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Combustion dynamics of biodiesel produced by supercritical methanol transesterification

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ABSTRACT

The fatty acid methyl ester (FAME) compositions and combustion characteristics of the biodiesel produced from three plant oils under different supercritical methanol conditions were investigated by gas chromatography and thermobalance analyzers. When the reaction temperature increased from 255 to 300 °C, the conversion efficiency of rapeseed oil into FAMEs in biodiesel increased from 13% to 98%. Such increase resulted in an improved combustion property of rapeseed biodiesel with decreasing combustion activation energy from 143.6 to 84.2 kJ/mol. The ignition temperatures of the biodiesel produced from rapeseed, soybean and palm oils gradually decreased from 257.6 to 240.2 and 238.0 °C, which implied that the biodiesel with more C=C double bonds had higher ignition temperature. The ignition temperature of biodiesel was lower than that of raw plant oil, but higher than that of petroleum diesel.

1. Introduction

Biodiesel is an environment friendly and renewable fuel because of its reproducibility, non-toxicity, and sulfur-free properties. Biodiesel can replace the petroleum diesel without significant modifications to the diesel engine that makes it a good renewable fuel. Supercritical methanol transesterification is a non-catalyst method for producing biodiesel which simplifies the tedious purification and separation steps of the biodiesel produced by conventional catalytic method [1].

Numerous studies have been conducted to characterize the combustion of biodiesel in a diesel engine [2–7]. The carbon monoxide, hydrocarbon, particulate matter and NO_x emissions of biodiesel burnt in a diesel engine were fully characterized. The combustion performance including the ignition delay, the heat release rate and the pressure rise rate of biodiesel burnt in a diesel engine were also investigated. To gain a further insight into the combustion of biodiesel, chemical kinetic mechanism studies related to the oxidation of biodiesel have been performed at the experimental and modeling levels. The chemical kinetic model for oxidation of methyl decanoate [8], methyl decenoates [9], then methyl stearate and oleate [10] were successfully developed. However, the fundamental study on combustion dynamics such as the combustion activation energy and the ignition temperature of biodiesel has not been conducted.

In recent years the application of thermal analysis to study the combustion behavior of oils had gained a wide acceptance among researchers [11]. Several investigators have obtained both qualitative and quantitative results from thermal gravimetric analysis (TGA) to predict the dynamics of liquid fuel combustion. Kok applied TGA to characterize the crude oil in the temperature range of 20–900 °C [11]. Murugan used TGA to examine the thermal behavior of fosterton oil mixed with reservoir sand [12]. Arrhenius model was used to obtain the kinetic parameters such as activation energy from the TGA data. Ambalae used TGA to obtained information on the pyrolysis and combustion behavior of both crude oil and its asphaltenes [13].

To advance the knowledge and understanding of biodiesel combustion, this work applied TGA to predict the combustion dynamics of the biodiesel produced by supercritical methanol transesterification reaction. The combustion dynamics and properties such as the activation energy and the ignition temperature of the biodiesel produced under different supercritical methanol transesterification conditions (temperature, pressure, time, and molar ratio of methanol to oil) were obtained from the TG/DTG curves. When the transesterification reaction temperature increased from 255 to 300 °C, the combustion activation energy decreased from 143.6 to 84.2 kJ/mol which led to an improved combustion property.

2. Materials and methods

2.1. Experimental materials

The rapeseed oil (density = 0.91 kg/L, heating value = 36 MJ/kg, molecular weight (MW) = 270.6), soybean oil (density = 0.92 kg/L, heating value = 38 MJ/kg, MW = 290) and palm oil (density = 0.94 kg/L, heating value = 40 MJ/kg, MW = 270) used in the experiments were purchased from Jinlongyu Company, China. The standard samples of various methyl esters such as palmitic acid (density = 0.85 kg/L, heating

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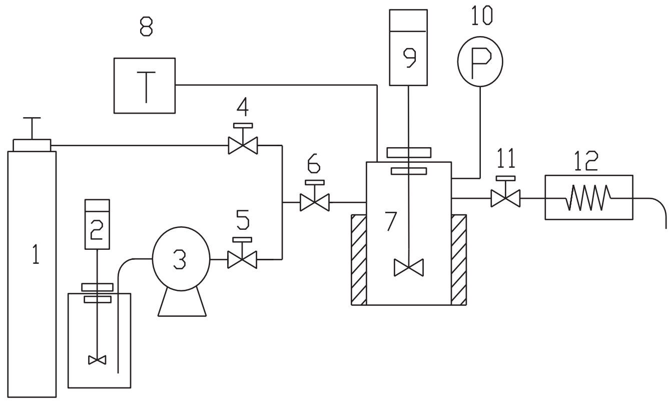

Fig. 1. Experimental system for biodiesel production by supercritical methanol transesterification. 1. N_2 cylinder, 2. magnetic stirrer, 3. high-pressure liquid pump, 4. gas control valve, 5. liquid control valve, 6. check valve, 7. supercritical reactor, 8. temperature controller, 9. mechanical stirrer, 10. pressure meter, 11. sampling valve, 12. sample cooler.

