Journal of Hazardous Materials 167 (2009) 625–629

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Study on volatility and flash point of the pseudo-binary mixtures of sunflowerseed-based biodiesel + ethanol

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ARTICLE INFO

Article history:
Received 4 October 2008
Received in revised form 30 December 2008
Accepted 7 January 2009
Available online 16 January 2009

Keywords:
Biodiesel
Transesterification
Vapor pressure
Ebulliometer
Flash point

ABSTRACT

Volatility and flash point for the pseudo-binary mixtures of sunflowerseed-based biodiesel + ethanol were measured over the entire composition range. The biodiesel was prepared by the transesterification of sunflowerseed oil in supercritical methanol without using any catalyst. The vapor pressures of mixtures of biodiesel + ethanol as a function of temperature were measured by comparative ebulliometry with an inclined ebulliometer. The vapor pressures versus composition at different temperatures and temperatures versus composition at different pressures were obtained from Antoine correlations. It is found that ethanol can adjust effectively the volatility and flash point of the biodiesel. The correlation of the flash points with the vapor pressure data for the pseudo-binary mixtures of biodiesel + ethanol displays agreement with the experimental data obtained by closed cup test.

1. Introduction

Biodiesel is a well-known alternative, renewable fuel which has been defined as the mono-alkyl esters of long-chain fatty acids, and is synthesized by transesterification of triglycerides in renewable feedstock with short chain alcohols [1–3]. Biodiesel comes from renewable sources and does not contribute to new carbon dioxide emission when compared with the conventional fossil-based diesel fuel. Additionally, it is biodegradable and nontoxic, has low emission profiles and so is environmentally beneficial [4–6]. Methyl esters of vegetable oils have outstanding physical and chemical advantages and low cost, so the methyl ester of sunflowerseed oil, rich in China, was prepared as biodiesel test sample in the present work.

Vapor pressure is one of the most essential thermodynamic properties that reflect the volatility, stability and safety of fuels. The flash point and vapor pressure involve the operability of ignition, combustion and storage of a fuel. To ensure the operation safety, the knowledge of volatility and flash point data for flammable liquids are very important. The lower volatility of biodiesel fuel is reportedly responsible for ignition delay, poorer atomization and combustion problems [7,8]. It is clearly that study on the vapor pressure for biodiesel system is valuable both to laboratory research and practical application. In the present work, ethanol was added to enhance the vapor pressure of biodiesel, since it has outstanding volatility and is commonly used as a blend with fuel [9,10]. The vapor pressure of mixtures of biodiesel + ethanol as a function of temperature was measured on an inclined ebulliometer. The vapor pressures versus composition at different temperatures and temperatures versus composition at different pressures were obtained from the Antoine correlations. A mathematical model was used to fit the flash point of biodiesel + ethanol system [11,12]. The result displays agreement with the experimental data obtained by closed cup test. The present work may be very useful to the development of environmentally friendly alternative fuels.

2. Experimental

2.1. Materials and characterization

The sunflowerseed oil used in this study was supplied from Inner Mongolia. Methanol with purity better than 99.5% and absolute ethanol with purity better than 99.7% was supplied by Sinopharm Chemical Reagent Company. The reagents were used without further purification.

2.2. Supercritical methanol transesterification method

The supercritical methanol reaction system employed in this work is shown in Fig. 1. The transesterification were performed in a 200-mL cylindrical autoclave made of stainless steel, equipped with a magnetic stirrer and condenser. In a typical run, the autoclave was charged with a given amount of methanol and sunflowerseed oil with a mole ratio of 20:1, the larger amount of methanol was

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0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2009.01.015

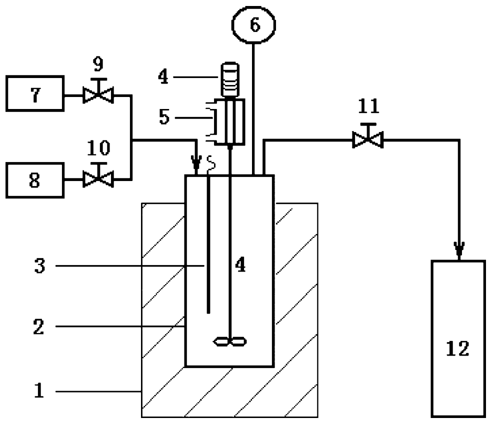

Fig. 1. Supercritical methanol transesterification system. 1, Electrical furnace; 2, autoclave; 3, temperature control monitor; 4, magnetic stirrer; 5, condenser; 6, pressure gauge; 7, sunflowerseed oil; 8, methanol; 9, 10, raw material entrance valve; 11, product exit valve; 12, product collecting vessel.

