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Thermal, oxidative and low temperature properties of methyl esters prepared from oils of different fatty acids composition: A comparative study

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ABSTRACT

Thermo-oxidative stabilities of castor oil methyl esters (COME) and waste cooking oil methyl esters (WCOME) were estimated using thermo gravimetric analysis technique (TGA). Low temperature properties of the methyl esters were investigated using ASTM and differential scanning calorimetry (DSC) techniques and compared. Thermo-oxidative onset temperature study showed that process of WCOME decomposition initiated and completed within a temperature range inferior to COME, because of higher percentage of polyunsaturated fatty acids in WCOME (44.41%) compared to COME (6.6%). Comparison of decomposition profile at 10 and 20 °C/min revealed that with increased heating rate degradation was found to be increased. WCOME in particular showed most unfavorable cold flow properties due to the presence of long chain saturated fatty acids (18 wt%). Comparison between ASTM and DSC method showed that DSC method could be a useful technique to estimate the low temperature properties, which also consume less time and sample amount.

1. Introduction

The energy is the most basic and fundamental requirement for human existence. A high percentage of the world's total energy output is generated from fossil fuels and it has been universally conceded that fossil fuels are finite and are depleting [1]. In addition, the threat of supply instabilities and increased public awareness about the impacts of fossil fuel emissions on the environment and their potential health hazards triggered governments around the world to impose restrictions on fossil fuel emissions. The negative effects of fossil fuel emissions on the environment have stimulated interest in alternative sources for fossil fuels [2]. In the search for alternative fuels, biomass sources have received more attention, among them vegetable oils (edible and non-edible) like soybean oil, palm oil, castor oil, and waste cooking oil can be a potential alternative to petroleum based diesel fuel [3,4]. Biodiesel is monoalkyl esters of fatty acids produced from vegetable oils. Biodiesel derived from vegetable oils seems to be a solution as it is renewable and ecofriendly in nature [5].

A major criticism often raised against bio-fuels is that, the use of vegetable oils for biodiesel production could divert the agricultural production away from food crops and thus it could cause food shortage and hike in food prices. Therefore, to overcome all these arguments and for better supply of food needs, edible waste and non-edible oils which does not have high commercial value are being used for biodiesel production [1,6,7]. The direct use of vegetable oils is not practical since it causes engine coking, carbon depositing and gel formation [8]. To overcome these problems, vegetable oils can be modified using different techniques such as dilution, pyrolysis, thermal cracking, and transesterification. Among these transesterification gaining much importance because it produces clean and environmentally safe fuel and the resulting fuel is quite similar to conventional diesel in its physico-chemical characteristics such as, calorific value, fire and flash point, cloud and pour point, density and viscosity etc. [9].

Apart from its advantages and applications, biodiesel also has some disadvantages like poor cold flow properties, degradation of fuel quality during long term storage and its combustion slightly increases nitrogen oxides emissions and poor thermo-oxidative stability. Storage stability can be defined as the relative resistance of a liquid fuel to physical and chemical changes brought about by interaction with its environment [10]. Stability also takes into account of sediment formation, changes in color and depends on the quantity of unstable materials present in the biodiesel. Microbial slimes, particulate solids, degradation products and cleanliness relative to the presence of water also influence the stability [11]. During the storage, fuel properties degrade due to the effects of thermal or thermo-oxidative decomposition from excess heat, oxidation (auto-oxidation) from contact with ambient air, hydrolysis from contact with moisture in tanks or fuel lines and microbial

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contamination from migration of dust particles or water droplets containing bacteria or fungi [10,11].

In general, most of the vegetable oil feed stocks consists of triacylglycerols with long chain fatty acid groups. Biodiesel derived from feed stocks with high C_{14+} fatty acid content like unsaturated (low melting point) and saturated fatty acids (high melting point) can significantly influences the cold flow properties. On the other hand, unsaturated organic compounds are more reactive to oxidation than saturated compounds with the same hydrocarbon chain length; apart from that polyunsaturated compounds are more reactive than monounsaturated compounds [12–14]. The effects of thermal and oxidative degradation on fuel quality during storage can be determined by ASTM, AOCS and European (EN) standard methods, but these methods are rigorous and time consuming [15–17]. Oxidation of biodiesel under elevated temperatures and purging with dry air or oxygen increases the viscosity, acid value and peroxide value. Increase in peroxide value may cause ignition delay of the fuel. However, extensive oxidative degradation causes decomposition of hydro peroxides which eventually decreases the peroxide value and cetane number which leads to an increase in the ignition delay time [18].

Recently, thermo-analytical techniques such as thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been applied to analyze thermal and oxidative stabilities of petroleum based fuel, biodiesel and synthetic lubricants [19–21]. However, from the reported literature [22–25] it was observed that conventional or non-isothermal differential scanning calorimetries are the reliable techniques to determine the cold flow properties.

