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Full Length Article

Variation of solid fraction with cold flow properties of biodiesel produced from waste frying oil

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A B S T R A C T

Biodiesel sample utilized in the study was produced from waste frying oil by a base catalyzed one step transesterification reaction. The feedstock oil and the samples produced were tested in accordance with the standards designated by European Committee for Standardization and also by American Society for Testing and Materials. Cold Flow Properties (CFP), namely Cloud Point (CP), Cold Filter Plugging Point (CFPP) and Pour Point (PP) were determined. Since the three CFP should occur at specific solid fractions during freezing, the objective was to examine in details the whole solidification history to estimate the corresponding solid fractions at these temperatures. The so-called computer-aided cooling curve analysis employed in metal casting industry was modified and applied to the current biodiesel sample. Indications of CP, CFPP and PP were noted as slope changes on the cooling curve and also on its first derivative curve. The Newtonian thermal analysis was utilized to estimate the solid fractions in the solid-liquid mixture at CP, CFPP and PP during solidification. The fraction of the solidified biodiesel in the mixture jumped from 0.18 to 0.39 when the CFPP temperature was reached. The visual observations were in agreement with the calculations.

1. Introduction

Biodiesel is a renewable fuel and may be a remedy to overcome the energy crisis and also global warming. It can be produced from renewable feedstock such as vegetable oil and animal fat. Despite its benefits, biodiesel has received substantial opposition not only due to the use of edible oils as its feedstock but also for occupying the limited agricultural lands to grow oil seed plants necessary in biodiesel industry [1]. Utilization of waste frying oil (WFO) may be a remedy for this conflict, i.e. food vs fuel. It also eliminates the detrimental environmental effects that may arise if WFO is disposed without any sewage treatment.

The most common biodiesel production method is the transesterification process in which feedstock and methanol react in the presence of a catalyst to yield fatty acid methyl esters (FAME), known as biodiesel fuel. The properties of WFO differ from those of refined and crude oils. The presence of heat and water accelerates the hydrolysis of triglycerides and increases the free fatty acid (FFA) content of WFO. Triglycerides containing high amounts of water and FFA cannot be easily transesterified and the pretreatment of WFO becomes necessary [2].

The major international biodiesel standards are EN 14214 [3] and ASTM D6751 [4]. In all specifications, the tendency of a fuel to gel or solidify at low temperatures is characterized by their Cold Flow Properties (CFP), i.e., Cloud Point (CP), Cold Filter Plugging Point (CFPP) and Pour Point (PP). They directly determine the usage of fuel according to the climatic conditions of a particular region. Since biodiesel starts to gel at higher temperatures than diesel fuel, determination of its CFP and their improvement are major challenges [5–10].

The CP is the temperature at which a cloud of wax crystals first becomes visible when fuel is cooled under conditions addressed by ASTM D2500 [11] or EN 23015 [12]. It may be considered approximately as the beginning of fuel freezing. The PP is described in ASTM D97 [13] and ISO 3016 [14] as the temperature at which wax crystallization becomes sufficient to gel the fuel. It is not the end of solidification, but is the lowest temperature at which the fuel can flow. In ASTM D6371 [15] and EN 116 [16] the CFPP is defined as the temperature at which the crystals grow and begin to adhere to each other plugging the diesel filters. It directly affects the diesel engine performance in winter. The CP is the highest temperature used for the characterization of cold flow and the PP is the lowest. The CFPP is usually between CP and PP. The CP is the only cold flow property that is considered in ASTM D6751 [4] standard whereas PP and CFPP rather than CP are taken into account in EN 14214 [3] standard.

The cooling curve recorded in a thermal analysis is a temperature versus time (T vs t) graph of a melt during freezing, hence it keeps the

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whole solidification history. Each phase change causes a thermal event which is displayed as a plateau on the cooling curve. It's widely employed in metal casting [17,18] and also for the petroleum waxes [19]. A plateau occurs in the vicinity of melting point of petroleum waxes having crystalline solids. Petroleum waxes with amorphous (non-crystalline) solids do not exhibit a plateau. A dT/dt vs t, i.e. 1st derivative, plot can disclose the small details and invisible information hidden in the T vs t graph. An analysis of the two plots can provide information about the phases evolved during liquid to solid transition. Various features of the solidified melt such as the latent heat, the type and the amounts of the phases that solidify can be found [17,18]. The definitions of CP, CFPP and PP, stated above involve crystallization of biodiesel and diesel fuels during solidification, therefore a plateau during freezing on their cooling curves should be expected.

The zero curve in a thermal analysis is an imaginary curve which is defined as the 1st derivative of a cooling curve in which the material examined does not undergo a phase change during freezing. Zero and dT/dt curves overlap in the fully liquid and fully solid phases but diverge from each other during liquid to solid transition period, i.e. in the two-phase region. The area enclosed by the two curves is directly related to the latent heat evolved and therefore, it can be used to determine the change of solid fraction with temperature during freezing. For the determination of the zero curve, the Newtonian approach assumes that there is no temperature change across the sample and that the heat transfer within the substance towards the casing occurs by convection. On the other side, the Fourier analysis considers the effect of temperature gradient across the sample and assumes that the heat transfer takes place by conduction. The extensive amount of data involved and dependency of variables on time and temperature necessitate computer usage for such a study and is called the computer-aided cooling curve analysis (CA-CCA). The analysis has been utilized extensively in metal casting for process and quality control [17,18].

