to determine the initial temperature T_i , the geometry and the gap, which, together with \dot{T}_h and $\dot{\gamma}_h$, constitute the information needed to impose the thermal and shear histories to the sample before a rheological test can be performed. Moreover, thermal cycle tests allow the determination of the crystallization temperature T_c and the dissolution temperature T_d , as illustrated shortly.

It is important to emphasize that by viscosity here we just mean the ratio of the instantaneous shear stress to the instantaneous shear rate. For materials of complex rheological behavior like the gelled biodiesel this ratio may be a function of several variables, especially the time of shearing. In thermal cycle tests the time of shearing before recording the data points is typically held fixed at values of the order of a few seconds, while steady state (if it exists at all) is expected to be achieved at much longer shearing times for these materials.

Therefore, while the viscosity $\eta \times T$ curves appearing in the thermal cycle test results shown in Figs. 1–9 are quite useful as already discussed, it is important to keep in mind that the absolute values of η that pertain to $T < T_c$ appearing therein are not to be confused with the steady-state viscosity discussed in Section 3.3 and appearing in Figs. 10 and 11.

2.2. Procedure to obtain the flow curves

We present flow curves as an example of rheological test result obtained with the procedure recommended in this paper. We also

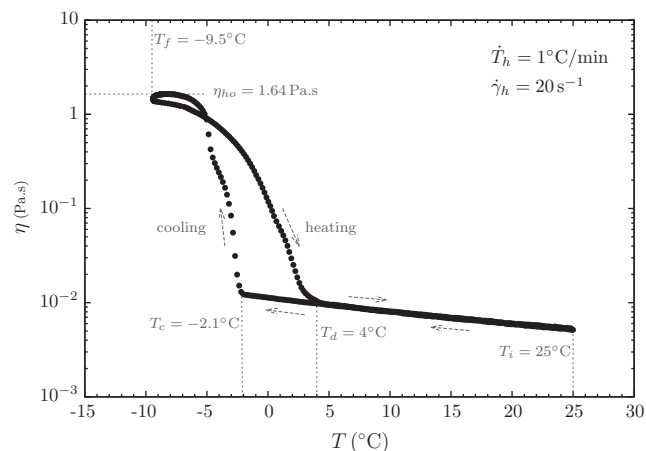


Fig. 1. A typical viscosity vs temperature curve obtained with the thermal cycle test.

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