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Study of oxidative stability and cold flow properties of *Citrillus colocynthis* oil and *Camelus dromedaries* fat biodiesel blends

Hassen Mohamed Sbihi[a,*], Imededdine Arbi Nehdi[a], Sadok Mokbli[b], Moufida Romdhani-Younes[c], Saud Ibrahim Al-Resayes[a]

[a] King Saud University, College of Science, Chemistry Department, P.O. Box 2454, Riyadh 1145, Saudi Arabia
[b] Superior Institute of Biotechnology of Sidi Thabet, Sidi Thabet 2020, Tunisia
[c] Faculty of Sciences of Tunis, Department of Chemistry, Laboratory of Structural Organic Chemistry, 2092 University of Tunis El Manar Tunis, Tunisia

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ABSTRACT

Biodiesel prepared from animal fat has been gaining increasing interest in the last few years. The main drawback of biodiesel is its poor low-temperature performance, which limits its use in cold climates. This study proposes a method of improving the low-temperature properties of young *Camelus dromedaries* (Hachi) fat biodiesel (*HB*) and improving select fuel properties [e.g., the cetane number (CN) and oxidative stability (OS)] of *Citrullus colocynthis* biodiesel (*CCB*), which has a high iodine value (IV). *HB* and *CCB* were blended in different volume ratios (100:0; 80:20; 60:40; 40:60; 20:80, and 0:100) and the fatty acid methyl ester (FAME) composition and fuel properties of the biodiesel blends were evaluated according to the American Society for Testing and Materials (ASTM) methods The correlation of the cloud point (CP), pour point (PP), cold filter plugging point (CFPP), kinematic viscosity (KV), CN, IV, and OS with the ratio of saturated to unsaturated FAMEs was determined. *HB* improved all the studied fuel parameters of *CCB*, and the international standards (ASTM D-6751 and EN 14214) were met. It is shown that the fuel properties of the biodiesel blends can be predicted using the FAME composition. The results of our study demonstrate that blending the biodiesel from Hachi fat and *C. colocynthis* seed oil provides a suitable alternative to biodiesel prepared using food crops.

1. Introduction

For many years, diesel fuels have been considered as one of the main contributors to the economic renaissance of most developed countries. Diesel fuels have many uses, especially in the transport sector and electrical and agricultural fields. However, diesel fuels have many negative environmental effects, such as pollution problems. In light of these considerations, there has been a growing demand for renewable and non-polluting resources. Wind power, solar energy, hydropower, biomass, and biofuels are the most promising alternative energy resources as replacements for diesel fuels. The primary advantages of biofuels are that they are (i) biodegradable, (ii) do not contain sulfur and aromatics, and (iii) are non-toxic. Moreover, biodiesel can be used in diesel engines with the same or better performance as achieved with normal diesel fuel. Nowadays, biodiesel as a renewable fuel is receiving much attention in the transportation sector. The consumption of biodiesel in European countries is forecast to reach 16,210 million liters in 2018, compared with the consumption of 14,363 million liters in 2011 (Flach et al., 2017). This corresponds to an increase in the biodiesel consumption by about 13% in seven years. Moreover, since 2008, the aviation sector has been conducting test flights with biodiesel (Flach et al., 2017). If these tests are successful, the demand for this biofuel will increase sharply.

Biodiesel is produced by converting the triglycerides of vegetable oils and animal fats to fatty acid methyl esters (FAMEs). The transesterification reaction can be carried out with catalytic and non-catalytic (under supercritical conditions) processes in the presence of simple alcohols, such as methanol, ethanol, propanol, et cetera (Yaakob et al., 2014). There are three kinds of catalytic processes: homogeneous, heterogeneous, and enzymatic biocatalysis. The most widely used route is homogeneous transesterification with a basic catalyst such as sodium hydroxide, potassium hydroxide, or sodium methoxide. The base transesterification process is preferred due to the higher reaction rate and low-cost reagents.

Silitonga et al. (2011) reported that biodiesel is mainly prepared from four categories of feedstock: edible vegetable oils such as soybean and sunflower, inedible vegetable oils such as *jatropha* and *algae*, recycled oils, and animal fats such as tallow and chicken. Moreover,

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[*] Corresponding author.
E-mail address: hmsbihi@ksu.edu.sa (H.M. Sbihi).