used to shift the reaction equilibrium to the right side and produce more methyl esters, the proposed product, which was rectified and then treated with silicon dioxide to remove impurities. In the experiments, the reaction temperature and pressure are 573 K and 18 MPa, and the reaction time is controlled at 30 min. The esters were extensively characterized for their properties, and it meets ASTM D6751 specifications for biodiesel, the value of molecular weight for the methyl ester is 288.6 g mol^{-1}, other detail data compared with canola oil methyl ester were listed in Table 1 [13–15].

2.3. Ebulliometric method

The apparatus was designed and constructed on the basis of the principle of the quasi-static method, which consists of a temperature control and measurement system, a pressure control and measurement system, inclined ebulliometers with pump-like stirrers, magnetic stirring systems [16]. The inclined ebulliometer can reduce the effect of height of liquid and the stirring function is useful for circulation of the solution. As a result, the reflux ratio and liquid holdup factor can be reduced. The temperatures inside the two ebulliometers were measured with two standard platinum resistance thermometers connected to Keithley 195A digital multimeters with an uncertainty of ±0.01 K. Vapor pressures at various temperatures were measured over the equilibrium pressure range from about 13.74 kPa to 100.79 kPa, the uncertainty of the calculated pressure was ±0.06 kPa. Mixtures of biodiesel + ethanol were prepared gravimetrically using an analytical balance with an uncertainty of ±0.1 mg.

The boiling points of a fuel sample and ethanol (a reference material) in two separate ebulliometers were measured under the same pressure, which could avoid directly measuring the equilibrium pressure because the pressure could be calculated from the well-known pressure–temperature behavior of ethanol.

Table 1
The properties of sunflowerseed-based biodiesel compared with Canola oil methyl ester.

Property	This work	Canola oil methyl ester	ASTM standard D 6751
Water (vol.%)	0.03	0.048	0.05
Boiling point (K)	608.76	609.15	588.15–623.15
Flash point (K)	412.15	380.15	373.15–443.15
Free glycerin (wt.%)	0.09	0.01	0.20
Total glycerin (wt.%)	0.15	0.12	0.24
Monoglycerides (wt.%)	0.79	0.90	-
Diglycerides (wt.%)	1.68	1.70	-
Triglycerides (wt.%)	0.00	0.00	-
Density at 15.6 °C (g cm^{-3})	0.879	0.883	0.87–0.89
Viscosity at 40 °C ($mm^2\ s^{-1}$)	4.22	4.34	1.9–6.0
Mass fraction of methyl ester (%)			
16:0	9.92	4.23	–
16:1	12.52	0.26	–
17:0	1.10	0.00	–
18:0	1.88	1.89	–
18:1	38.10	61.33	–
18:2	30.53	19.09	–
18:3	5.95	8.71	–

Table 2
Bubble-point vapor pressure data for biodiesel (1) + ethanol (2) systems.

$w_2 = 1.0000$		$w_2 = 0.7992$		$w_2 = 0.6002$		$w_2 = 0.4007$	
T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
320.04	25.47	310.49	15.14	310.29	14.75	313.51	17.07
323.40	30.01	316.29	20.58	317.05	21.00	318.54	22.07
326.87	35.47	321.16	26.32	321.30	26.00	323.33	27.96
329.26	39.61	324.80	31.45	325.14	31.35	327.00	33.27
331.60	44.14	328.33	37.22	328.73	37.14	330.28	38.82
333.33	47.74	331.02	42.17	331.64	42.50	332.90	43.68
335.28	52.14	333.76	47.79	333.64	46.47	335.50	49.00
337.36	57.20	336.06	52.97	336.23	52.22	337.84	54.31
339.35	62.27	338.27	58.37	338.29	57.16	340.20	60.14
345.26	80.00	340.21	63.55	340.38	62.54	341.98	64.79
346.66	84.93	342.19	69.19	342.27	67.80	343.92	70.34
348.38	91.07	344.04	74.78	344.13	73.34	345.75	75.88
350.82	100.40	345.77	80.47	345.77	78.59	347.60	81.83
		346.82	83.98	348.03	86.21	349.64	88.90
		348.21	88.96	349.96	93.31	351.06	93.98
		351.23	100.45	351.75	100.22	352.77	100.47

