International Journal of Latest Engineering Research and Applications (IJLERA) ISSN: 2455-7137

Volume – 09, Issue – 01, January 2024, PP – 95-104

Phase Equilibrium for Washing Step during Biodiesel Production from Vegetable Oil and Animal Fat Mixtures

Jalal Mustafa Hasan[1], Cevdet AKOSMAN[2], Arkan Jasim Hadi[3]

[1](Department of Chemical Engineering, Soran University, Kurdistan, Iraq)

[2](Department of Chemical Engineering, Firat University, Elazig, Turkey)

[3](Department of Chemical Engineering, Soran University, Kurdistan, Iraq)

Abstract: The ternary liquid-liquid equilibrium data of the biodiesel-methanol-water system involved in biodiesel production provides important tools for the development and design of the equipment. In this investigation, the effects of temperature and amount of beef tallow in corn oil on ternary phase equilibrium data for the system of biodiesel-methanol-water were experimentally determined.

The biodiesel samples (0%, 10%, and 20% v/v beef tallow) were produced using the mixtures of corn oil and beef tallow with methanol (methanol to oil: 1/6, n/n) using potassium hydroxide of %1 (w/w) at 60 °C. The solubility data were determined using the cloud point titration method for biodiesel-methanol-water systems at temperatures of 25 °C, 35 °C,45 °C, and at atmospheric pressure. It was found that the effect of temperature on the solubility curves of the ternary liquid-liquid system of biodiesel-methanol-water was negligible at low methanol compositions but had little effect at high methanol compositions. The ternary liquid-liquid solubility curves of biodiesel-methanol-water systems did not significantly change with increasing the beef tallow concentration in corn oil.

Keywords: Biodiesel, Beef Tallow, Corn Oil, Phase Equilibrium.

1. INTRODUCTION

Due to the trajectory of human civilization development in the last few centuries, fossil fuels have become one of the most essential resources in the world to sustain the existence of human societies. However, this dependency on fossil fuels carries a risk with it as fossil fuels are not renewable, but take millions of years to form under very peculiar conditions. Furthermore, the use of such fuel in internal combustion engines causes various environmental problems due to carbon dioxide gases released into the atmosphere, which in turn plays a part in increased average ambient temperatures. As the problems associated with fossil fuel consumption became clear, renewable energy resources became a topic of interest as they were seen as good alternative candidates for meeting the ever-increasing energy demands of human societies. Amongst these, biodiesels were of particular interest worldwide [1,2]. The most widely recognized approach to producing biodiesel is the transesterification process, which refers to a catalyzed chemical reaction including vegetable oil and alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol [3]. The production of biodiesel cannot be practiced using vegetable oils alone because of their high substance of free unsaturated fats. Biodiesel can be produced using different sources, for example, blends of vegetable oils or mixtures of vegetable oils and animal fats. Biodiesel acquired from blends of multi-feed stocks can have better physical properties. Likewise, it could be monetarily helpful to form biodiesel by using cheap feedstock with expensive feedstock [4].

The investigation of LLE for the water-washing step in methyl biodiesel production is significant because this progression decides the last biodiesel purity as indicated by the biodiesel standard quality necessities and takes into consideration assessing conceivable ester losses to the water-rich phase. Furthermore, information about the LLE of biodiesel-water-alcohol systems is important for optimizing this purification step, which can decrease the large quantity of water used in this phase [5]. Liquid-liquid phase equilibrium studies of ternary systems are necessary for both industrial and theoretical applications. To establish optimum conditions for the separation and purification of biodiesel, knowledge of the exact phase equilibrium of the components included in the production of biodiesel is crucial. To choose the more effective solvent for the phase separation and purification of biodiesel, it is also necessary to know the phase equilibrium of the components concerned. As far as one could know, ternary liquid-liquid equilibrium data concerning the of production biodiesel from a blend of animal fat and vegetable oil have not been studied too much. Regarding the importance of this knowledge, few experimental data on the LLE behavior of water + alcohol + pure methyl esters, pure ethyl esters, and methyl and ethyl biodiesels are available [6,7,8,9].

Bessa et al., [5] determined LLE for a system containing cottonseed biodiesel-water-methanol and ethanol systems experimentally at various temperatures. Yan et al. [10] investigated the LLE for ternary system palm oil biodiesel-methanol-water at 30 and 40 °C. Basso et al.[11] studied crambe oil biodiesel. Santos et al. [1] studied liquid-liquid phase equilibrium for three component systems biodiesel-water-methanol at temperatures 25, 30, and 40 °C.

LLE solubility data concerning producing biodiesel from a blend of animal fat and vegetable oil have not been studied till now. These data might be important from a thermodynamic perspective to understand the animal fat impact on biodiesel production systems. The purpose of this investigation is to experimentally determine solubility curves for a ternary system of biodiesel from corn oil and beef tallow mixtures, methanol, and water.