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Sierra-Cantor and Guerrero-Fajardo (2017) indicated that at present, three-hundred and fifty sources of fats and vegetable oils are used for biodiesel preparation, and edible vegetable oils account for 95% of these sources. According to the UN Human Rights Council, the use of this feedstock is "a crime against humanity" because edible vegetable oils are some of the principal sources of human food (Sarin, 2012). To avoid the use of food crops, many researchers have turned to using low-cost feedstocks such as animal fats (Sbihi et al., 2014; Bhatti et al., 2008) or inedible vegetable oils (Borugadda and Goud, 2012) to make biodiesel. However, the challenge is the availability and quantity of these raw materials. More recently, animal fats and inedible vegetable oils have been increasingly used as feedstock sources for biodiesel production because they are a lower cost source of triglycerides. However, the major inedible oils such as *Jatropha curcas*, *Pongamia pinnata*, *Prunus sibirica*, and *Datura stramonium* contain significant levels of monounsaturated and polyunsaturated fatty acids (Sarin, 2012). Highly unsaturated fatty acid methyl esters (UFAMEs) show low oxidative stability and excellent cold flow properties (Shahidi, 2005).

It is known that the cold flow properties (CFPs) govern the flow behavior of diesel and similar fluids at low temperatures. For biodiesel, experts have evaluated the CFPs based on three parameters: the cloud point (CP), pour point (PP), and cold filtering plugging point (CFPP). Moreover, Sierra-Cantor and Guerrero-Fajardo (2017) reported that the CFPs of biodiesel depend mainly on the fatty acid profile. Biodiesel with a higher content of UFAMEs generally exhibits good CFPs. In contrast, biodiesel with a higher content of saturated fatty acid methyl esters (SFAMEs) generally exhibits inferior CFPs. In addition, Lanjekar and Deshmukh (2016) and Knothe and Dunn (2003) claimed that the molecular weight, ramification, and the presence of polar groups in FAMEs affect the CFPs. Moreover, Moser (2014) reported that increasing the carbon number in the structure of the alcohol used for the transesterification reaction improves the CFPs of biodiesel. Several studies have been conducted to enhance the CFPs, and have shown that the addition of alcohols (Abe et al., 2016; Verma et al., 2016), ethers (Ali et al., 2014), and diesel (Atmanli, 2016) significantly improved the CFPs.

Compared to petroleum diesel, biodiesel is prone to oxidation due to the presence of double bonds in the FAMEs (Fu et al., 2017). Biodiesel reacts with oxygen during storage to form undesirable products such as aldehydes, carboxylic acids, and high-molecular-weight molecules that can damage the combustion engine (Anwar and Garforth, 2016). Moreover, the presence of undesirable products in biodiesel increases the kinematic viscosity (KV) and forms gums, sediments, and other deposits (Anwar and Garforth, 2016). Thus, a high content of polyunsaturated fatty acid methyl esters (PUFAMEs) that contain bis-allylic methylene groups in biodiesel has a significant negative effect on the oxidation stability (OS) of the fuel (Anwar and Garforth, 2016).

Different approaches have been used to improve the oxidation stability of biodiesel. Kumar (2017) reported that reducing the percentage of PUFAMEs enhanced the OS. Moreover, the addition of natural or synthetic antioxidants (Moser et al., 2013; Nikolic et al., 2014) or diesel (Silitonga et al., 2013; Jain and Sharma, 2014) had a strong impact on the OS of biodiesel. Dharma et al. (2017) and Wang et al. (2016) stated that the OS of *Jatropha Curcas* biodiesel (*JCB*) was 3.23 h at 110 °C and the CP, PP, and CFPP were 3, 2, and 2 °C, respectively, whereas, the biodiesel standards EN 14214 and ASTM D-6751 require an OS limit of 6 h and 3 h at 110 °C, respectively. *Datura stramonium* biodiesel had an OS of 2.40 h, which is below the biodiesel standards, due to the high content of PUFAMEs (Wang et al., 2016). Fan et al. (2016) showed that lowering the iodine value of biodiesel obtained from apricot seed oil from 136.50 g I_2/100 g to 107.70 g I_2/100 g enhanced the OS from 1.98 h to 3.18 h. Moreover, the CFPP changed from −12.5 °C to −8.70 °C, which is an excellent value; this is attributed to the high content of PUFAMEs such as linoleic acid.