value = 41 MJ/kg, MW = 270.5), stearic acid (density = 0.85 kg/L, heating value = 42 MJ/kg, MW = 298.51), oleic acid (density = 0.90 kg/L, heating value = 41 MJ/kg, MW = 296), linoleic acid (density = 0.90 kg/L, heating value = 40 MJ/kg, MW = 294.5), and linolenic acid (density = 0.91 kg/L, heating value = 40 MJ/kg, MW = 292.46) were obtained from Fluka Company, USA. Methanol (density = 0.80 kg/L, MW = 32) and n-Heptane (density = 0.68 kg/L, MW = 86) were used as solvents. Isopropyl myristate (density = 0.86 kg/L, heating value = 41 MJ/kg, MW = 270) was used as an internal standard sample.

2.2. Supercritical methanol transesterification of plant oils

The schematic diagram of batch-type reactor system for the transesterification of plant oil using supercritical methanol as solvent is shown in Fig. 1. The system comprises a reactor (Weihai autocontrol WHFS-1 series), a high pressure liquid pump (Hangzhou zhijiang petrochemical plunger pump 2 J-W series), and a temperature controller. The maximum tolerable temperature and pressure of the system were 400 °C and 25 MPa respectively.

The average molecular weight of rapeseed, soybean and palm oils were measured by chemical titration. The plant oil and methanol with different molar ratios (29:1, 36:1, and 42:1) were fully mixed before entering the reactor at set temperatures (255, 275, and 300 °C) and pressures (9, 11, and 17 MPa). The reactants were stirred (160 r/min) in the reactor during the reaction. The liquid samples were extracted during or after the reaction. Biodiesel was separated by distillation and methanol was recovered after the reaction.

2.3. FAME compositions in biodiesel

The biodiesel compositions were analyzed with a Kexiao 1690 gas chromatograph. Isopropyl myritate was used as the internal standard for quantification. The injection and detection temperatures were 275 °C. The temperature program was set as follows: the initial temperature of 150 °C was hold for 3 min, then increased to 230 °C (5 °C/min), and hold again for 3 min.

2.4. Thermal gravimetric analysis of biodiesel

The combustion dynamics and properties of the biodiesel produced under different supercritical methanol transesterification conditions (temperature, pressure, reaction time, and molar ratio of methanol to oil) were identified by thermal analysis. The burning profiles were determined on a thermobalance (Mettler Toledo, TGA/SDTA851). The combustible mass of the biodiesel sample was kept at (20 ± 1) mg. In an air flow of 50 ml/min, the furnace temperature was increased from 40 to 720 °C at three heating rates (20, 40,and 80 °C/min). The weight of sample was monitored continuously as a function of temperature. The thermal gravimetric (TG) or DTG curves were obtained.

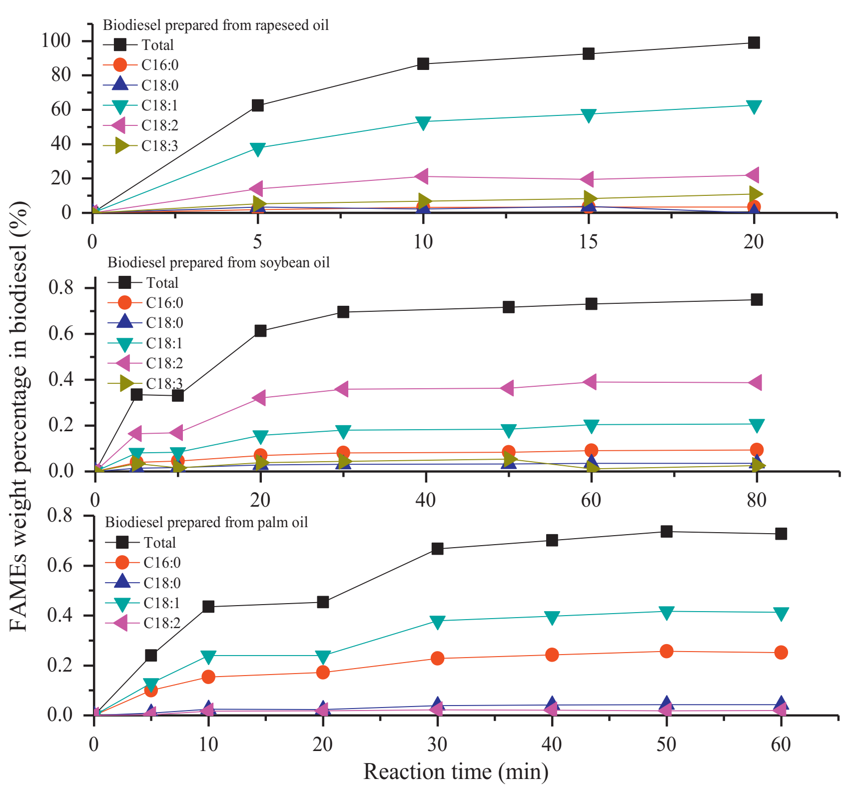

Fig. 2. FAME compositions in biodiesels prepared from rapeseed oil, soybean oil, palm oil.