2. MATERIALS AND METHODS

2.1. Material Used

Refined and winterized food-grade corn oil was used as vegetable oil while beef tallow served as animal fat. Corn oil was obtained from a local shop and beef tallow was collected in a local butcher shop. Distilled water, anhydrous grade methanol (99.95 % Sigma Aldrich, Louis, MO, USA), AR grade Isopropyl alcohol, toluene Sigma -Aldrich, and AR grade KOH (GIDC Vatwa, Ahmedabad, Gujarat) were used as reagents in the experiments.

2.2. Biodiesel Production Procedure

2.2.1. Potassium Methoxide Solution

To prepare potassium methoxide solution as a catalyst, 10 g of potassium hydroxide (1% by weight of oil mixture) was added to 250 ml of methanol (with a molar ratio of oil to methanol:1/6). The solution was stirred and heated to 60 °C until the potassium hydroxide in the methanol was completely dissolved.

2.2.2. Corn Oil and Beef Tallow Mixture

The beef tallow used in the experiments was subjected to several preparatory steps. Firstly, it was melted at 65°C to eliminate solid particles and water. The resultant liquid was then filtered using a vacuum filter and later dried in a furnace at 105°C. To prepare a mixture of corn oil and beef tallow, 1000 ml of pure corn oil (0% beef tallow), 900 ml of corn oil mixed with 100 ml of beef tallow (10% beef tallow), and 800 ml of corn oil mixed with 200 ml of beef tallow (20% beef tallow) were used.

2.2.3. Biodiesel Production Procedure

The transesterification process is the most common method used for biodiesel production. Transesterification is the reaction of oil or fat with a mono-alkyl alcohol to form glycerol and esters with the aid of a catalyst as shown in "Fig." 2.1.

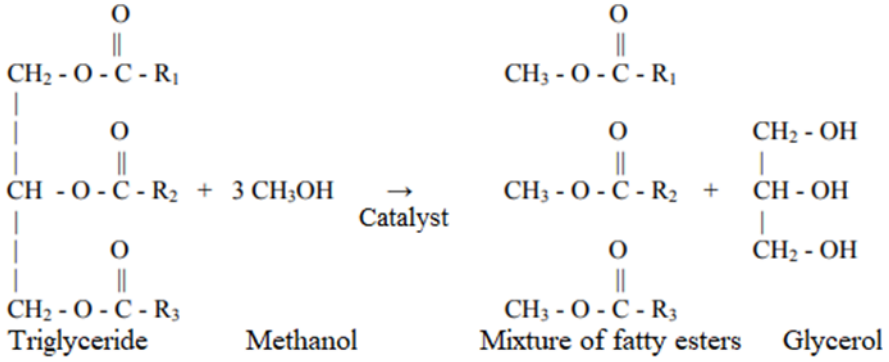

Figure 2. 1. Transesterification of triglycerides with alcohol

Where R1, R2, and R3 are long chains of carbons and hydrogen atoms, sometimes called fatty acid chains. Biodiesel samples were produced using a batch transesterification system, as illustrated in "Fig."2.2. To produce biodiesel samples, an amount of 1000 ml mixture of corn oil and beef tallow was poured into a three-necked flask and heated to a temperature of 60 °C. The prepared solution of potassium methoxide was then combined with the oil and fat mixture. The reaction was stirred at 600 rpm at 60 °C for 2 hr. When the transesterification reaction was completed, it was left to cool down. The mixture was then left for at least 12 hours in a separation funnel to separate the glycerol and biodiesel phases. The light layer (biodiesel) appeared at

the top, while the heavier layer (glycerol) appeared at the bottom. Glycerol was easily separated by draining from the bottom. For biodiesel purification, the unreacted methanol and potassium hydroxide were removed by washing with hot water by 3 or 4 times. Finally, the wet biodiesel was dried to remove water and the remaining excess methanol in a furnace at 105 °C overnight. The same procedure was used for producing biodiesel samples with different concentrations of beef tallow (%0, %10, and %20 v/v) used in this study.

