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Study on volatility and flash point of the pseudo binary mixtures of sunflower-based biodiesel + methylcyclohexane

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ABSTRACT

The transesterification of sunflower seed oil was carried out in supercritical ethanol without using any catalyst to produce biodiesel. In the present work, methylcyclohexane was added to enhance the vapor pressure of biodiesel. The vapor pressures of mixtures of biodiesel + methylcyclohexane as a function of temperature were measured by comparative ebulliometry with an inclined ebulliometer. The vapor pressures versus composition at different temperatures were obtained. Experimental data of vapor pressures and equilibrium temperatures were correlated by the Antoine equation. A mathematical model was used to predict the flash point of the pseudo binary mixtures. With the regular solution theory, the predictive flash point displays agreement with the experimental data obtained by closed cup test.

1. Introduction

Because of limited resources of fossil oil and environmental concerns there has been a focus on biodiesel as a fuel [1–3]. Biodiesel has been defined as the mono-alkyl esters of long-chain fatty acids derived from renewable feedstock, and is synthesized by transesterification of triglycerides in vegetable oils with short chain alcohols. Biodiesel comes from renewable sources and does not contribute to new carbon dioxide emission. Additionally, it is biodegradable and nontoxic, has low emission profiles and so is environmentally beneficial [4–6]. Due to the great molecular similarities of biodiesel to paraffinic diesel fuel compounds, this alternative fuel has a chance of fulfilling the demands that diesel engine makes of its fuel. Essentially, no engine modifications are required to substitute biodiesel for diesel fuel that can maintain the engine performance. Ethyl esters of vegetable oils have outstanding advantages because ethanol and vegetable oils are derived from agricultural products and are renewable and biologically less objectionable in the environment. In the present work, the ethyl ester of sunflower seed oil, rich in China, was prepared as biodiesel test sample.

Vapor pressure is one of the most essential thermodynamic properties that reflect the volatility, stability and safety. The values of the vapor pressure and flash point involve the operability of storage, ignition and combustion of a fuel. The lower volatility of biodiesel fuels is reportedly responsible for ignition delay, poorer atomization and combustion problems [7]. Methylcyclohexane is one kind of cycloparaffins (one major component in fossil fuel) which has outstanding volatility, and it is usually studied as "model" fuel [8]. In this paper, the biodiesel and methylcyclohexane are selected as alternative paraffinic and cycloparaffin sample respectively. The vapor pressure of mixtures of biodiesel and methylcyclohexane as a function of temperature were measured by the comparative ebulliometry using an inclined ebulliometer [9,10]. The vapor pressures versus composition at different temperatures were obtained. A mathematical model was used to predict the flash point of mixtures of biodiesel + methylcyclohexane [11,12]. With the regular solution theory, the predictive flash point displays agreement with the experimental data obtained by closed cup test. In industrial application, these results are useful for choosing optimum mixed ratio of biodiesel and cycloparaffin as alternative fuel, and the prediction data of flash point are necessary for avoiding hazard in the process of production and storage of biodiesel.

2. Experimental

2.1. Materials and characterization

The sunflower seed oil used in this study was supplied from Inner Mongolia, and the fundamental physical properties were listed in Table 1. Methylcyclohexane with purity better than 98% as claimed by the supplier, Sinopharm Chemical Reagent Company, was used with further distillation. Absolute ethanol with purity bet-

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Table 1
The fundamental physical properties of sunflower seed oil.

Substance	Viscosity at 40 °C/mm^2 s^{-1}	Density at 15.6 °C/kg m^{-3}	Average molecular weight/g mol^{-1}	Refractive index at 20 °C
Sunflower seed oil	29.21	932.45	863	1.4751

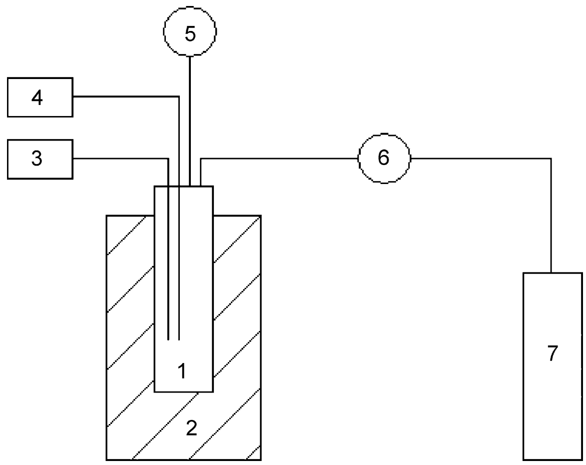


Fig. 1. Supercritical ethanol transesterification system. 1, Autoclave; 2, Electrical furnace; 3, Raw material entrance valve; 4, Temperature control monitor; 5, Pressure gauge; 6, Product exit valve; 7, Product collecting vessel.

