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LIQUID-LIQUID EQUILIBRIA OF TERNARY MIXTURE CONTAINING CASTOR OIL BIODIESEL, METHANOL AND GLYCEROL AT DIFFERENT TEMPERATURES AND ATMOSPHERIC PRESSURE

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ABSTRACT

In this work, ternary liquid-liquid equilibrium (LLE) data (binodal solubility curves and tie-lines) for castor oil biodiesel + methanol + glycerol at six different temperatures (25, 35, 40, 50, 55 and 60) °C and atmospheric pressure were determined using modified cloud point titration and gas chromatographic analysis. Temperature and time interval influences on the phase diagrams were studied. Spectrometric analysis of the biodiesel and oil were also investigated. The distribution coefficients and solvent selectivities were calculated. The results showed high values of methanol distribution and selectivities at the investigated conditions. Methanol solubilized preferentially in the glycerol heavy phase. The distribution coefficients and solvent selectivity values showed methanol as a good solvent for the separation of castor oil biodiesel from glycerol. The analysis of the biodiesel and oil using Fourier transform infra-red (FTIR) spectrometry showed that the most prominent functional group was methyl ricinoleate which impacted on the character of the biodiesel. The knowledge of the phase equilibrium behaviour of the system is important in the design of efficient separation process, optimization of biodiesel purification and development of appropriate models to elucidate on the purification process.

Keywords: *Liquid-liquid equilibria; Castor oil biodiesel-methanol-glycerol system; Ternary phase diagrams; Spectrometric analysis; Distribution coefficient; Solvent selectivity*

1.0 INTRODUCTION:

The use and application of biodiesel for industrial and domestic processes is gradually gaining wide-spread attention partly due to price fluctuation in the energy market occasioned by the unstable nature of fossil fuel economy but more importantly, due to environmental concerns (Borugadda and Goud, 2012; Atabani et al., 2013; D'Amato et al., 2017). Biodiesel production most often is associated with the presence of impurities such as non-reacted alcohol, glycerol and catalyst. Product requirement constraints are imposed by the relevant standards (ASTM D-6751, ASTM D-9751 and EN 14214) and as such, these impurities must be removed which is mostly achieved by washing with water. The direct product of the biodiesel production can be assumed to be a ternary mixture of the specific biodiesel, alcohol and glycerol systems. Biodiesel has excellent fuel properties which include renewability, biodegradability, and environmentally benign (Vicente et al., 2004; Encinar et al., 2005). The properties of any biodiesel are usually strongly affected by the purity of the end-product. Industrially, biodiesel is produced by alcoholysis of vegetable oils and/or animal fats. However, a major area of concern in the reaction sequence is the immiscibility of the reactants; usually methanol or ethanol and the vegetable oils or animal fats. As a result of this challenge, mass transfer limitations at the beginning of the process are always generated. Consequently, the products of the reaction (biodiesel and glycerol) are not miscible which is an important characteristics used for the initial separation stage in most industrial processes. Phase equilibrium description of any system consisting of biodiesel, alcohol and glycerol is a fundamental requirement for understanding, designing, optimizing and reducing cost of the biodiesel production process.

Castor oil contains about 30% to 55% oil by weight depending on the breed and has the highest viscosity amongst vegetable oils (Adama et al., 2018; Mosquera et al., 2016; Nangbes et al., 2013; Ogunniyi, 2006). It contains naturally occurring triglycerides giving it the appearance of a pure compound. It is used for various purposes including the production of biodiesel. Castor oil biodiesel has many excellent properties that influences its use as combustion fuel. The major character of the biodiesel is the high concentration of the ricinoleate ester that greatly influences the behaviour of both the oil and

biodiesel (Adama et al., 2018; Mosquera et al., 2016; Nangbes et al., 2013; Ogunniyi, 2006)
Liquid-liquid equilibrium data are important prerequisite needed to attain biodiesel final product specification (Knothe and Van Gerpen, 2009) due to the fact that a settling unit operation process is used mostly. Therefore, distribution coefficients as well as selectivity are essential parameters needed to ascertain any solvent's ability to promote and enhance phase separation. Consequently, experimental data of multi-component liquid-liquid equilibrium systems are essential for design, operation and optimization of any extraction process (Seader and Henley, 2006). It can be used to understand the process of purification and separation of the light phase from the heavy phase in biodiesel production. Several studies have been presented that describes the liquid-liquid equilibrium (LLE) data of biodiesel, glycerol, and methanol or ethanol systems (Adama et al., 2021; Noriega et al., 2016; Do-Carmo et al., 2014; Rostami et al., 2013; Ardila et al., 2013; Machado et al., 2012; Franca et al., 2009; Machado et al., 2011; Mesquita et al., 2011; Follegatti-Romero et al., 2010; Ming-Jer Lee et al., 2010). In our previous studies (Adama et al., 2018 and 2021), we investigated the tie lines for the purification of castor oil biodiesel/methanol/glycerol system at 20 °C and 30 °C and the component distribution associated with phase separation and purification of tropical almond biodiesel at different temperatures respectively. Further studies on the production, characterization and application of phase system analysis for purification of biodiesel produced from tropical almond seed oil was also investigated (Adama et al., 2020). However, the investigations were limited to few parameters.