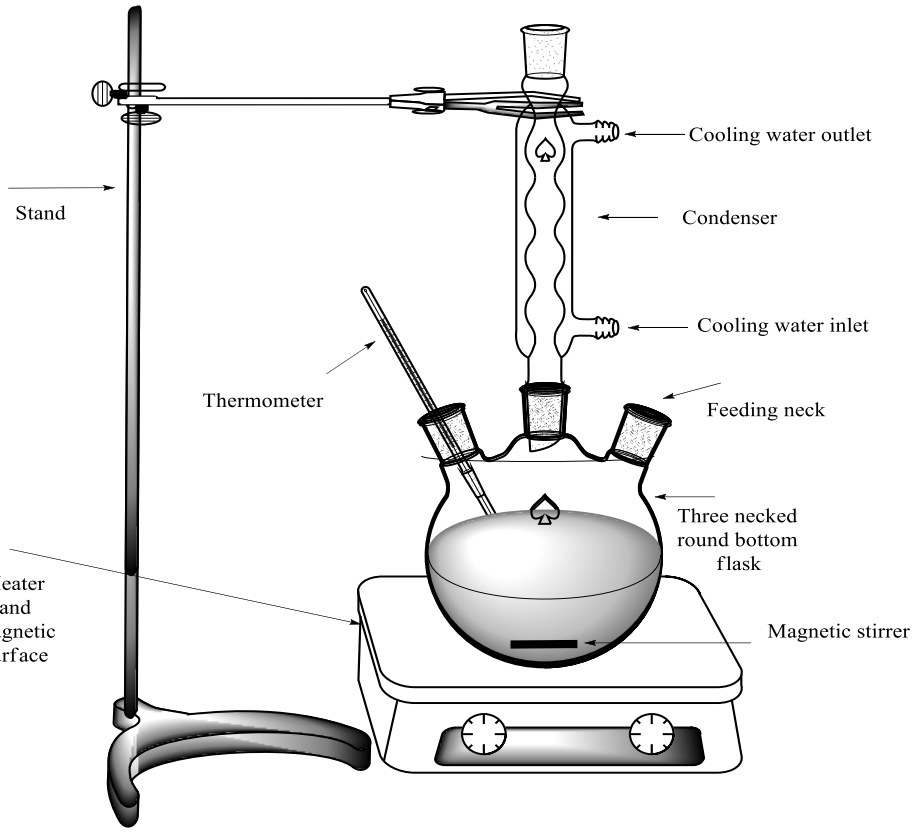

Figure 2. 2. Experimental setup for biodiesel production

2.3. Procedure for Solubility Curve Measurements

The experimental setup for measuring solubility data is shown in "Fig." 2.3. The equilibrium cell was a glass cell of 100 cm^3. A water bath equipped with a temperature controller and a well-isolated furnace capable of keeping the temperature within the precision $\pm$ 0.2 °C were used. The cloud point titration method was used to determine the solubility curves data for biodiesel-water-methanol systems at constant temperature and stirring rate (600 rpm). For the measurements of solubility data for the water-rich phase, binary mixtures of biodiesel-methanol having different compositions were first prepared in the cell and placed in the water bath. Then it was titrated with water until a visible change could be detected in the ternary mixture, from transparent to cloudy aspect. The observed points were considered the saturation point of water in the mixture of biodiesel-methanol-water. Similarly, for the solubility data measurements of the biodiesel-rich phase, binary water-methanol mixtures in different compositions were used for titration with biodiesel until the color of the mixture was changed from clear vision to turbidity. The observed points were the biodiesel saturation point in the biodiesel-water-methanol mixture. The solubility values were calculated the initial weights of components of binary mixtures, and the amounts of biodiesel and water spent in the titrations. Determinations of solubility curves for biodiesel-water-methanol systems were carried out at 25, 35, and 45 °C.

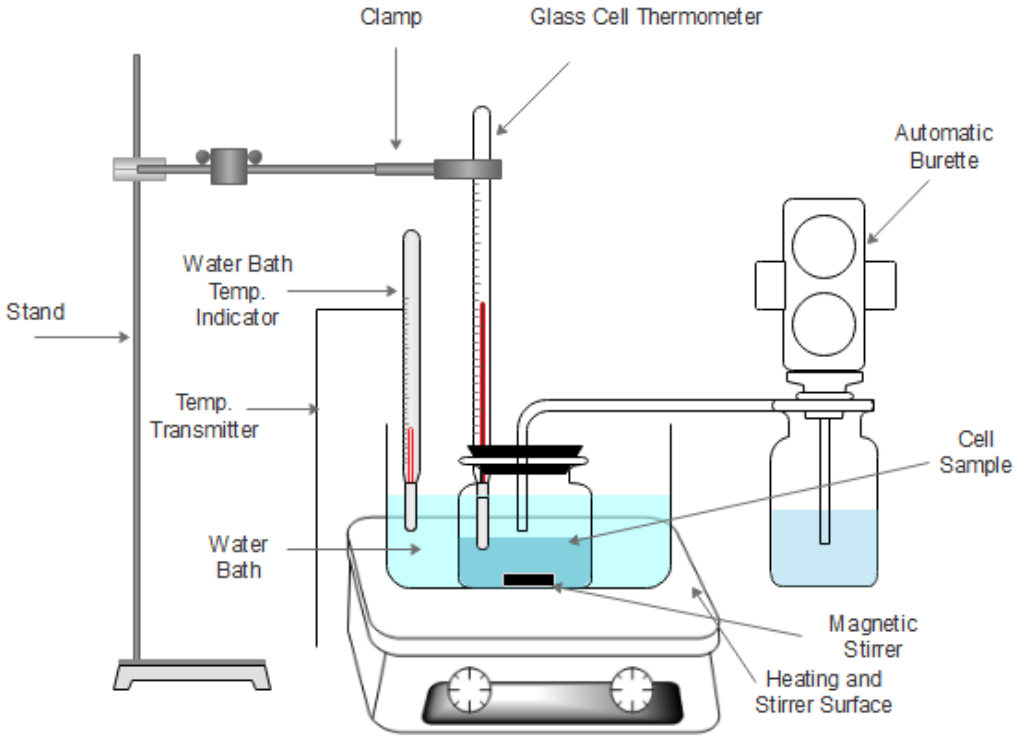

Figure 2. 3. Experimental setup for measurements of solubility data.