$w_2 = 0.2994$		$w_2 = 0.2008$		$w_2 = 0.1013$		$w_2 = 0.0799$	
T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
311.34	14.87	313.82	16.29	315.77	15.88	317.37	16.14
316.97	19.88	318.87	21.02	321.36	20.92	323.47	21.62
322.30	25.93	324.19	27.18	326.06	25.99	328.38	27.06
326.42	31.55	327.99	32.47	331.05	32.23	332.10	31.82
330.14	37.38	331.18	37.47	334.29	36.88	335.76	37.11
333.04	42.61	334.44	43.23	337.61	42.56	338.97	42.20
335.57	47.68	337.34	49.00	340.40	47.80	341.92	47.59
338.26	53.58	339.70	54.17	343.12	53.14	344.69	53.11
340.50	58.99	341.73	58.98	345.35	58.06	347.45	58.66
342.57	64.32	344.08	64.95	347.83	63.95	349.64	63.87
344.40	69.35	345.81	69.69	349.95	69.43	351.66	68.91
346.16	74.57	347.65	74.97	354.11	80.80	353.91	74.60
347.89	79.91	349.62	80.91	356.23	86.95	356.09	80.30
350.25	87.77	351.57	87.37	358.35	93.72	357.94	85.78
351.91	93.71	353.45	93.80	360.21	100.54	360.20	92.36
353.76	100.62	355.36	100.79			362.54	100.30

$w_2 = 0.0600$		$w_2 = 0.0402$		$w_2 = 0.0205$		$w_2 = 0.0000$	
T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
317.72	14.50	325.84	15.77	334.90	13.74	396.96	25.98
323.54	19.30	331.10	20.55	344.64	19.24	412.13	30.36
328.68	24.43	336.12	25.61	350.68	23.77	432.56	35.41
334.03	30.68	340.88	30.98	355.22	28.72	443.16	40.23
337.34	35.24	344.84	36.45	361.46	33.90	458.24	44.45
340.66	40.60	348.91	42.21	365.92	38.94	469.87	48.78
343.74	45.55	352.16	47.14	370.25	43.77	483.76	53.63
346.24	50.25	355.53	52.99	373.19	48.71	495.81	57.40
349.14	55.65	358.53	58.49	377.79	54.61	510.14	61.65
351.58	60.92	360.57	63.19	382.23	61.45	523.22	66.38
353.95	66.51	363.61	68.83	386.52	68.19	535.56	71.19
356.99	73.64	366.12	74.08	389.90	72.74	545.12	74.48
359.16	79.50	368.17	79.20	394.01	79.78	557.78	79.14
361.35	85.13	370.55	84.04	399.68	92.50	565.23	82.95
363.89	92.85	374.37	91.59	403.01	99.54	578.98	87.69
366.14	99.98	377.59	99.69			592.11	93.92
						608.76	100.37

Table 3
Boiling temperatures and Antoine equation constants of ethanol.

Pure chemicals	T_b (K)	Antoine equation constants		
		A	*B*	*C*
Ethanol				
Ref	351.45	16.664	3667.71	46.966
Expt	351.03	16.750	3678.79	47.800

2.4. Flash point measurements

The flash points of pseudo-binary mixtures with different compositions of biodiesel and ethanol were measured on a closed-cup flash point analyzer, SYD-261, manufactured by Changji Instrument Co., Ltd. (China). This apparatus is operated according to the Chinese standard test method, GB/T 261, in reference to ASTM D93 test method. The flash point analyzer incorporates control devices to adjust the heating rate of 1–2 °C/min for the test sample, the test interval is 0.5 °C, and the uncertainty of this method was ±1 °C.

3. Results and discussion

3.1. Vapor pressures of the pseudo-binary mixtures

The vapor pressures of the pseudo-binary mixtures of biodiesel and ethanol at various temperatures were measured, over the entire composition range. The experimental data are listed in Table 2, where *T* is the temperature, *p* is the vapor pressure and *w* is the mass fraction. Table 3 gives boiling temperatures and Antoine equation constants (compared with literature data) of ethanol [17].