The limited knowledge and information data-base on the liquid-liquid equilibrium behaviour of castor oil biodiesel/methanol/glycerol ternary system important for greater elucidation on actual purification process in terms of components distribution and phase behaviour using ternary phase diagrams necessitated this research. The binodal solubility curve compositions as well as the tie line data were determined. The distribution or partition coefficient and the solvent selectivity were calculated to ascertain the behaviour of the ternary mixture in real-life industrial biodiesel purification processes.

2.0 MATERIALS AND METHODS

2.1 Materials

Castor oil biodiesel was produced, separated and purified according to previous work (Adama et al., 2018). The study also presented the fatty acid profile of the castor oil biodiesel. Other chemicals as reported include glycerol (99 %-100 % JDA, Acros Organics, USA), Methanol (Merck, Germany, 99.5 % purity) and potassium hydroxide pellets (85 % BDH Labtech Chemicals, Poole, England). The equipment used for the liquid-liquid experiments were burette, mechanical agitator - the stirrer, analytical balance, pipette, thermostatic water-bath with a circulation pump for temperature control, conical flasks, stopwatch, beakers and analytical instrument for analysing the composition of the mixture - Gas chromatograph-mass spectroscopy/flame ionization detector (GCMS/FID).

2.2 Methods

The procedures for characterization of the castor oil and castor oil biodiesel, spectroscopic analysis of the oil and biodiesel and the liquid-liquid equilibrium experiments were performed as in our previous works (Adama et al., 2018; 2020 and 2021) in addition to approaches employed by several other researchers (Machado et al., 2012; Mesquita et al., 2012; Ardila et al., 2013; Rostami et al., 2013; Noriega et al., 2016). The binodal solubility curve and tie line data for the castor oil biodiesel ternary system at the investigated temperatures and time intervals were determined by a modified cloud point method using titration procedure under isothermal conditions. The modification involved withdrawing samples from the mixture at 2 min intervals for 32 min under constant agitation. Each sample, at a different time interval, was then analyzed using GC for the component composition from the withdrawn mixture.

3.0 RESULTS AND DISCUSSIONS

Figure 1 shows the Fourier Transform Infra-Red (FTIR) spectrometry of the castor oil biodiesel and castor oil respectively.

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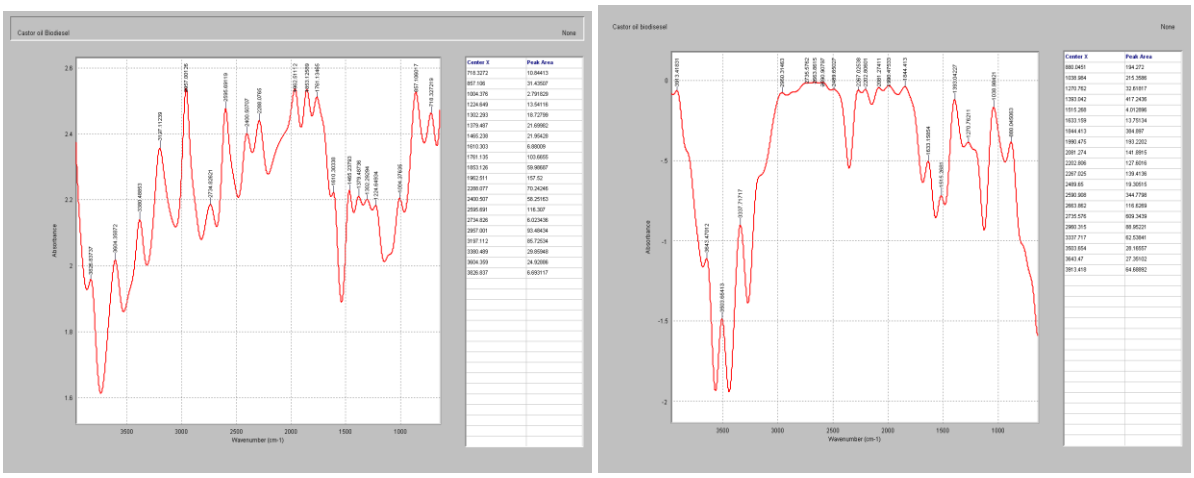
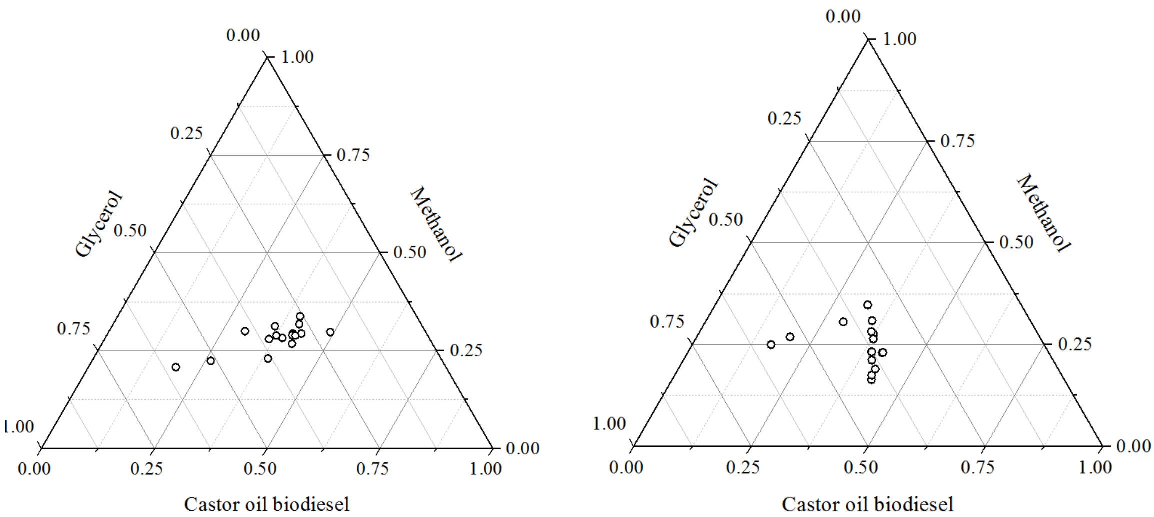