2.4. Biodiesel Characterization

The most common physical and chemical biodiesel properties such as density, acid value, viscosity, and composition of fatty acids were determined for each of the feedstocks and methyl ester fatty acids formed. The chromatographic analysis of raw materials and FAME (Fatty Acid Methyl Ester) was carried out by Shimadzu Inc., Kyoto, Japan, using a GC (Gas Chromatography) analyzer (GC- 6C 2010 plus model). The capillary column was 0.25 mm in diameter and 100 m in size within the GC analyzer. All fatty acid methyl ester results are tripled and mean values were included. By using the molecular masses of the triglycerides similar to the methyl esters of fatty acids from biodiesel, molecular masses of biodiesel, corn oil, and beef tallow samples were determined by equation1".

$$M_w = \sum M_{wi} * x_i \quad (1)$$

M_w: is the molecular weight of oil, fat, or biodiesel

M_{wi}: is the molecular weight of individual methyl esters

x_i: is the percentage of fatty acid methyl ester

By using a density bottle with 25 ml in volume, the density of both feedstocks and biodiesel samples was determined. A digital exactness electronic analytical balance was used to measure the weight of the samples, the density measurements were carried out at 25 °C and correlated at 15 °C. The viscosity of biodiesel samples and feedstocks was determined by the viscometer, which is identified as the Canon Fenske Routine (PSL ASTM-IP 75). The measuring samples were heated to 40 °C and the measured viscosities were converted to kinematic viscosity by viscosity conversion table. According to ASTM D664, the FFA (Free Fatty Acid) content and acid number of the feedstocks and all biodiesel samples were determined. 125 ml of solvent was prepared by combining 50 percent isopropyl alcohol with 50 percent toluene by volume, and five grams of the sample were dissolved in the prepared solvent. 2 ml of 1% alcoholic phenolphthalein was added and titrated with 0.1 M KOH solution. The calorimeter oxygen bomb (11350 automatically adiabatic model, Julian Peters Co., Moline, IL, USA) was used to determine the heat values of biodiesel samples and raw materials.

3. RESULT AND DISCUSSION

3.1 The Characteristics of Feedstocks and Biodiesel

Table 3.1 and Table 3.2, show the chemical compositions and some physical properties of corn oil and beef tallow, respectively. From Table 3.1, the chemical compositions of corn oil and beef tallow are within the range found in the literature. Generally, the amount of saturated fatty acids in vegetable oils is lower than the

amount of saturated fatty acids in animal fats. As can be seen in Table 3.1, the saturated fatty acid content of corn oil is 14.55 %, while the saturated value of beef tallow is 41.11 %. As can be observed in Table 3.2, the percentages of FFA (are considerably low for both corn oil and beef tallow, (i.e., 0.197 % and 0.539 %, respectively). Table 3.3 provides measured properties of biodiesel derived from the mixtures of corn oil and beef tallow.

Table 3. 1. Fatty acid methyl ester compositions of oils and fat used in this study (% wt.)

Fatty acid methyl ester	Corn oil	Beef tallow
Myristic acid methyl ester	0	3.77
Palmitic acid methyl ester	11.97	21.73
Palmitoleic acid methyl ester	0	1.66
Stearic acid methyl ester	2.58	15.6
Oleic acid methyl ester	25.12	46.2
Linoleic acid methyl ester	58.72	7.43
Linolenic methyl ester	0.65	0.10
Arachidate methyl ester	0	0.326
Others	0.98	3.51
Saturated	14.55	41.11
Unsaturated	84.52	55.38

Table 3. 2. Measured properties of vegetable oils and animal fat used in this study

Properties	Corn oil	Beef tallow
Molecular weight, g/mol	869	858
Density (at 15 °C), g/cm^3	0.91	0.87
Kinematic viscosity (at 40 °C), cP	33.1	171.8
Acid value, mg KOH/g	0.393	1.041
FFA, %	0.197	0.539
Water content, %	< 0.05	< 0.05
Calorific value, MJ/kg	39.5	40.65

Table 3. 3. Measured properties of biodiesel produced from mixtures of corn oil and beef tallow

Properties	Beef tallow content (v/v, %)		
	0	10	20
Biodiesel conversion	0.97	0.94	0.92
Density at 15 °C, g/cm^3	0.88	0.875	0.871
Viscosity at 40 °C, mm^2/s	4.52	4.69	5.28
Flashpoint, °C	170	163	150
Acid value, mg KOH/g oil	0.447	0.383	0.375
Acid content, %,	0.231	0.185	0.193
Heat value, MJ/kg	38.50	37.25	37.75
Water content, %	< 0.05	< 0.05	< 0.05

3.2. Solubility Data Results

The solubility (binodal) data for ternary mixtures containing biodiesel-methanol-water for each biodiesel sample obtained at temperatures 25, 35, and 45 °C are shown in Tables 3.4-3.6 The corresponding solubility curves for each biodiesel sample are shown in "Fig."3.1-3.3. The Figures show that the solubility curves for the biodiesel-methanol-water system match the typical solubility curves found in the literature [5,12]. From the Figures, it can be seen that the ternary liquid-liquid system of biodiesel-methanol-water under investigation constitutes a pair of partially soluble systems. The main result of these findings is that the solubility of biodiesel and water in each other is too small, while methanol is completely dissolved in both water and biodiesel. This can be attributed to the long chains and low polarities of esters. The presence of double bond (s) in a molecule has a greater effect on the solubility of water in the long-chain esters than the length of the carbon chain does.

