Energy 68 (2014) 57–60

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Cold flow properties of biodiesel obtained from corn oil

Nazmiye Rasimoglu, Hakan Temur*

Atatürk University, Engineering Faculty, Department of Chemical Engineering, 25240 Erzurum, Turkey

ARTICLE INFO

Article history:
Received 27 March 2013
Received in revised form
26 January 2014
Accepted 13 February 2014
Available online 20 March 2014

Keywords:
Biodiesel
Cold flow properties
Cold filter plugging point
Cloud point
Pour point

ABSTRACT

In this study, it is aimed to investigate the effects of parameters of transesterification on the cold flow properties of corn oil based biodiesel such as cloud point, pour point and cold filter plugging point. Reaction parameters examined were the transesterification temperature (in the range of 20–60 °C), reaction time (10–60 min), alcohol-to-oil ratio (3.15:1–12.85:1 in moles), amount of catalyst (0.25–2 $g_{catalyst}$/100 mL corn oil) and stirring speed (300–800 rpm). As a result, it has been observed that when the transesterification reaction period is kept longer than 10 min, there were no changes in cold flow properties of the biodiesel obtained. In addition, better cold flow properties were monitored when alcohol-to-oil ratio was kept between 3.15:1 and 4.15:1. While no effect of reaction temperature on cold flow properties was observed above 20 °C, amount of basic catalyst used in the experiments gave the lowest cold flow properties at the percent of 0.75. Stirring speed has been ineffective in terms of cold flow properties in the transesterification process.

1. Introduction

The energy need of the world increases because of the growing population and increasing energy consumption as a result of the industrial developments in worldwide. The most consumed energy source in the world is fossil fuels today. 85% of the energy need of the world is met by fossil fuels [1]. In addition, about 40% of the fossil energy consumption worldwide is composed of oil despite the fact that it showed a decline in 2009 because of the worldwide economic recession [2]. Diesel fuel is the most consumed oil product among all petroleum distillates although its contribution to global air pollution is the one of the highest. It is an important source for air pollutants such as NO_x, SO_x, CO, CO_2, particulate matter, and VOCs (volatile organic compounds) which have serious potential to give damage to health of any living being [3]. It is evident that alternative diesel fuels have a vital importance to be able to reduce air pollution worldwide.

Biodiesel is an alternative and environmentally friendly diesel fuel which can be obtained from renewable biological resources such as vegetable oils and animal fats. The main production method of biodiesel is transesterification of oils and fats, in which vegetable oils or fats react with a monohydric alcohol along with an acidic or basic catalyst to yield a mixture of fatty acid alkyl esters and glycerol [4]. Basic transesterification is used wider because of the shorter reaction period and higher product yield. Use of some excess alcohol is required because of reversible nature of the reaction in both methods.

Properties of biodiesel such as exhaust gas emissions, internal lubricity, and its renewability nature are comparable with petroleum diesel; however, poor cold flow properties of biodiesel are one of the obstacles hindering its common use [5]. Biodiesel contains saturated fatty acyl esters in considerable amounts. They are mainly responsible for high CP (cloud point), PP (pour point) and CFPP (cold filter plugging point) temperatures. Cloud point is the temperature by which liquid lipid material begins to have a cloudy appearance because saturated esters get solidify and become crystallized. This causes blockages in the pipes and filters of the fuel systems of the vehicles. If the temperature decreases further, it solidifies increasingly and finally liquid flow will completely stop. The lowest temperature it can continue to flow is called as pour point. Cold filter plugging point is defined as the highest temperature at which a given amount of a fuel sample cooled under certain experimental conditions cannot pass through a standard filter in a specific time [6]. Cold flow properties of biodiesel and diesel fuels are specified by ASTM (American Society for Testing and Materials) D6751 in US and EN (European Standards) 14214 in Europe. In both standards, the cold flow properties of biodiesel such as CP, PP and CFPP are specified to be reported in degrees Celsius depending on the season and the location.

Although minor constituents such as saturated monoacylglycerols or free steryl glucosides may cause clogging problems in fuel pipes and filters of the vehicles, it is clearly known that cold

* Corresponding author. Tel.: +90 442 231 4587; fax: +90 442 236 0957.
E-mail address: htemur@atauni.edu.tr (H. Temur).

http://dx.doi.org/10.1016/j.energy.2014.02.048
0360-5442/

flow properties of biodiesel are mainly affected by fatty acid monoalkyl ester composition of the biodiesel [5,7]. Many studies have been lately focused on improving cold flow properties of biodiesel. Of these, blending biodiesel with different improving agents [5,8–10], winterization [11], use of different alcohols in transesterification and use of oils with modified fatty acid profile [12] are noticeable examples. But one important problem with all these solutions is that it is not possible to obtain a biodiesel sample having favorable cold flow properties without causing a negative effect in another property such as cetane number or oxidative stability. The reason is that biodiesel characteristics such as cold flow properties, kinematic viscosity and density are improved with the increasing unsaturated fatty acid content while some others, such as cetane number and oxidative stability, are improved with the increasing saturated fatty acid content. It is also concluded that monounsaturated fatty acid methyl esters such as oleic acid methyl esters are the most appropriate biodiesel components [13,14].

In this study, it is aimed to investigate the effects of transesterification parameters on the cold flow properties of a biodiesel sample obtained from corn oil. The target of the study is to obtain optimum transesterification conditions giving as low as possible cold flow temperatures.

