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Full Length Article

Comparision of fuel properties of biodiesel fuels produced from different oils to determine the most suitable feedstock type

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A R T I C L E I N F O

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A B S T R A C T

Energy, having primary importance in ensuring the prosperity and development of countries, has recently become one of the most strategic parameters in the international arena. Although there is no problem with oil and gas reserves for the next few decades, the issues such as searching for new alternative energy sources, producing and delivering them to consumers will be the most critical issues in energy sector. Today, almost all countries of the world (developed and developing) put in place new energy strategies to increase the share of alternative energy sources in their total energy consumption. Biodiesel is one of the most promising alternative energy sources. Biodiesel can be produced from a lot of different feedstocks such as vegetable oils, waste frying oils and fats, soapstock, algae, etc. However, produced biodiesel's fuel properties significantly depend on the physico-chemical properties and fatty acid composition of its feedstock. In this study, methyl ester biodiesel fuels were produced by using the same transesterification reaction conditions from ten different vegetable oils including soybean, sunflower, corn, cottonseed, canola, olive, safflower, hazelnut, rapeseed, and algae. These oils' fatty acid distributions and some critical fuel properties of biodiesel fuels obtained from these oils were detected and compared with each other to determine the best feedstock type for biodiesel production. The highest ester content value was measured for the biodiesel fuels produced from algae (98.7%) and olive oil (98.6%). In addition, cetane numbers of these two biodiesels were the highest (59 for algae biodiesel and 58 for olive oil biodiesel). The best cold flow properties were determined for biodiesel fuels obtained from algae, corn, and canola oils with the cold filter plugging point (CFPP) values of −14 °C, −13 °C and −13 °C, respectively.

1. Introduction

The major part of all energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). Fossil energy sources are limited and can be found only in certain parts of the world [1]. The decrease of fossil fuel reserves and the rising concerns about the vital impacts of greenhouse gas emissions on the environment have created a need for finding alternative energy sources to replace traditional ones [2]. The scarcity of conventional fossil fuels, the increase of concentrations of combustion-generated pollutants in the atmosphere and the rising costs of environmental problems in the world economy made biomass sources more attractive [3]. Within the context of alternative energy policies, the usage of agriculture-based various biomass sources has found a wide application area all over the world, thanks to their attractive properties such as compatibility with existing fuel distribution infrastructure, better exhaust emission profile, renewability, sustainability, etc. The usage of biofuels especially in transportation sector is so critical in terms of reducing greenhouse gas emissions. Biodiesel, as an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats. This fuel is biodegradable, non-toxic and has low emission profiles and better lubricity properties as compared to petroleum diesel [4]. In addition to its environmental benefits, well-organized and designed biodiesel production from agricultural sources may improve the rural development and consequently reduce immigration from villages to cities, which is a big problem for developing countries [5]. However, biodiesel production from inedible feedstocks, such as waste frying oils and fats, is more accurate in order not to cause increases in edible vegetable oil prices and disturb the balance in food supply [6,7]. In addition to waste feedstocks, algae can also be considered as a potential biodiesel feedstock. Algae-based biodiesel, which is defined as the third generation biofuel, could be an alternative energy source since it has many advantages. Algae are organisms that make use of sunlight and CO_2 more effectively compared to other oil plants, and their cleavage potentials and growth rates are also quite high. It is very favorable that the agricultural areas are not used during the cultivation of algae and they can reproduce with high speed even in very small areas. Moreover, some algae species contain more oil than field crops and they are not affected by seasonal changes

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and climatic conditions. These superiorities make algae very advantageous feedstocks for biodiesel production [8]. As mentioned above, biodiesel fuel can be produced from lots of feedstock containing triglyceride. Feedstcok choice of the biodiesel industry is generally affected from the annual vegetable oil production quantity of that country. The most used feedstock is soybean in USA, rapeseed in European Union countries, palm oil in some tropical countries such as Malaysia and Indonesia. Biodiesel is a fuel comprised of alkyl monoesters of long chain fatty acids derived from the processed feedstock. It should be strongly underlined that fatty acid composition of the feedstock does not significantly change during transesterification reaction at which biodiesel fuel is obtained. Because of this, almost all critical physico-chemical fuel properties of a biodiesel fuel (i.e. viscosity, density, cetane number, iodine value, calorific value, lubricity, oxidation stability, cold flow properties) strongly depend on the feedstock's fatty acid characteristics such as the chain length and the number of double bonds [9–11]. Canakci and Sanli [12] analyzed some critical fuel properties of biodiesels produced from different biomasses and compared them with those of petroleum-based diesel fuel. They have concluded that freezing points of biodiesel fuels, especially produced from fats having high saturation level, were unacceptably high. However, it was reported that if the branched-chain alcohols such as 2-propanol were used in transesterification reactions, positive results in the cold-low properties could be obtained. Ramos et al. [13] investigated the fatty acid compositions of various vegetable oils used in biodiesel production. Also, they detected the fuel properties of biodiesel fuels produced from these vegetable oils, and correlated them with the fatty acid contents (degree of unsaturation) of the feedstocks. They have reported that cetane number and oxidation stability values improved with increasing carbon chain length and decreasing unsaturation level (especially poly-unsaturated fatty acids). In addition, unsaturated fatty acids caused higher iodine values and lower CFPPs. Biodiesel fuels produced from almond, olive, corn, rapeseed and high oleic sunflower oils had comparatively better properties because they had more mono-unsaturated fatty acid content. Elangovan and Jeryrajkumar [14] produced biodiesel fuels from different feedstocks by varying the transesterification reaction conditions. In this study, they measured kinematic viscosity, density, flash point, heating value, and then calculated the correlation coefficients between these fuel properties. They mentioned that these fuel properties strongly depend on the feedstock type and marginally affected from reaction parameters. In addition, they observed strong positive correlation between these fuel features and all of them increased with increasing carbon chain length and degree of saturation. Dmytryshyn et al. [15] produced biodiesel fuels from four vegetable oils (canola oil, green seed oil, processed waste fryer grease and unprocessed waste fryer grease) by using methanol and potassium hydroxide, and subsequently compared their fuel properties such as density, viscosity, cloud point and pour point. They reported that the highest methyl ester yield was obtained from canola oil. The product yield with green seed oil was also satisfactory. The most of the physico-chemical fuel properties of canola methyl ester and green seed methyl ester were similar and not much different from those of petroleum-based diesel fuel. Nevertheless, due to a low lubricity property of the green seed methyl ester, the authors recommended lubricity improver for this biodiesel fuel to protect the engine from friction and wear problems. In the literature there are numbers of studies which characterize the fatty acid compositions of various vegetable oils and measure the physico-chemical fuel properties of biodiesels obtained from these vegetable oil feedstocks. However, in these papers, the number of vegetable oil samples and measured fuel properties were generally inadequate. The purpose of this study was to determine the best vegetable oil as biodiesel feedstock. For this aim, the fatty acid compositions of ten different vegetable oils were determined at first. And then, the measured fuel properties of methyl ester biodiesels, which were produced with the same transesterification reaction conditions, were compared with each other's and the specifications given in European Biodiesel Standard (EN-14214).