The water content in the biodiesel-rich phase is higher than the biodiesel content in the water-rich phase. The solubility of methanol in the water-rich phase was higher than in a biodiesel-rich phase for all biodiesel

samples. It can be observed from the lower part of the solubility curves, that the biodiesel solubility in the water-rich phase and the water solubility in the biodiesel-rich phase are relatively low for the low methanol compositions in the mixtures. At high methanol concentrations, the affinity of methanol in water is higher than that in biodiesel for biodiesel samples studied. Since biodiesel has non-polar molecules while methanol and water have polar molecules, methanol is preferably dissolved in water when these three components are mixed. Similar results were reported in the literature findings [1,5,11]

The effect of temperature on the ternary solubility is insignificant at higher water and biodiesel concentrations, and therefore clear visual differences between phases were not noticed. On the other hand, when the temperature increases, the heterogeneous phase region decreases for the high methanol concentration. When the beef tallow concentration is increased in biodiesel this effect decreases. This may be due to the biodiesel structure produced from various sources such as vegetable oil and animal fats. The type and quantity of methyl esters forming biodiesel depend on the oil and fat sources used. Generally, the saturated fatty acid content in vegetable oil is lower than in animal fats. As can be observed in Table 3.1, the saturated fatty acid value in corn oil was 14.55 % while the saturated fatty acid content in beef tallow was 41.11%. The solubility of methanol decreases slightly as the ratio of saturated fatty acid methyl ester increases in biodiesel at all temperatures studied.

It was also noticed that from the solubility curves, the immiscibility region is higher for temperatures 25 °C, compared to the region obtained for higher temperatures. Hence, it could have resulted that, when the temperature increases, the two phases region decrease, thus, working at room temperature is preferable, and it makes it easier to separate three components. As a result, the low immiscibility between water and biodiesel samples used in this investigation shows that biodiesel purification can be efficiently achieved by a liquid-liquid extraction process using water as a solvent.

Table 3. 4. Solubility data (in mass fraction) for the ternary system of biodiesel (1)-methanol (2)–water (3) at 25°C

0% beef tallow			%10 beef tallow			%20 beef tallow		
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$
99.89	0	0.10002	90.11	9.748	0.140	95.46	4.419	0.114
95.81	4.049	0.140	74.73	24.99	0.268	74.78	25.01	0.200
90.06	9.718	0.220	62.57	37.08	0.340	62.42	37.26	0.313
85.99	13.62	0.380	50.27	49.29	0.428	50.45	49.38	0.160
74.51	24.88	0.600	37.41	62.08	0.500	37.57	62.30	0.120
62.58	37.01	0.400	25.05	74.40	0.542	25.04	74.81	0.141
50.26	49.21	0.520	12.87	86.11	1.005	12.95	86.86	0.182
37.36	62.03	0.600	5.737	92.91	1.352	6.026	92.54	1.42
24.91	74.38	0.702	0.114	1.690	98.19	0.087	12.74	87.17
12.88	86.30	0.806	0.156	12.72	87.11	0.121	37.41	62.46
5.738	92.82	1.432	0.215	24.87	74.90	0.156	50.02	49.82
0.121	1.694	98.18	0.285	37.32	62.39	0.174	62.37	37.45
0.225	12.75	87.01	0.336	49.91	49.74	0.198	75.01	24.78
0.347	24.82	74.82	0.417	62.23	37.34	0.307	85.87	13.81
0.433	37.26	62.29	0.485	74.79	24.71	1.058	91.25	7.683
0.572	49.85	49.57	0.641	87.14	12.21	5.903	92.66	1.428
0.762	61.97	37.26	2.094	90.28	7.624	-	-	-
1.375	74.12	24.49	5.642	92.91	1.449	-	-	-
2.384	85.63	11.98	-	-	-	-	-	-
3.461	89.51	7.026	-	-	-	-	-	-
5.741	92.82	1.431	-	-	-	-	-	-

Table 3. 5. Solubility data (in mass fraction) for the ternary system of biodiesel (1)-methanol (2)–water (3) at 35 °C