2. Experimental

The edible corn oil used in the experiments was supplied from a local grocery store. The density of the corn oil was 0.868 g/mL at 15 °C. Corn oil has a good oxidative stability in spite of its high unsaturated fatty acid content [15]. The fatty acid content of the corn oil used in the study is given in Table 1. The corn oil sample was analyzed by a gas chromatograph (Agilent 6890N gas chromatograph, Waldbronn, Germany) with a DB-23 capillary column (60 m × 250 μm × 0.15 μm). Column temperature increased from 100 to 200 °C with a rate of 5 °C/min and from 200 to 250 °C with a rate of 4 °C/min. FID (flame ionization detector) (H_2 and dry air) at 280 °C and helium gas (as a carrier with 1.2 mL/min) were used. Injection block temperature was maintained at 250 °C. The gas chromatography analysis has shown that the corn oil used in the experiments seems to have a higher percent of saturated fatty acid and a lower percent of linoleic acid than those of common corn oil samples [16] though it was supposedly used as a corn oil sample. However, this does not affect the overall goal of the study. Alcohol used in the experiments was methyl alcohol from Merck with 99.8% purity. Anhydride potassium hydroxide with 99.98% purity from Merck was used as a catalyst. Transesterification reaction was carried out in a 500 mL jacketed glass reactor. 200 mL corn oil sample was put into the reactor and heated until the reaction temperature at first. KOH was dissolved in the methanol in a separate flask and the mixture was heated until the same temperature as heated corn oil. Then, catalyst–methanol mixture was poured into the corn oil and the reaction started with agitation. After reaction period ended, mixture was taken into a separating funnel and left there 8 h to separate methyl esters from glycerol. After separation, methyl ester mixture was washed out three times with distilled water by the one tenth in volume. It is left alone 6 h for each washing cycle and then separated from the aqueous phase. After washing, methyl ester mixture was taken into a vacuum rotary evaporator for dehumidifying. The methyl ester mixture obtained from evaporation was used to analyze cold flow properties of biodiesel as B100 (pure biodiesel) according to the standards of EN 23015 for CP, ISO (International Organization for Standardization) 3016 for PP, and EN 116 for CFPP. The average molecular weight of the corn oil was found to be 900.0 g/mol.

The reaction parameters affecting cold flow properties of biodiesel were considered to be reaction temperature, reaction time, alcohol-to-oil ratio, amount of catalyst and stirring speed. Chosen parameters and their levels are shown in Table 2. When a parameter was examined, others were kept constant at a fixed value prespecified by means of the literature [4] in order to see only effect of the parameter under inspection. These unchanged levels of parameters are marked with an asterisk (*) in Table 2.

Table 1
Fatty acid content of the corn oil used in the experiments.

Fatty acid component	% (weight)
k	9.47 ± 0.42
C18:0 (stearic acid)	39.24 ± 1.35
C18:1 (oleic acid)	44.62 ± 3.42
C18:2 (linoleic acid)	0.36 ± 0.25
C18:3 (linolenic acid)	0.29 ± 0.06
C20:2 (arashidonic acid)	0.05 ± 0.02
C20:5 (eicosapentaenoic acid)	0.37 ± 0.03

3. Results and discussions

Each experiment has been repeated at least 3 times and standard deviations in the measurements of cold flow temperatures were at the range of ±0.33 the parameters. The change in the cold flow properties of biodiesel at different parameter levels was plotted as the cold flow properties versus the parameter tested.

3.1. The effect of reaction time

When the effect of reaction time was examined, other parameter levels were kept constant at the level of 50 °C reaction temperature, 1:5.03 (in moles) alcohol-to-corn oil ratio, 1 g_{KOH}/100 mL_{oil} catalyst ratio and 400 rpm stirring speed. The effect of transesterification time on cold flow properties of the biodiesel was given in Fig. 1.

As seen in Fig. 1, reaction time has no important influence on cold flow properties of biodiesel between examined intervals. It shows that after 10 min from the beginning of the reaction, the transesterification process was completed significantly and there observed no change in the cold flow properties of fatty acid methyl ester content. It has been reported from another study [4] that approximate yield of 80% was observed after only in a couple of minutes in the case of sunflower oil and soybean oil reacting with methanol.

3.2. Effect of alcohol-to-corn oil ratio

Effect of alcohol-to-corn oil ratio on cold flow properties is shown in Fig. 2. As seen in the figure, the alcohol-to-corn oil ratios smaller than 4.15:1 (in moles) give lower cold flow properties. In other words, while an increase in amount of alcohol enhanced the amount of ester products in compliance with Le Chatelier's principle at the beginning of the reaction, higher amounts of alcohol caused a decline in the ester formation at later stages of the reaction. This was probably because the solubility of glycerol in the

Table 2
Examined parameters and their levels in production biodiesel from Corn oil.

Parameter	Levels examined
Reaction temperature (°C)	20, 30, 40, 50*, 60
Reaction time (min)	10, 20, 30*, 40, 50, 60
Alcohol-to-oil ratio (in moles)	3.15:1, 4.15:1, 5.03:1*, 6.29:1, 8.43:1, 12.58:1
Catalyst ratio (g_{KOH}/100 mL_{oil})	0.5, 0.75, 1*, 1.5, 2
Stirring speed (rpm)	300, 400*, 500, 600, 800