A B

Figure 1: (A) Castor oil biodiesel FTIR Spectrum (B) Castor oil FTIR Spectrum

The Figure 1 indicated the presence of several functional groups. The dominant functional groups of the biodiesel and oil were =C-H, C-O-C, RO-H, R-OH and C=O for the biodiesel and =C-H, CH_2, C=O and O-H groups for oil. However, other functional groups present are CH_2, C≡O, -C≡C-, >C=C<, RC≡N and OH in both the oil and biodiesel which had minimal influence on the oil and biodiesel to absorb infrared radiation at the investigated absorbance range (cm^{-1}). The use of infrared spectroscopy in the analysis of the oil and biodiesel was based on the principle that almost all molecules absorb infrared light at those frequencies where the infrared light affected the dipolar moment of the molecule. In the castor oil and biodiesel molecules, the differences of charges in the electronic fields of their atoms produce the dipolar moment of the molecules. The molecules with dipolar moments allowed infrared photons to interact with other molecules causing excitations to higher vibrational states. The results of the analysis of the tie line data for the castor oil biodiesel mixture composition (castor oil biodiesel/glycerol/methanol) at the investigated temperatures (25, 35, 40, 50, 55, and 60) °C and time of 2 mins to 32 mins, at 2 mins interval for the overall phase mixture composition before phase separation are presented in Figure 2.

From Figure 2, it could be observed that the tie line data predicted and showed how castor oil biodiesel, methanol and glycerol components distributed in the phase mixture composition (feed composition) before separation at the various temperatures and time intervals. The components were observed to be evenly distributed and concentrated at each temperature in the feed composition to appreciable extent at the various time intervals during investigation.