Due to the absence of phase diagrams of multicomponent biodiesel fuel, estimation of solid fractions at CP, PP and particularly at CFPP during freezing becomes a complex issue. The present study was aimed to examine the cold flow behavior of biodiesel produced from WFO during solidification by employing the CA-CCA technique in conjunction with the Newtonian thermal analysis. Estimation of the solid fraction in the solid-liquid region of biodiesel particularly, at the CFPP was a prime interest since the amount of crystals formed while the fuel is freezing affects directly the plugging of the filters.

2. Methodology

2.1. Sample preparation and characterization

The base catalyzed one step transesterification reaction method was used to produce biodiesel from WFO [2,20–22] which was collected from the Engineering Faculty Cafeteria in Near East University. Prior to the reaction, WFO was filtered for the removal of food residues and solid precipitates then, heated to 100–120 °C for water removal [2]. The fatty acid composition of the feedstock was analyzed via Gas Chromatography (GC) in accordance with EN ISO 5508 [23] standard. The titration of WFO showed that its free fatty acid (FFA) content was less than 3% (2.2% as oleic acid) and the feedstock was suitable for base catalyzed transesterification reaction [24]. The amount of additional catalyst (NaOH) required for neutralization of FFA was also calculated.

Biodiesel, glycerol, excess methanol and other undesired products were separated from the resulting mixture with the aid of a separation funnel after transesterification. Biodiesel collected was purified by washing and then by heating to 110 °C. Thirteen different parameters of the final product was also tested following the relevant standards. The results obtained were tabulated with the required limits and the related standards.

Among the above properties, CP, PP and CFPP were determined following ASTM D2500 [11], EN 23015 [12], ASTM D97 [13], ISO 3016 [14], ASTM D6371 [15] and EN 116 [16] standards. Since, unlike metals, the liquid biodiesel was transparent to light, the solidification process could be followed visually.

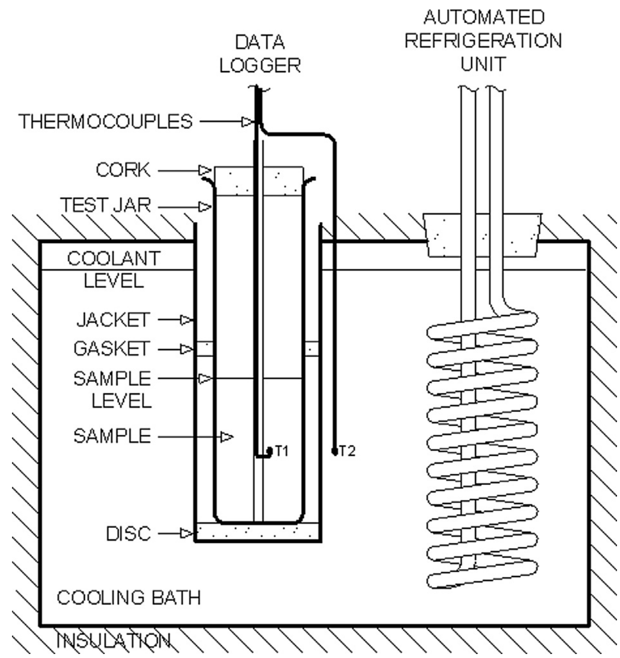

Fig. 1. Experimental setup built following the ASTM standards.

2.2. Experimental setup

The experimental setup for CA-CCA of biodiesel sample, schematically presented in Fig. 1, was built in accordance with the specifications given in the standards [11–16] referred above to assure compatibility. An insulated cooling bath was filled with ethanol as the coolant. Ethanol was cooled down while its temperature was controlled by an automated refrigeration unit. A stirrer was used for thermal homogeneity of the ethanol in the cooling bath. An aluminum cylinder jacket was placed in the middle of the cooling bath. A 6 mm thick cork disk was placed at the bottom of the jacket as a thermal insulator. The glass test jar was filled with biodiesel sample to a level of 54 mm corresponding to a sample volume of about 45 ml. The test jar was then fitted into the jacket and a uniform air gap of 5 mm in the radial direction between the test jar and the jacket was ensured by a gasket.

Two T-type thermocouples for temperature readings are also shown in Fig. 1. Thermocouple T1 was positioned 27 mm above the bottom and 3.5 mm away from the central axis of the test jar in order to measure the temperature of biodiesel sample (T). Thermocouple T2 was placed to measure the temperature of ethanol (T_0) in the vicinity of the jacket close to the mid-section at which T1 was fixed.

2.3. CA-CCA and derivation of solid fraction during freezing of biodiesel sample

Prior to data collection for CA-CCA, the cooling bath was cooled down to -20 °C and the biodiesel sample was heated up to 50 °C which was about 40 °C above the expected CP value. Temperature readings from thermocouples were recorded using a data logger with 1 s intervals and the data was stored for the analysis. The average of 30 successive measurements was calculated to smoothen the curves using Eq. (1) below, rendering the data free of any noise.

$$T_n = \frac{\sum_{i=30(n-1)}^{30(n-1)+29} T_i}{30} \quad t_n = \frac{\sum_{i=30(n-1)}^{30(n-1)+29} t_i}{30} \quad n = 1,2,3,4,..... \tag{1}$$