The Antoine equation is used to correlate the vapor pressure, and the equation is given by

$$\ln p = A - B/(T - C) \tag{1}$$

where *p* is the vapor pressure in kPa, *T* is the equilibrium temperature in K, and *A*, *B*, *C* are constants. This equation can be put into the following form to determine these constants, $\ln p = A - (AC + B)/T + C \ln p/T$, In this form, $\ln p$ is dependent variable, $1/T$ and $\ln p/T$ are the independent variables. The regression method is used to find *A*, *B* and *C* for pseudo-binary systems with experimental data listed in Table 2. The Antoine equation constants of the pseudo-binary mixtures of biodiesel + ethanol are listed in Table 4, together with the errors given by the average relative deviation:

$$ARD = \sum_{i=1}^{n} \frac{\left|(p_{\text{cal}} - p_{\text{exp}})/p_{\text{exp}}\right|_i}{n} \tag{2}$$

where *n* is the number of the experimental datum points.

The low vapor pressure of 'pure' biodiesel can result in ignition delay and combustion problems. The addition of ethanol has a critical effect on the vapor pressure of the biodiesel. The vapor pressure lines of p–w_2 at several temperatures and T–w_2 at several pressures are shown in Figs. 2 and 3, along with the departures of the equilibrium pressure or temperature from the ideal behavior. Clearly, the mixtures of biodiesel + ethanol have large positive deviations on the values of pressures from Raoult's law. The pressure

Table 4
Correlation results of vapor pressure by Antoine equation for biodiesel (1) + ethanol (2) systems.

w_2 (%)	Datum points	Temperature range (K)	Antoine equation coefficients			ARD (%)
			A	$B \times 10^{-3}$	*C*	
100.00	13	320.04–351.82	16.750	3.679	47.800	0.06
79.91	16	310.49–351.23	16.377	3.461	57.065	0.02
60.02	16	310.29–352.75	16.568	3.593	51.347	0.04
40.07	16	313.51–352.77	16.097	3.372	59.146	0.04
29.94	16	311.34–353.76	15.731	3.215	64.641	0.05
20.08	16	313.82–355.36	15.228	3.009	71.869	0.05
10.13	15	315.77–360.21	14.286	2.692	82.049	0.23
7.99	16	317.37–362.54	12.848	2.053	113.401	0.13
6.00	16	317.72–366.14	12.071	1.763	130.034	0.22
4.02	16	325.84–377.59	8.876	0.730	206.578	0.61
2.05	15	334.90–403.01	9.852	1.304	155.055	1.14
0.00	17	396.96–608.76	6.731	1.168	60.616	0.85

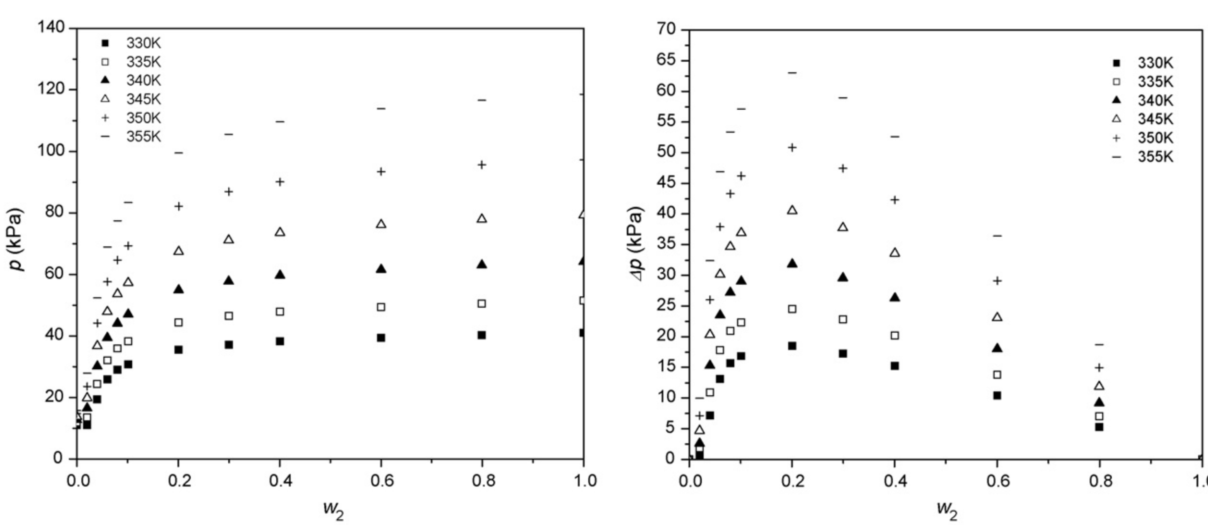

Fig. 2. Vapor pressure versus composition at several temperatures (left) and departures of equilibrium pressure from the ideal behavior (right).