(A) **(B)**

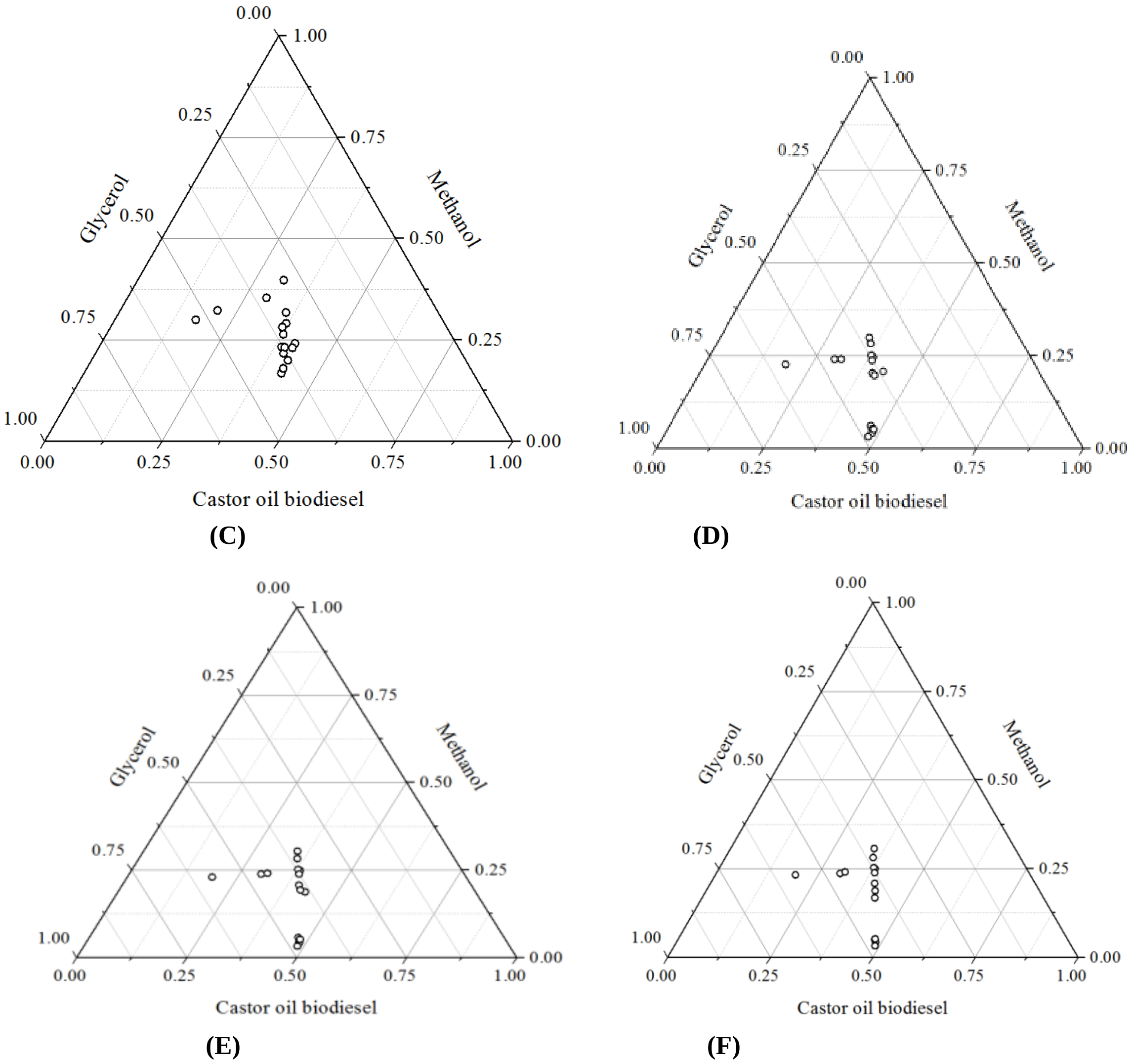


Figure 2: Tie-line plot for overall mixture composition before phase separation at (A) 25 °C (B) 35 °C (C) 40 °C (D) 50 °C (E) 55 °C (F) 60 °C

The results of the analysis of the tie line data and plots for castor oil biodiesel light phase and glycerol heavy phase mixture composition after phase separation at the investigated temperatures and time intervals are presented in Figure 3.

Figure 3 shows the tie line plots for castor oil biodiesel light phase and glycerol heavy phase after phase separation at the investigated temperatures and time of 2 mins to 32 mins at 2 mins intervals. From the ternary phase diagram plot, it can be observed that the compositions between the equilibrium light phase and the heavy phase were represented by the tie lines data. This also represented the conjugate phases in equilibrium which were the extract and the raffinate phases of the ternary mixture. The figures showed non-horizontal tie lines at the investigated compositions. It was observed that the solubility of methanol in the heavy glycerol phase was greater and higher than in the light biodiesel phase as seen by the size of the phase region bordering methanol and glycerol and the gradient of the tie lines. Methanol readily solubilizes in the heavy glycerol phase due to its strong affinity for glycerol; hence increase in the size of the two phase region bordering the glycerol and methanol.

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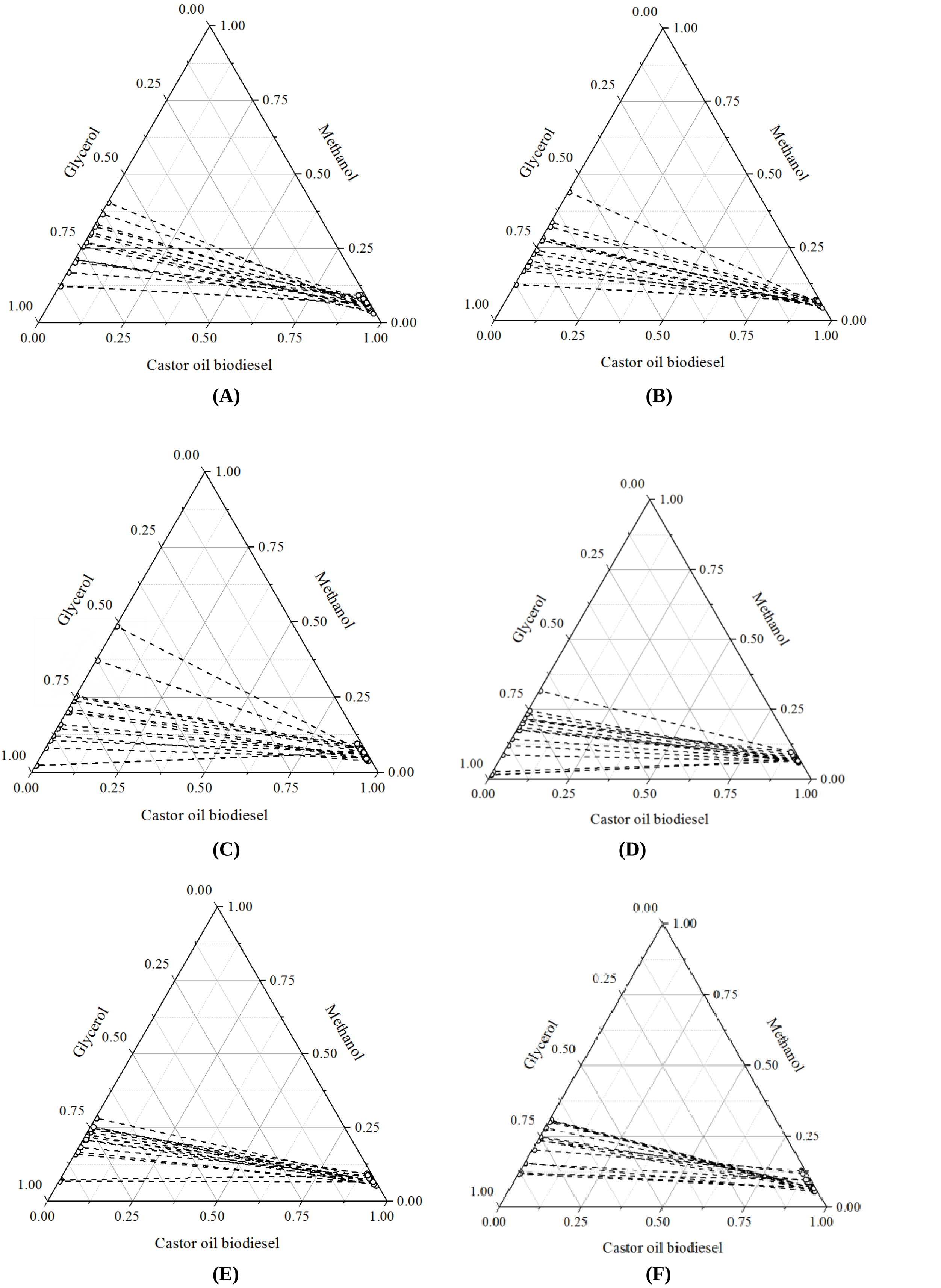