0% beef tallow			%10 beef tallow			%20 beef tallow		
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$
98.42	1.298	0.279	92.64	6.993	0.360	94.89	4.968	0.131
95.03	4.587	0.379	74.68	24.79	0.521	74.73	24.89	0.361
92.48	6.995	0.520	62.02	37.29	0.683	62.15	37.39	0.443
87.22	12.09	0.681	37.11	62.03	0.846	37.34	62.10	0.546
74.50	24.73	0.761	24.99	73.99	1.009	25.18	74.22	0.589
61.95	37.23	0.802	12.48	86.21	1.307	12.89	86.42	0.675
37.06	61.74	1.186	7.227	90.87	1.896	7.242	90.97	1.779
25.02	73.74	1.233	0.174	12.45	87.37	0.128	3.374	96.49
12.45	85.86	1.686	0.260	37.60	62.13	0.174	37.64	62.18
7.253	90.77	1.973	0.330	49.67	49.99	0.226	49.73	50.04
0.156	1.055	98.78	0.364	64.14	35.49	0.260	64.21	35.53
0.173	3.318	96.50	0.416	74.87	24.70	0.329	74.95	24.71
0.191	12.45	87.34	0.599	81.12	18.27	0.528	81.05	18.41
0.226	25.09	74.67	1.410	86.18	12.40	1.757	85.94	12.29
0.313	37.58	62.10	2.956	89.95	7.089	2.955	89.93	7.107
0.364	49.65	49.97	7.048	90.94	2.007	7.054	90.96	1.977
0.434	64.11	35.45	-	-	-	-	-	-
0.537	74.83	24.63	-	-	-	-	-	-
0.740	81.00	18.25	-	-	-	-	-	-
2.276	85.64	12.07	-	-	-	-	-	-
3.626	89.31	7.055	-	-	-	-	-	-
7.229	90.79	1.973	-	-	-	-	-	-

Table 3. 6. Solubility data (in mass fraction) for the ternary system of biodiesel (1)-methanol (2)–water (3) at 45 °C

0% beef tallow			%10 beef tallow			%20 beef tallow		
$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$	$100*W_1$	$100*W_2$	$100*W_3$
98.63	1.245	0.120	96.50	3.326	0.167	92.77	7.062	0.160
95.15	4.669	0.179	61.76	37.39	0.846	74.63	24.83	0.521
61.77	37.12	1.100	49.56	49.40	1.030	60.25	39.07	0.663
36.97	61.54	1.484	36.96	61.83	1.202	37.19	62.00	0.806
24.85	73.34	1.808	24.98	73.60	1.411	25.08	73.90	1.012
12.47	85.30	2.222	12.40	85.57	2.026	12.45	86.11	1.428
7.651	90.11	2.233	7.283	90.55	2.165	7.298	90.53	2.165
0.173	1.046	98.77	0.104	3.388	96.49	0.145	3.430	96.42
0.261	12.45	87.28	0.174	49.75	50.04	0.244	51.55	48.19
0.330	37.61	62.05	0.305	64.15	35.49	0.288	64.18	35.52
0.364	49.63	49.99	0.467	74.80	24.65	0.416	74.90	24.67
0.451	64.07	35.47	0.877	80.65	18.33	0.597	80.81	18.58
0.589	74.80	24.60	2.925	84.19	12.44	2.609	85.11	12.27
0.775	80.97	18.25	4.256	88.06	7.045	3.458	89.43	7.102
2.279	85.62	12.09	7.289	89.63	1.985	7.335	90.62	2.040

3.595	89.39	7.00	-	-	-	-	-	-
7.848	90.190	1.961	-	-	-	-	-	-

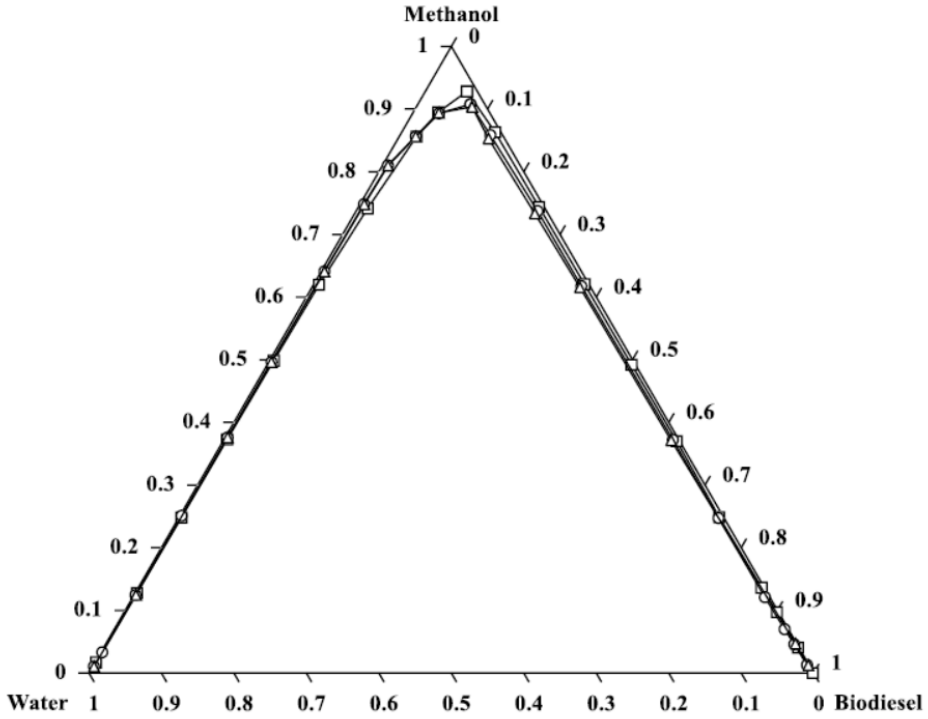

Figure 3. 1. Solubility curves for pure corn oil biodiesel-methanol-water system at different temperatures. (□) 25 °C, (○) 35 °C, (△) 45 °C, in mass fraction