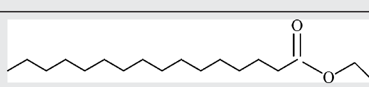
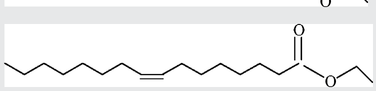
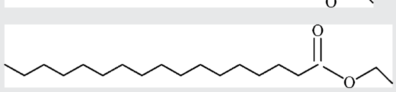
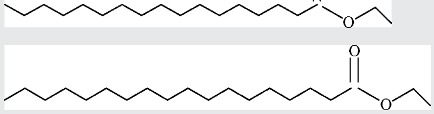
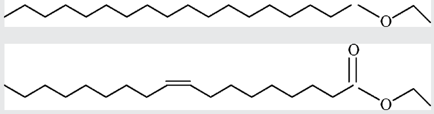
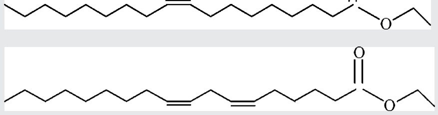
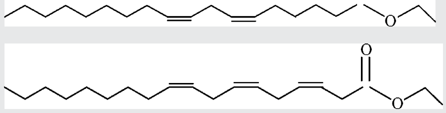
ter than 99.7% was also supplied from Sinopharm Chemical Reagent Company.

2.2. Supercritical ethanol transesterification method

The supercritical ethanol transesterification system employed in this work is shown in Fig. 1. All the runs of transesterification were performed in a 200 ml cylindrical autoclave made of stainless steel in which the pressure and temperature were monitored in real time, covering up to 33 MPa and 823 K, respectively. In a typical run, the autoclave was charged with a given amount of sunflower seed oil and liquid ethanol with a mole ratio of 1:20, the larger amount of ethanol was used to shift the reaction equilibrium to the right side and produce more ethyl esters, the proposed product [13–16], which was rectified and then treated with silicon dioxide to remove impurities. The purity of the sunflower-based biodiesel by this method can reach better than 99%. In this paper, the reaction pressure and temperature are 12 MPa and 573 K, and the reaction time is controlled at 30 min.

The predominant composition range of biodiesel was analyzed by a Hewlett Packard 6890/5973 gas chromatography–mass spectrometry. The C_{16}–C_{18} fatty acid ethyl esters are the major components listed in Table 2. The esters were extensively characterized according to ASTM specifications for biodiesel, the results compared with canola oil methyl ester were listed in Table 3 [17–19].

Table 2
The composition of biodiesel.

Fatty acid ethyl ester	Structure	Mass fraction
16:0		0.0992
16:1		0.1252
17:0		0.0110
18:0		0.0188
18:1		0.3810
18:2		0.3053
18:3		0.0595

2.3. Ebulliometric method

The apparatus was designed and constructed on the basis of the principle of the quasi-static method, which consisted of inclined ebulliometers with pump-like stirrers, magnetic stirring systems, a pressure control and measurement system, and a temperature control and measurement system. The structure and operation of the apparatus were described in detail previously [9,20]. Mixtures of biodiesel + methylcyclohexane were prepared gravimetrically using an analytical balance with an uncertainty of ±0.1 mg.

The quasi-static method is based on that the feed composition instead of the equilibrium mole fraction of liquid phase is reasonable under appropriate circumstances. The equation of the composition analysis for the ebulliometer is [20]

$$\frac{x_0 - x}{x} = \frac{(R + \alpha)(K - 1)}{1 + R} \quad (1)$$

where R is the reflux ratio under steady state, x_0 is the feed composition, x is liquid mole fraction, a is the liquid holdup factor, $\alpha = (N_g - RN_1)/N$, N_g and N_1 are the number of moles retained in the vapor and liquid phases, respectively, N is the total number of moles of the system, K is the phase equilibrium constant ($K = y/x$), y is vapor mole fraction. When R approaches zero, $\alpha = N_g/N$, the equation is equivalent to that of the static method

$$\frac{x_0 - x}{x} = (K - 1)\alpha \quad (2)$$

The inclined ebulliometer can reduce the effect of height of liquid and the stirring function is useful for circulation of the solution.

Table 3
The properties of sunflower-based biodiesel and Canola oil methyl ester.

Property	This work	Canola oil methyl ester	ASTM standard
Water/vol.%	0.04	0.048	0.05
Boiling point/K	608.26	609.15	588.15–623.15
Flash point/K	418.15	380.15	373.15–443.15
Free glycerin/wt.%	0.13	0.01	0.20
Total glycerin/wt.%	0.18	0.12	0.24
Mono-glyceride/wt.%	1.08	0.90	–
Di-glyceride/wt.%	2.09	1.70	–
Tri-glyceride/wt.%	0.00	0.00	–
Density at 15.6 °C/g cm^{-3}	0.885	0.883	0.87–0.89
Viscosity at 40 °C/mm^2 s^{-1}	4.97	4.34	1.9–6.0