Figure 3: Tie-line plot for castor oil biodiesel/glycerol/methanol system after phase separation at (A) 25 °C (B) 35° C (C) 40 °C (D) 50 °C (E) 55 °C (F) 60 °C

10.51975/23380101.som

The binodal solubility curve composition plots at the investigated temperatures and time intervals for castor oil biodiesel phase mixture composition are presented in Figure 4.

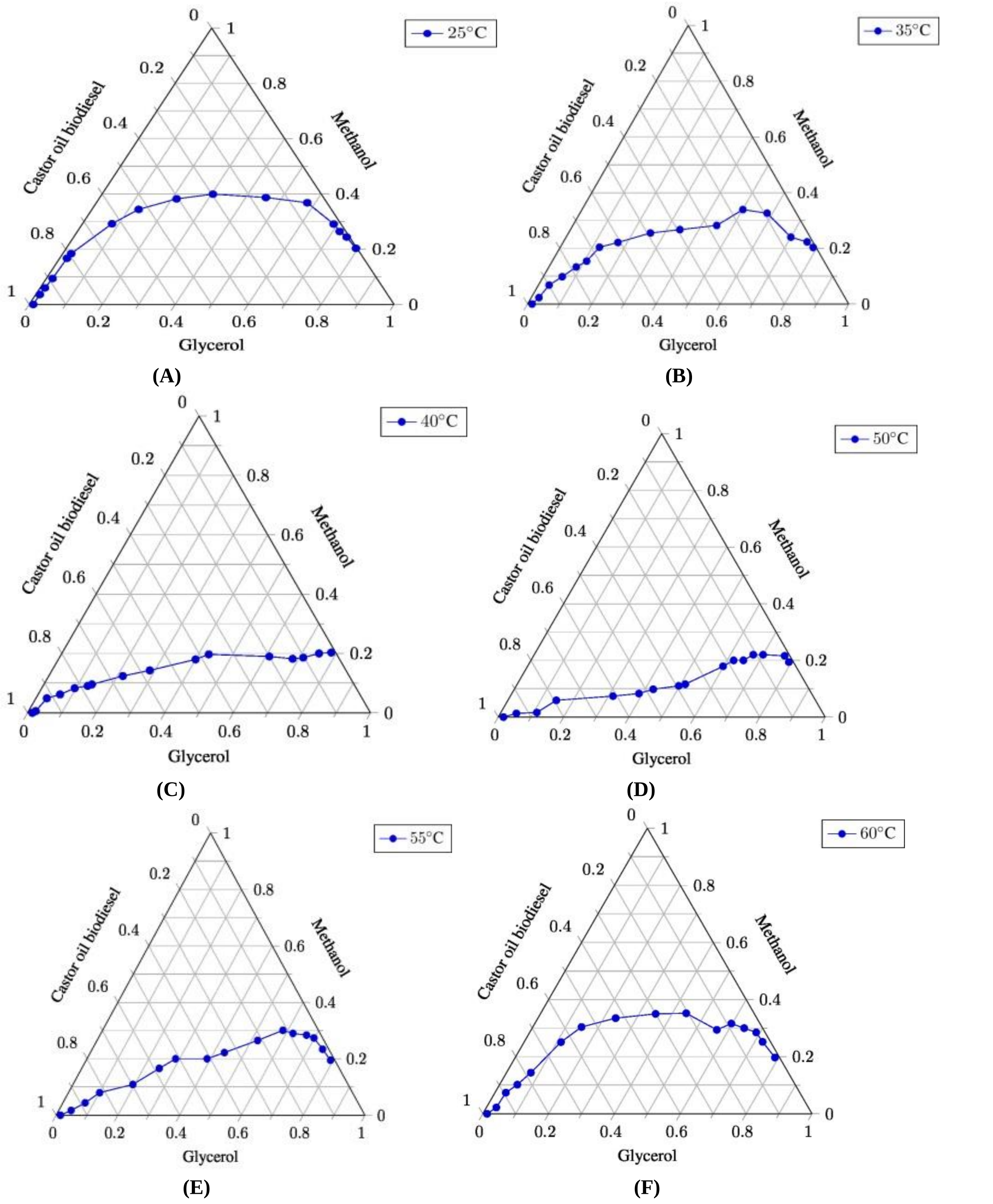

Figure 4: Binodal solubility composition plots for castor oil biodiesel/glycerol/methanol system at (A) 25 °C (B) 35 °C (C) 40 °C (D) 50 °C (E) 55 °C (F) 60 °C