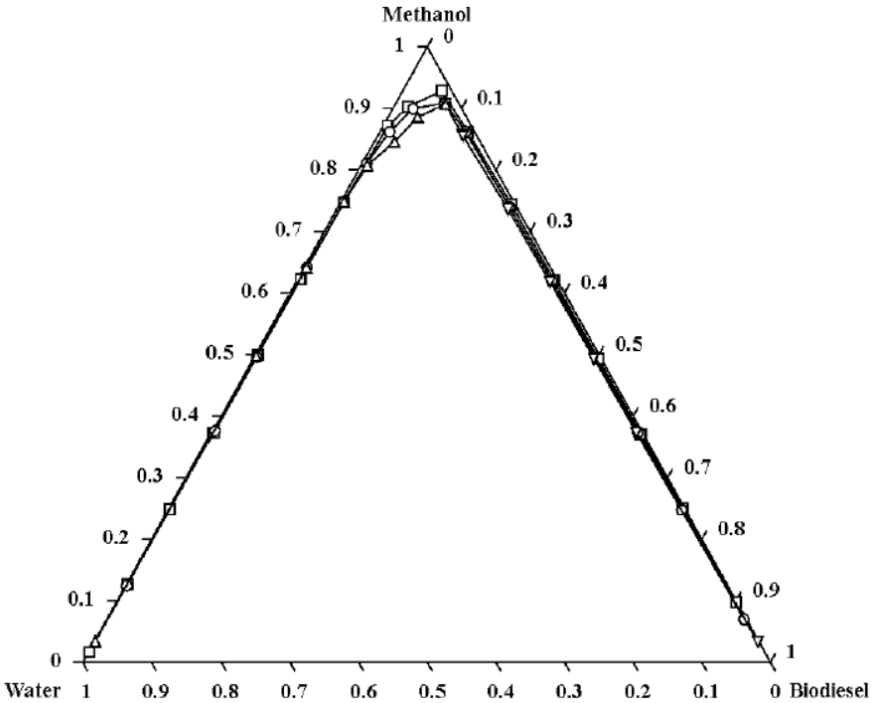

Figure 3. 2. Solubility curves for %10 beef tallow in the corn oil biodiesel-methanol-water system at different temperatures. (□) 25 °C, (○) 35 °C, (△) 45 °C, in mass fraction

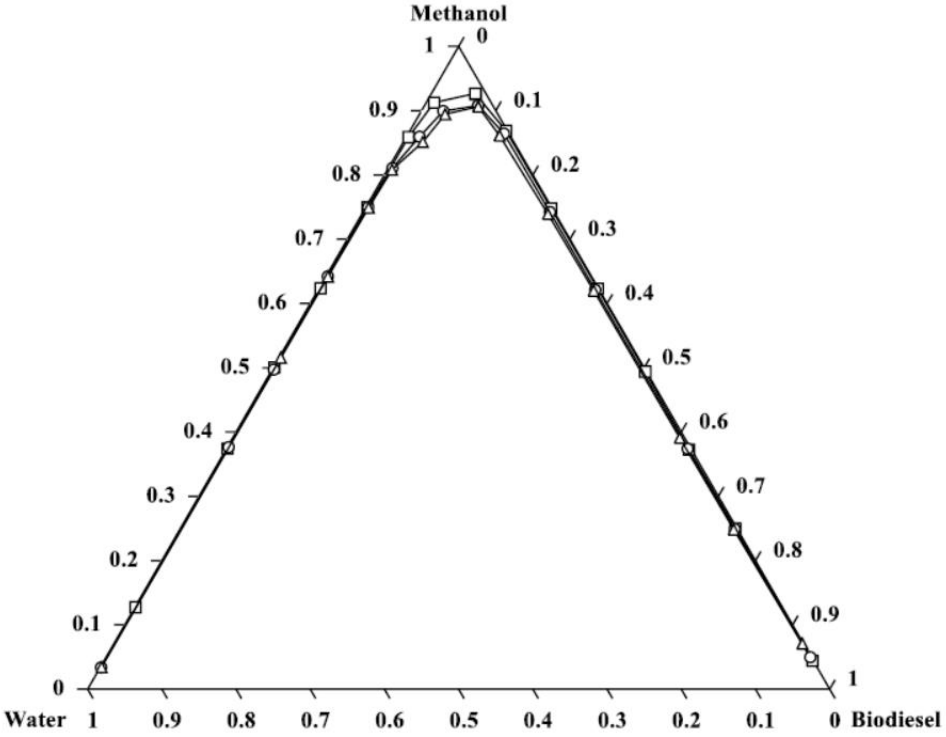

Figure 3. 3. Solubility curves for %20 beef tallow in the corn oil biodiesel-methanol-water system at different temperatures. (□) 25 °C, (○) 35 °C, (△) 45 °C, in mass fraction