2. Materials and methods

In this study, biodiesel fuels were produced from ten different vegetable oils including algae, soybean oil, sunflower oil, corn oil, cottonseed oil, canola oil, olive oil, safflower oil, hazelnut oil, rapeseed oil. All of these vegetable oil feedstocks were purchased from various companies in Turkey. Prior to transesterification reactions, the fatty acid compositions of the vegetable oils were determined. The fatty acid distributions of safflower oil, hazelnut oil, and rapeseed oil were cited from the related literature. The fatty acid contents of the rest of the vegetable oils were measured in Dicle University Science and Technology Application and Research Center. For this purpose, Shimadzu GCMS-TQ8030 gas chromatography device was used with the AOCS Official method Cd 3A-63. Methanol (99.7% purity) and potassium hydroxide (99.9% purity) was supplied by Sigma-Aldrich, Turkey. Transesterification experiments were carried out in a 500 ml four-necked batch reactor. The reactor was equipped with a reflux condenser, to avoid methanol losses, a magnetic stirrer, a thermocouple connected to a heater plate for temperature control, and two stoppers to remove samples and to feed the raw materials, respectively. The reactor was initially charged with the oil and preheated to the desired temperature. The potassium hydroxide catalyst was dissolved in the methanol and the resulting solution was added to the reactor. Reaction conditions of methanol:vegetable oil molar ratio of 6:1, 0.75% w/w potassium hydroxide, reaction temperature of 60 °C and reaction duration of 60 min were kept constant in all transesterification reactions. After the reaction time was completed, the reaction mixture was transferred to the separation funnel. The mixture was left to rest for overnight for complete glycerin phase separation. The glycerin accumulated in the bottom was drained off. The methyl ester product was washed four-times with deionized water, and subsequently, it was centrifuged to remove the aqueous layer compound by methanol, residual catalyst, and glycerol. The residual methanol and water were separated from the biodiesel fuel via rotary evaporation under vacuum at 110 °C for 1 h. The obtained biodiesel fuels were stored in refrigerator at 4 °C. In order to compare the biodiesel fuels, which were obtained from different vegetable oil feedstocks, their some critical fuel properties (ester content, flash point, water and sediment content, viscosity, density, sulfur content, copper strip corrosion, cetane number, cold filter plugging point, carbon residue, acid number, free and total glycerin, phosphorous content, distillation temperature, potassium content and oxidation stability) were measured. These fuel properties were detected in METU Oil Research Center, Batman Refinery Fuel Analysis Laboratory of Turkish Oil Refineries Co. (TUPRAS), Batman University Vocational School of Technical Sciences Fuel Analysis Laboratory.

3. Results and discussion

3.1. Fatty acid compositions of vegetable oil feedstocks

There are three main types of fatty acids that can be present in a triglyceride molecule: saturated (Cn:0), monounsaturated with one double bond (Cn:1), and polyunsaturated with two or three double bonds (Cn:2,3). Each biodiesel feedstock has its own fatty acid structure, and almost all of the critical fuel properties of any biodiesel fuel strongly depend on the fatty acid contents of the feedstock from which it is produced [16]. Because of this, fatty acid compositions of biodiesel feedstocks should be investigated in detail. The fatty acid profiles of the vegetable oils used in this study were summarized in Table 1. As seen, vegetable oils investigated in this study were mostly comprised of monounsaturated and polyunsaturated fatty acids. Based on the fatty acid distribution, two additional parameters can also be calculated for biodiesel feedstocks: the degree of unsaturation (DU), and long chain