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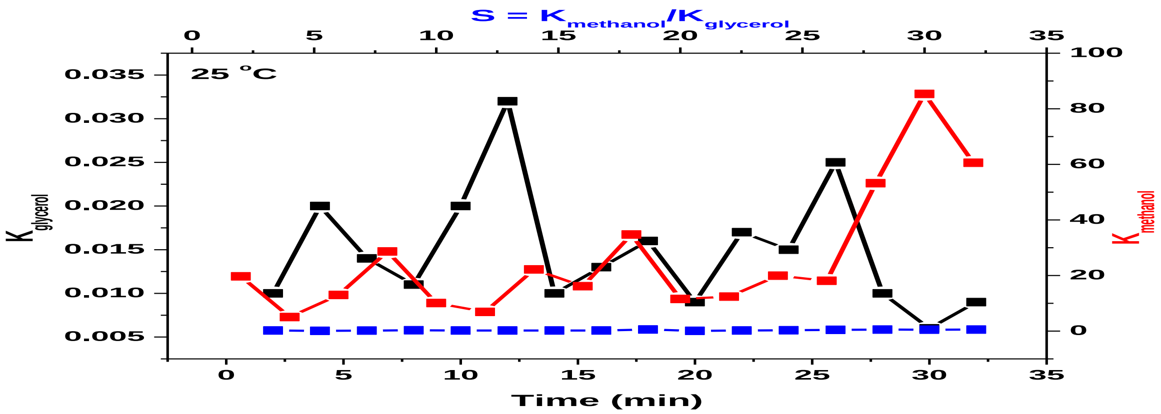
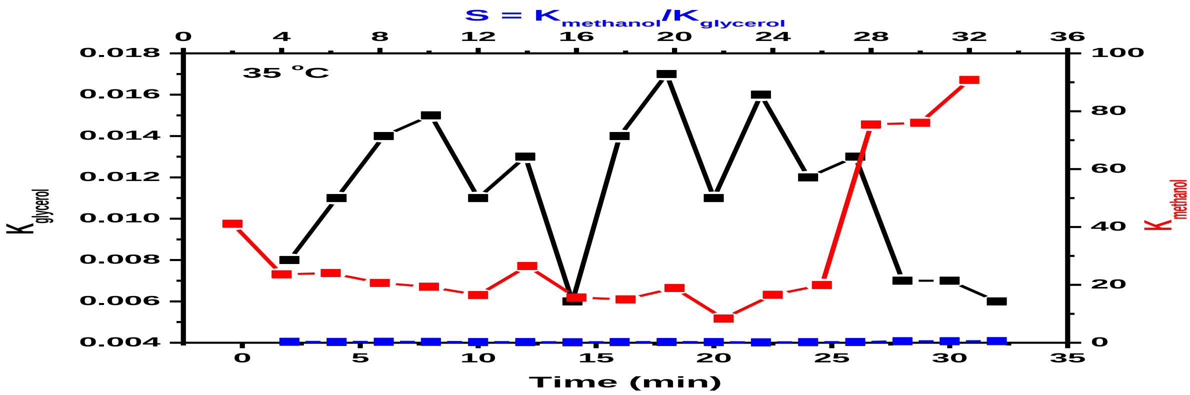
Figure 4 shows the binodal solubility curve composition plots for castor oil biodiesel/glycerol/methanol system, at the different withdrawal time intervals and temperatures. Several measurements of different pairs of the conjugate solutions of the light phase and the heavy phase at each temperature and time interval were obtained at the different temperatures and time intervals. From experimental analysis, it was observed that castor oil biodiesel and glycerol were partially miscible and soluble in methanol. However, castor oil biodiesel and glycerol were totally immiscible in each other. This behaviour was observed to be in agreement with other studies (Mesquita et al., 2011; Rostami et al., 2013). It could be seen from the binodal solubility curve composition diagrams of the different figures that the castor oil biodiesel had higher solubility in the heavy phase at the studied temperatures and time intervals investigated.

The results of the ternary equilibrium data for distribution coefficient of glycerol ($K_{glycerol}$), methanol ($K_{methanol}$) and selectivity (S) at the different temperatures and withdrawal times for castor oil biodiesel/methanol/glycerol phase compositions are presented in Figure 5.

In Figure 5, it can be verified that the distribution coefficient of methanol ($K_{methanol}$) in the biodiesel light phase was higher causing the biodiesel to drag the greatest amount of methanol present in the biodiesel light phase. This gives an appreciable purification of the biodiesel phase of the biodiesel with minimal fraction of glycerol in the biodiesel which was in agreement with studies conducted on different biodiesel ternary systems (Machado et al., 2011; Ardila et al., 2013, Adama et al., 2021). Thus, the drying process of the biodiesel was greatly favoured. At other temperatures, the distribution coefficient of methanol with regards to temperature and time intervals was observed to exhibit consistent values of relatively less than one. This behaviour of the distribution coefficient may be explained in terms of the polarity of the hydroxyl group of the methyl ricinoleate molecule making the distribution of the more polar components (methanol) to increase in the biodiesel light phase which can be readily separated.