4. CONCLUSION

This study experimentally investigated the phase equilibrium of biodiesel from mixtures of corn oil and beef tallow-methanol-water at different temperatures and atmospheric pressures. The measured properties of biodiesel production from the mixture of corn oil and beef tallow are within the range found in the literature. The results indicate typical solubility curves found in the literature due to the immiscibility of biodiesel in water and the complete dissolution of methanol in both water and biodiesel. The solubility curves did not change significantly with increasing beef tallow concentration in corn oil biodiesel. However, the solubility of methanol in the biodiesel-rich phase decreased as beef tallow concentration increased. As the concentration of methanol increases in both the water-rich phase and biodiesel-rich phase, the solubility curves separate from the axis, and thus indicate a significant increase in solubility of methanol in biodiesel and water. This behavior is crucial for removing of methanol from the raw biodiesel by liquid-liquid extraction in which water is an extracting agent.

REFERENCES

[1] Santos, T., Gomes, J. & Puna, J. Liquid-liquid equilibrium for the ternary system containing biodiesel, methanol, and water. *Journal of environmental chemical engineering.* 2018; 6, 984-990..

[2] Demirbas A. Political, economic and environmental impacts of biofuels: A review. *Applied energy*. 2009 Nov 1;86:S108-17.

[3] Hossain, A. & Mazen, M.. Effects of catalyst types and concentrations on biodiesel production from waste soybean oil biomass as renewable energy and environmental recycling process. *Australian journal of crop science*. 2010;4, 550..

[4] Park, J.-Y., Kim, D.-K., Lee, J.-P., Park, S.-C., Kim, Y.-J. & Lee, J.-S. Blending effects of biodiesels on oxidation stability and low-temperature flow properties. Bioresource Technology.2008. 99, 1196-1203.

[5] Bessa, A. M. M., Pinheiro, R. S., Evangelista, N. S., Carmo, F. R. D., Sant'ana, H. B. D. & Santiago-Aguiar, R. L. S. D. Liquid–Liquid Equilibrium for Cottonseed Biodiesel+ Water+ Alcohol (Methanol/Ethanol) Systems at (293.15 and 313.15) K: Experimental Data and Thermodynamic Modeling. *Journal of Chemical & Engineering Data*. 2015;60, 707-713.

[6] Lee, M.-J., Lo, Y.-C. & Lin, H.-M. Liquid-liquid equilibria for mixtures containing water, methanol, fatty acid methyl esters, and glycerol. *Fluid Phase Equilibria*. 2010; 299, 180-190..

[7] Follegatti-Romero, L. A., Oliveira, M. B., Batista, E. A., Coutinho, J. A. & Meirelles, A. J. Liquid-liquid equilibria for ethyl esters+ ethanol+ water systems: Experimental measurements and CPA EoS modeling. *Fuel.* 2012;96, 327-334..

[8] Mohadesi, Majid. "Liquid-Liquid Equilibrium for Ternary Systems Containing Biodiesel+ Glycerol+ Alcohol (Ethanol or Methanol): Thermodynamic Modeling." *Journal of Chemical and Petroleum Engineering 54.2* (2020): 285-295..

[9] De Azevedo Rocha, Enio G., et al. "Liquid–liquid equilibria for ternary systems containing ethylic palm oil biodiesel+ ethanol+ glycerol/water: Experimental data at 298.15 and 323.15 K and thermodynamic modeling." *Fuel 128.* (2014): 356-365.

[10] Yan, X. Y., Cheng, Y. C. & Hu, X. P. Liquid-Liquid Equilibrium for (Water+ Palm Oil Biodiesel+ Methanol) Ternary System at Different Temperatures. *Advanced Materials Research. Trans Tech Publ*. 2012; 867-871..

[11] Basso, R. C., De Almeida Meirelles, A. J. & Batista, E. A. C. Liquid–liquid equilibrium of pseudo ternary systems containing glycerol+ ethanol+ ethylic biodiesel from crambe oil (Crambeabyssinica) at T/K=(298.2, 318.2, 338.2) and thermodynamic modeling. *Fluid phase equilibria*. 2012; 333, 55-62.

[12] Pinheiro, R. S., Bessa, A. M. M., De Queiroz, B. A., Duarte, A. M. S. F., De Sant'ana, H. B. & De Santiago-Aguiar, R. S. Optimization of the methylic biodiesel purification process by the intermediate of liquid-liquid equilibrium data for ternary systems containing methanol+ water+(soybean, corn or brown shell of coconut) biodiesel. *Fluid Phase Equilibria*. 2014.;361, 30-36.