Table 5
The flash point results for biodiesel (1) + ethanol (2) systems.

w_2 (%)	T_{fp}^{expt} (K)	$T_{fp}^{correlation}$ (K)	l_{ij}	V_1 (mL mol^{-1})	V_2 (mL mol^{-1})
100.00	285.15	285.15	~	~	~
79.91	285.15	285.57	−0.110	326.3	58.9
60.02	285.65	286.21	−0.110	326.5	59.0
40.07	286.15	287.23	−0.108	326.8	59.1
29.94	286.65	288.04	−0.106	327.7	59.2
20.08	288.65	290.47	−0.108	328.1	59.3
10.13	294.15	294.43	−0.102	328.4	59.4
7.99	295.15	296.73	−0.102	328.6	59.4
6.00	298.65	299.95	−0.102	328.9	59.5
4.02	303.15	305.09	−0.102	329.3	59.6
2.05	312.65	314.87	−0.100	329.8	59.7
0.00	412.15	412.15	~	~	~

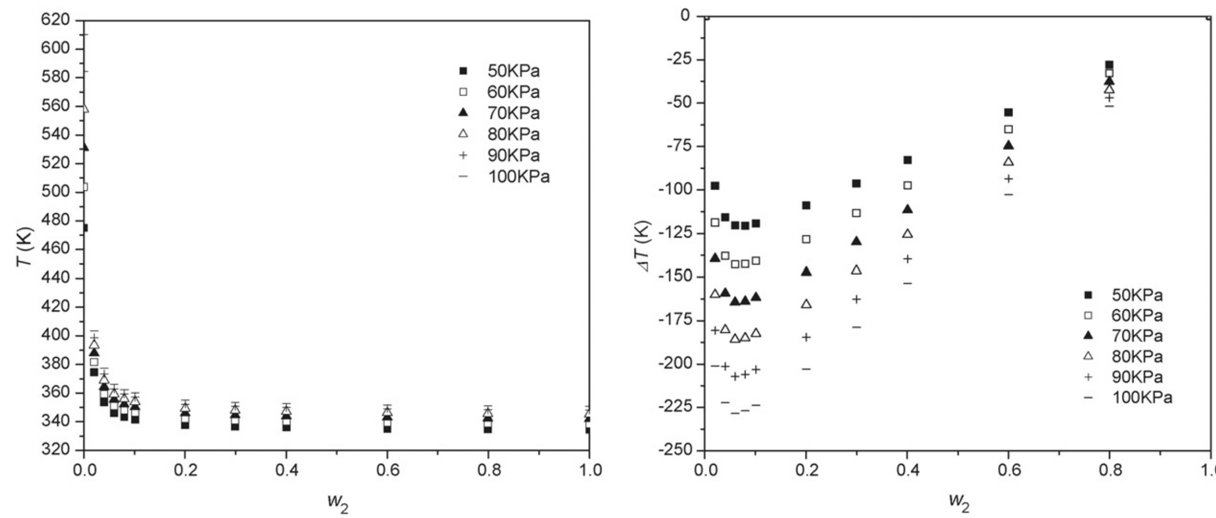

Fig. 3. Bubble-point temperature against composition at several pressures (left) and departures of equilibrium temperature from the ideal behavior (right).

departure increases with increasing temperature and the maximum pressure departure Δp among the six temperatures is about 63.02 kPa at 355.00 K, and the maximum temperature departure at 100 kPa is about −228.4 K. These results may be very useful to the development of environmentally friendly alternative fuels.