(A)



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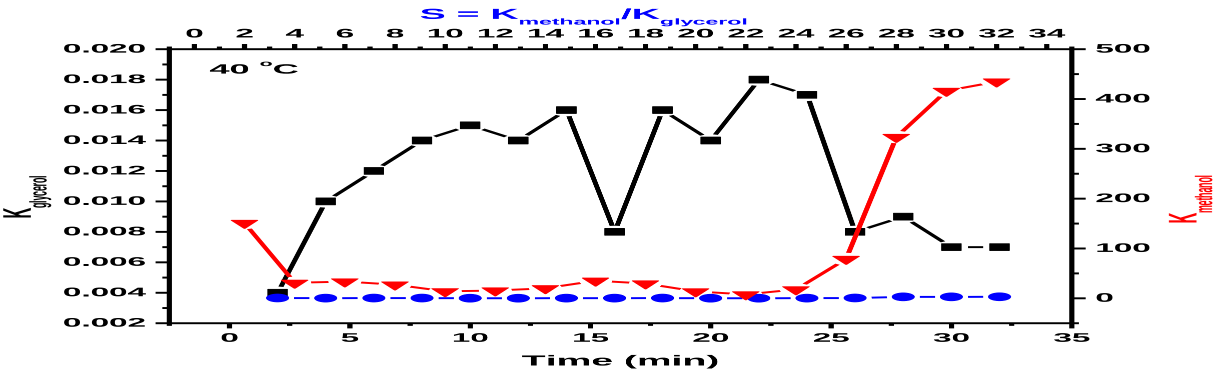

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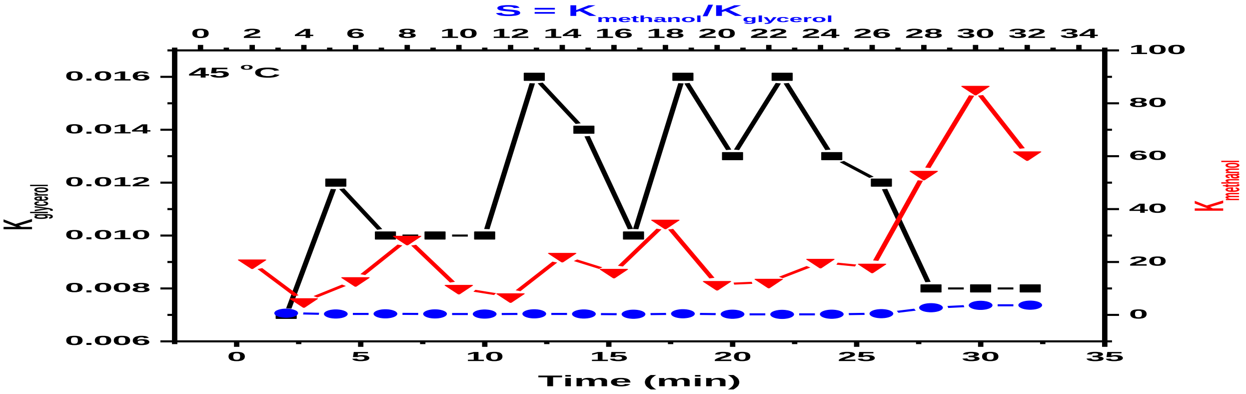