Vegetable oil or animal fat biodiesel, which has lower contents of UFAMEs, especially linoleic and linolenic acids, has high stability to oxidation as a result of the fewer double bonds (Polaina and MacCabe, 2007). The OS of Babassu, coconut, and palm biodiesel (*PB*) were 15.70 h (Sanford et al., 2009), 8.80 h (Monirul et al., 2017), and 8.85 h (Benjumea et al., 2008), respectively. In comparison, beef tallow biodiesel had negative cold flow properties due to the high content of SFAMEs. The CP and CFPP of beef tallow biodiesel were 16 °C and 14 °C, respectively (Karmakar et al., 2010).

Few researchers have addressed the mixing of biodiesel from different feedstocks for improving the quality of biodiesel. Sarin et al. (2007) showed that the OS of *JCB* was improved by blending with *PB*. The OS stability of the biodiesel blend (*JCB* 40% + *PB* 60%) exceeded the requirement of biodiesel standard EN 14214. Moreover, Sierra-Cantor and Guerrero-Fajardo (2017) reported that a certain biodiesel blend (*PB* 20% + soybean (*SB*) 60% + rapeseed (*RB*) 20%) had a CFPP of −6 °C and OS of 6.56 h. Zuleta et al. (2012) stated that biodiesel blends with up to 25% *PB* did not exhibit enhanced cold flow properties.

Giwa et al. (2010, 2014) showed that biodiesel produced from *Citrullus colocynthis* seed oil (*CCB*) had lower OS (1.32 h and 1.41 h) due to the high linoleic (C18:2Δ9c,12c) acid content (61.41% and 64.01%). The combination of the low-cost, non-edibility, and high triacylglycerol content of Hachi fat (*HF*) and *C. colocynthis* seed oil (*CCSO*) make them promising as alternative feedstocks for biodiesel production. According to global statistics, approximately three-billion liters of Hachi biodiesel (*HB*) can be obtained in Saudi Arabia and twenty-seven billion around the world (Sbihi et al., 2014). *Citrillus colocynthis* belongs to the Cucurbitaceae family, usually known as melons. It is widely distributed in desert regions of the world including Asia (Saudi Arabia), Africa, and the Mediterranean region. The fruit of this plant contains 200–300 seeds (Sawaya et al., 1986). The seeds of *Citrillus colocynthis* are rich in fat and contain between 20% and 35% oil (Gupta and Chakrabarty, 1964). Nehdi et al. (2013) reported that the total oil yield was approximately 400 liters/ha. Furthermore, the oil consists mainly of unsaturated fatty acids, particularly linoleic and oleic acids (80–85%).

To the best of our knowledge, mixed biodiesel from animal fats has not been reported. Furthermore, *CCB* has not been studied as a blend with either vegetable oils or animal fat as a biodiesel combined with *HB*.

The OS and CFPs are important criteria that determine the biodiesel quality. In our previous study (Sbihi et al., 2014), we indicated that *HF* can be used as a possible alternative source for biodiesel production, but it has poor CFPs. Thus, biodiesel produced from *HF* cannot be used in cold climates.

The properties of biodiesel depend upon the FAME composition, and the values of the major parameters are related to the amount of SFAMEs and UFAMEs. Therefore, the aim of this study is to prepare a biodiesel blend from *HF* and *CCSO*, with different volume ratios of FAMEs, to ensure that it meets the international standards for industrial use. Thus, the shortcomings in the properties of *HF* biodiesel alone or *CCSO* alone can be overcome. First, we determine the composition and the fuel properties of the mixtures with various ratios of FAME. The relationship between the biodiesel properties and FAME composition is explored and the mixtures are optimized to achieve FAME compositions that conform to the common international standards. We also determine the thermal behavior of the mixtures with different FAME ratios by thermogravimetric analysis (TGA).

2. Materials and methods

2.1. Biodiesel production

The raw materials used in this study were obtained from Riyadh, Saudi Arabia. *C. colocynthis* seeds were collected from Wadi Hanifa in the Nejd region (Riyadh Province) and *HF* was collected from the slaughterhouse (Central Riyadh). The raw *HF* was cut into small pieces and then placed in a glass beaker. The mixture was subsequently heated at 70–80 °C and the heated oil was rapidly filtered to obtain pure *HF*.