In the present work, methyl esters from castor and waste cooking oils were synthesized and their thermo-oxidative stabilities were investigated using thermo gravimetric analysis (TGA) and differential thermo gravimetric analysis (DTG) under different atmospheres (inert gas nitrogen and reactive gas oxygen) using different heating rates. In addition, low temperature properties of the methyl esters were investigated by conventional ASTM D97 standard method and differential scanning calorimetry (DSC) technique and both the methods were compared.

2. Experimental details

2.1. Materials

The waste cooking oil (fish fried soybean) was collected from hostel mess, IIT Guwahati, Guwahati, India and mechanically extracted castor oil was obtained from Cherukupalli, Andhra Pradesh, India. Potassium hydroxide flakes, methanol were consumed in transesterification, and other reagents used to determine the physico-chemical properties were procured from Merck, India Ltd.

2.2. Methods

2.2.1. Alkali-catalyzed transesterification

Transesterification reaction was carried out in a 500 ml special glass reactor (3 mm thick), sealed tightly and fitted with condenser at the top. The reaction glass vessel was placed in a temperature controlled water bath. As the free fatty acid (FFA) value of both the samples was <1 (CO-0.57, WCO-0.73), a single step transesterification procedure was followed. FFA is the half of the acid value and it was determined by AOCS official method Te 1a-64. The reaction was carried out using 1:6 oil to alcohol molar ratio and 1 wt% KOH as catalyst. Initially, oil sample was charged into the reactor and heated up to desired reaction temperature 60 °C, in order to cease the loss of methanol from reaction, because beyond this temperature evaporation of methanol was observed. The alkali catalyst KOH (1 wt.%) was dissolved in methanol to form sodium methoxide solution and was prepared freshly in order to avoid moisture absorbance and to maintain the catalytic activity. The prepared sodium methoxide solution was slowly added to the preheated oil. The system was totally closed to the atmosphere to prevent the loss of alcohol, and stirred for 90 min. After completion of reaction, the mixture was cooled and transferred into a separating funnel and allowed to settle overnight for separation. The upper layer contains methyl esters, residual methanol and catalyst, whereas the lower layer contains glycerol and impurities.

The glycerol layer was drawn off using separating funnel and the methyl ester layer was washed with warm millipore water (40 °C) until washing water had a pH that of millipore water. Methyl ester was dried at 60 °C under vacuum by using rotary evaporator (BUCHI Rotavapor, Model R 200) to remove the water content. The obtained yield of methyl ester was 95% and the physico-chemical properties of prepared methyl ester were estimated according to the standard ASTM and AOCS methods.

2.2.2. Chemical composition (GC)

The fatty acid composition of the castor and waste cooking oil samples was determined using Nucon 5765 gas chromatograph equipped with a flame ionization detector (Nucon Engineers, Delhi, India) and fused silica capillary column BPX-70, 60 m × 0.25 mm × 0.25 μm (SGE, India). The column temperature was programmed to increase from 180 °C to 240 °C at 4 °C/min. The detector and injector temperatures were fixed at 240 °C and 230 °C, respectively. The carrier gas used was nitrogen (40 psi) at a flow rate of 45 ml/min, air and hydrogen flow rates were 30 ml/min and 300 ml/min, respectively. The sample injection volume was 1.0 μl with a split flow of 60 ml/min. Presence of saturated fatty acid methyl esters in the sample increases the cloud point, cetane number and improves the stability whereas more polyunsaturation reduces the cloud point, cetane number and stability [26]. The fatty acid composition of castor oil and waste cooking oil is shown in Table 1.

2.2.3. Thermo gravimetric analysis (TGA)

Thermo gravimetric method determines the thermal properties of esters as a function of temperature. The non-isothermal analysis was performed in thermo gravimetric analyzer model TG/SDTA851e, METTLER TOLEDO at two different heating rates of 10 and 20 °C/min from room temperature to 700 °C. The maximum temperature (700 °C) was used, so that the sample weight remains constant till the end of analysis, implying that all the chemical reactions have been completed. Inert nitrogen gas was used as a purge gas at flow rate of 40 ml/min during thermal stability study and oxygen gas was used as a reactive gas at a flow rate of 100 ml/min for oxidative stability study. Different amounts of samples were used during the analysis, but all the samples were measured in mg in an open silica crucible. TG curves as well as its derivative curves (DTG) were used to analyze the onset temperature of the esters. Onset temperature was used to indicate the resistance of esters against thermal and oxidative degradation and it was determined by extrapolating the horizontal baseline of TGA curve at 1% degradation, and the intercept of this line with the tangent can be defined as the onset temperature as shown in Fig. 1.

2.2.4. Differential scanning calorimetry (DSC)

DSC experiments were performed on DSC instrument (model DSC1, star^e system, Mettler Toledo), with computer based controller. Dynamic DSC measurements were carried out in an aluminum crucible with a small variation in sample mass of approximately 6–10 mg and placed in the DSC module with a similar empty pan as reference. The procedure involved heating of the sample from ambient temperature to 50 °C, then held under isothermal