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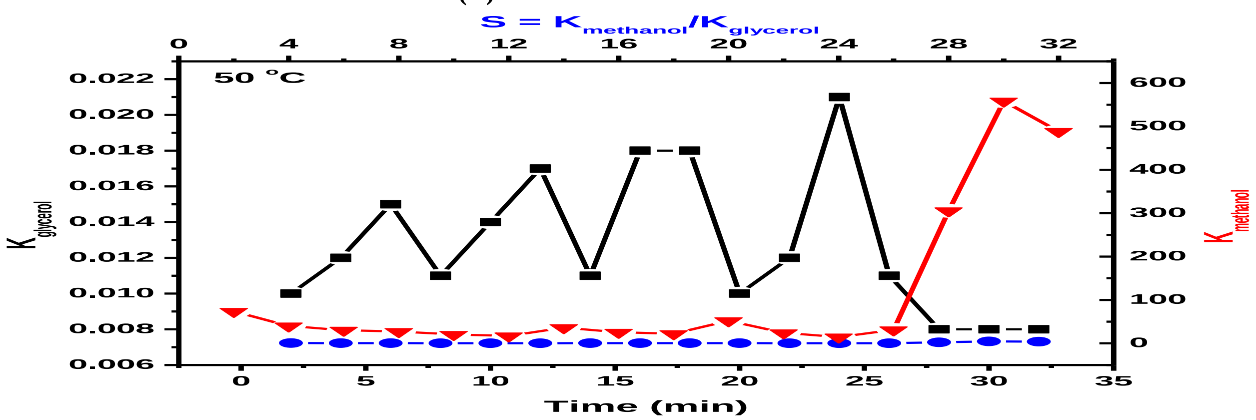
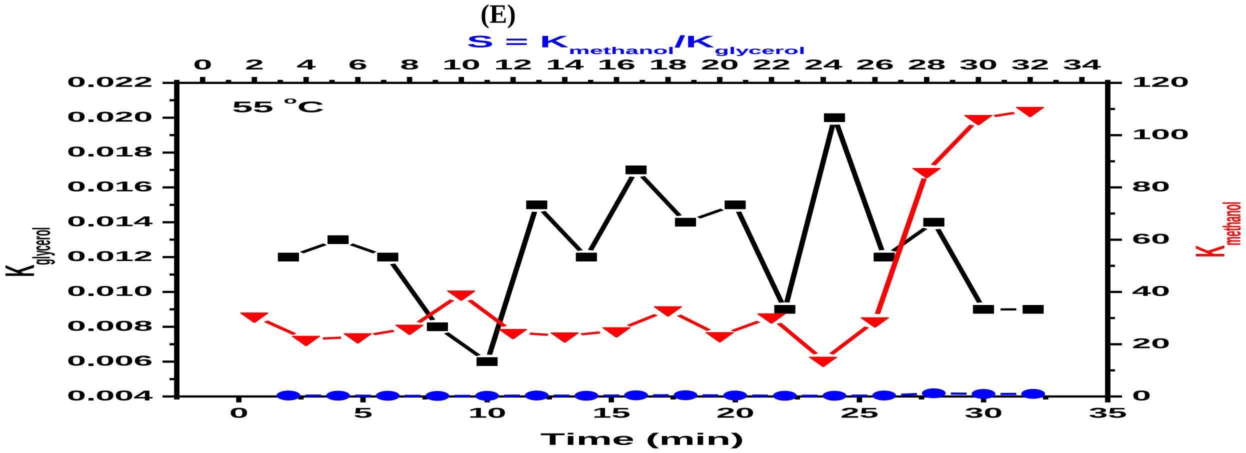


(E)



(F)

Figure 5: Distribution coefficients of glycerol ($K_{glycerol}$), methanol ($K_{methanol}$) and selectivity (S) at (A) 25 °C (B) 35 °C (C) 40 °C (D) 50 °C (E) 55 °C (F) 60 °C and withdrawal times for castor oil biodiesel/methanol/glycerol phase compositions

The selectivity of biodiesel in the biodiesel light phase showed its preference to solubilize methanol; the solute or glycerol; the diluent. At all system temperatures and atmospheric pressure, the solubility values (*S*), were between 2 and 488. Also, it was observed that a decrease in the mass fraction of methanol in the glycerol heavy phase gave an increase in the selectivity of biodiesel for methanol. This was due probably to the presence of methanol in the glycerol heavy phase that solubilizes an amount of glycerol in addition to methanol, thus affecting the selectivity (*S*) values. This observation was also in agreement with studies conducted (Machado et al., 2011 and Ardila et al., 2013). For ternary systems, increasing the temperature gives an increase in selectivity, *S*, as verified by low methanol mass fraction values. At the investigated conditions, similar '*S*' profile were observed. Increasing the methanol mass fraction in the glycerol heavy phase gives a decrease in selectivity of the biodiesel. This could be probably due to the presence of methanol in the glycerol heavy phase which enhances the solubility of the phase in the biodiesel light phase. This then solubilizes an amount of glycerol with methanol; which act as a glycerol carrier; thereby diminishing the solubility '*S*' values. This observation is in agreement with studies conducted (Machado et al., 2012).

Basically, distribution coefficient and selectivity parameters are essential in the comprehension of the solvent's ability to promote phase separation. Essentially, lower values for distribution coefficients implies higher concentrations of glycerol in the glycerol heavy phase and lower amounts of glycerol solubilized in the biodiesel light phase. Selectivity is directly related to the extraction capability of the solvent and it was observed that all values of the selectivity was larger than 1. However, the alcohol concentration is the main factor that affects biodiesel product solubility and selectivity (Franca et al., 2009). The agreement of the tie lines with the feed composition indicated low experimental error by loss of mass or analysis accounted for the quality of the LLE data obtained. The entire work complements the researches conducted by several other researchers (Franca et al., 2009, Machado et al., 2011 and Ardila et al., 2013).

4. CONCLUSION

Liquid-liquid experimental data consisting of binodal solubility curves and tie-lines were obtained for ternary system of castor oil biodiesel, methanol and glycerol at six different temperatures and atmospheric pressure (25, 35, 40, 40, 55 and 60) °C using modified cloud point titration method and gas chromatographic analysis. Distribution coefficient and selectivity analyses were performed. The system presented high values of methanol distribution and selectivity at the investigated conditions. The separation factor was greater than 1 at all investigated conditions. This indicated that methanol solubilized preferentially in the glycerol heavy phase. It also showed that methanol is a good extraction solvent for the separation of castor oil biodiesel and glycerol mixtures. The effect of temperature was observed to be negligible for the system studied. Spectroscopic analysis of the castor oil biodiesel and castor oil indicated the presence of several functional groups with methyl ricinoleate being the most pronounced. The knowledge of the phase equilibrium for the castor oil biodiesel, methanol and glycerol system is important in optimizing biodiesel purification process as well as developing models for simulating and optimizing ternary systems behaviour.

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