3.2. Correlation of flash points from vapor pressure data

The flash point of a substance is that temperature at which its vapor pressure is sufficient to form a combustible mixture with air. The specific flash point value is generally measured by a flash point analyzer with closed-cup test methods. In the present work, a mathematical model was used to correlate the flash point of mixtures of biodiesel + ethanol [11].

$$1 = \sum \frac{p_i x_i \gamma_i}{p_{i,\mathrm{fp}}} = \frac{p_1 x_1 \gamma_1}{p_{1,\mathrm{fp}}} + \frac{p_2 x_2 \gamma_2}{p_{2,\mathrm{fp}}} \tag{3}$$

where p_i is the vapor pressure of each pure species, it varies with temperature according to the Antoine equation, x_i is the liquid mole fraction of a flammable substance i, and γ_i is the activity coefficient in liquid phase. The saturated vapor pressure of pure liquid i at flash point, $p_{i,\mathrm{fp}}$, can be estimated by substituting its flash point, $T_{i,\mathrm{fp}}$, into the Antoine equation.

The activity coefficient γ_i (i = 1, 2) can be estimated from the regular solution model [18],

$$\ln \gamma_i = \frac{(1-\phi_i)^2[(\delta_i-\delta_j)^2 + 2l_{ij}\delta_i\delta_j]V_i}{RT} \tag{4}$$

$$\delta_i{}^2 = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m},i} - RT}{V_i} \tag{5}$$

$$\phi_i = \frac{x_i V_i}{\sum(x_i V_i)} \tag{6}$$

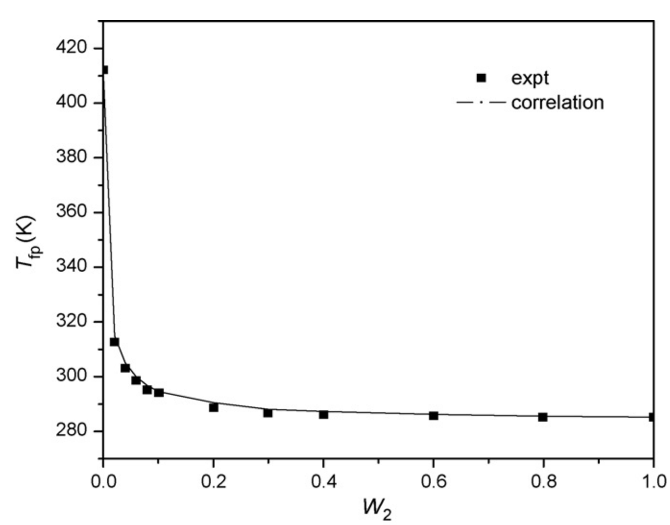

Fig. 4. Comparison of the flash point correlation curves with experimental data for mixture of biodiesel (1) + ethanol (2).

where V_i is the molar volume of species i, l_{ij} is the variable parameter, and its absolute value is small than 1, $\Delta_{vap}H_{m,i}$ is the average initial enthalpy of vaporization, and the average value of biodiesel and ethanol is 61.7 kJ mol^{-1} and 41.6 kJ mol^{-1}, respectively. The flash points of the pseudo-binary system can then be correlated with these equations. The flash points of the mixtures covering the entire composition range of ethanol in biodiesel were tested and listed in Table 5.

The experimental data were plotted against the correlative results in Fig. 4. It can be clearly seen that the correlative values for the flash point simulation based upon regular solution theory display agreement with the experimental data. These results suggest that ethanol can be used to reduce the flash point and improve combustion of biodiesel, but ethanol may also increase the potential hazard of the storage and safety. It is important that appropriate content of ethanol should be controlled to improve combustion and ensure safe storage of the pseudo-binary mixture, which may be used as alternative fuel in the future.

4. Conclusions

- The transesterification of sunflowerseed oil was carried out in supercritical methanol without using any catalyst. Vapor pressures for the pseudo-binary mixtures of biodiesel + ethanol were measured with satisfactory results by comparative ebulliometry. The correlative flash points for the same system were presented against the experimental data.
- The bubble-point lines of equilibrium temperature or vapor pressure versus composition were correlated with the Antoine equation. The phase line indicated that the pseudo-binary mixtures of biodiesel + ethanol had large positive deviations on the value of pressure and negative deviations on temperature from the ideal behavior.
- The flash points of the mixtures covering the entire composition range of ethanol in biodiesel were tested by closed cup test. The correlation of the flash points with the vapor pressure data for the pseudo-binary system displays agreement with the experimental data. The biodiesel blended with appropriate content of ethanol may be used as alternative fuel in the future.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (20703036) and the Natural Science Foundation of Zhejiang Province (Y407093).

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