



## Original Research Article

### Tie Line Analysis of Ternary Phase Diagram for Purification of Castor Oil Biodiesel/Methanol/Glycerol System at 20 °C And 30 °C

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#### ABSTRACT

*The final product of biodiesel production is often taken as a ternary mixture of the specific biodiesel, methanol and glycerol to certain degree of purity. Tie line analysis of ternary phase diagram for castor oil biodiesel/methanol/glycerol system was investigated in this research to provide experimental data for the purification of the biodiesel system. Measurements were carried out at temperatures of 20°C and 30°C and time of 2 mins to 32 mins at intervals of 2 mins using cloud point titration procedure under isothermal conditions. Gas chromatography (GC) methodology using ASTM D6584 standard was employed for the analysis of the mixture component mass compositions to obtain the tie line data. The distribution coefficient,  $K$ , and solvent selectivity,  $S$ , were evaluated to ascertain the extracting capacity of methanol and for the location of immiscibility of the ternary components. The influence of temperature on  $K$  and  $S$  were also investigated. The results obtained revealed that two liquid phases existed at the investigated temperatures and the optimum areas of influence of the mixture components were located using the tie line ternary phase diagrams. Methanol was observed to preferentially distribute to the lower glycerol-rich phase than the upper biodiesel-rich phase though biodiesel solubilized more methanol than glycerol.*

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## 1. INTRODUCTION

Alternative means of meeting energy needs of mankind are increasingly becoming important in most scientific research due to the depleting fossil fuel sources and increasing damage to the environment (Audu

2012; Noriega et al., 2016). The use of bio-materials for fuels and energy processes has several advantages and many requirements except that they are biological materials (biomass) (Martinez et al., 2014; Homrich and Ceriani 2016). Over the last hundred years, close to ninety percent of all fuels consumed worldwide for energy generation and transportation has been attributed to fossil fuels (Guldhe et al., 2015). Biodiesel is a renewable fuel produced from vegetable oil and animal fats (Wannachod et al., 2016). Conventionally, biodiesel separation and purification are based on the unit operation processes of distillation, extraction and adsorption (Hajek et al., 2016; Vavra et al., 2017). Generally, ternary phase diagrams describe the phase behaviour of mixtures of components and require the establishment of the two-phase systems for the three components involved. The phase diagram displays the regions of the potential space where the various phases of the system are stable (Sanjid et al., 2014; Silitongaa et al., 2016; Vijayaraj and Safhiyagnanam 2016). The phase diagram represents graphically, the co-existing phases and those of stability regions when equilibrium is established among phases of a given system (Noriega et al., 2016; Wales et al., 2016).

Understanding the limits of biodiesel purification methods and selecting appropriate combinations of feedstock and purification steps are important steps required to achieve consistent quality of fuel (Martinez et al., 2014; Stojkovic et al., 2014; Mathimani et al., 2015; Baskar and Aiswarga, 2016). Adequate knowledge about the phase equilibrium which involves the determination of the tie lines composition in the ternary mixture is essential for better understanding of the process, improvement of the reaction rate, selectivity of the desired product and the separation process for the product mixture (Hajek et al., 2016; Vavra et al., 2017). Researches on biodiesel production are largely concentrated on the transesterification process and its improvement. Regrettably, only a handful of experimental results on equilibrium phase performance of biodiesel mixtures have been reported in addition to statistics on the significance of the phases separated after transesterification and the distribution of the components between the phases (Andreatta et al., 2008; Berrios and Skelton 2008; Franca et al., 2009; Stephen and James 2011; Goncalves et al., 2014; Guldhe et al., 2015; Maghami et al., 2016; Hakim et al., 2016). Several studies showed that equilibrium data for liquid-liquid ternary systems were needed to properly situate the heterogeneous and homogeneous reactions and purification process (Franca et al., 2009; Rostami et al., 2013; Do- Carmo et al., 2014; Noriega et al., 2016; Homrich and Ceriani 2016; Wales et al., 2016; Hakim et al., 2016; Maghami et al., 2016). This can be utilized for understanding the process of purification and separation of the biodiesel-rich phase from the glycerol-rich phase. According to Noriega et al., (2016) and Vavra et al., (2017), limited works presently exist on the equilibrium phase characteristics of biodiesel mixtures due to the extremely high variations in the feedstock used and composition of methyl esters in different biodiesel fuels. In this regard, the equilibrium data of the different biodiesels in terms of the biodiesel/glycerol/methanol mixture composition was observed to show high variations.

In this research, investigation of the tie line compositions for the purification of castor oil biodiesel/methanol/glycerol system at 20°C and 30°C and different time intervals was undertaken to provide ternary equilibrium phase data/diagram for castor oil biodiesel mixture system. The influence of temperature on the distribution coefficient,  $K$ , and solvent selectivity,  $S$ , were evaluated from the tie line data to establish the extracting ability of the solvent on the phase mixture components.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Castor seed (*Ricinus communis L*) was obtained from Awo-akpali and Ukpaba villages of Ankpa, Kogi State, Nigeria. The extraction of the castor oil from the castor seed was done using a hydraulic press equipped with a temperature controller. The extracted castor seed oil was centrifuged at 1200rpm for about thirty (30) minutes to remove any debris in the oil. Other materials used included glycerol > 99% and methanol > 99%. These were of high analytical grades. The equipment used included burette, mechanical agitator – stirrer,

analytical balance, pipette, water-bath for temperature control, conical flasks, stop watch, beakers and gas chromatography flame connected with flame ionization detector (GC-FID).

## 2.2. Methods

### 2.2.1. Biodiesel production

Castor seed oil was used in the production of the biodiesel. The reaction mechanism employed in the production of the biodiesel was transesterification. The reaction temperature was maintained at 60°C with the stirrer speed set at 1200rpm. Constant agitation was maintained throughout the reaction. Potassium hydroxide at a concentration of 5%w/v was used as the catalyst. Samples of the biodiesel were stored in small containers and thereafter analyzed using Thermo Scientific Trace GC Ultra AS 3000 Auto-Sampler GC-FID.

### 2.2.2. Castor oil biodiesel fatty acid characterization

The content of the biodiesel was determined by GC method using FAME norm in accordance with ASTM D6584, EN14214, EN14103 and EN14105. The instrument used was a Thermo Scientific Trace GC Ultra AS 3000 auto-sampler gas chromatography connected to a flame ionization detector (FID). The criteria which were both qualitative and quantitative for the analysis of biodiesel produced, are specified in EN14214 and EN14103 for fatty acid methyl ester (FAME) and linolenic acid methyl esters content respectively. Calibration was made of all FAME components by relative response to a single component; methyl heptadecanoate. The range of FAME(s), for which the method was applicable fall within the range of C<sub>14:0</sub> and C<sub>24:1</sub>. Quantification was done with the aid of Chem Station Data handling software. The fatty acid composition of the castor oil biodiesel is presented in Table 1.

### 2.2.3. Determination of phase diagram of biodiesel/methanol/glycerol (tie line compositions)

The tie-line composition/data for castor oil biodiesel ternary system at 20°C and 30°C and various time intervals was determined by the cloud-point method using titration procedure under isothermal conditions employed by several researchers (Franca et al., 2009; Mesquita et al., 2012; Machado et al., 2012; Ardila et al., 2013; Rostami et al., 2013). These entailed the determination of the biodiesel – rich phase composition data and glycerol-rich phase composition data (tie-lines composition data).

The mass fraction of biodiesel, methanol and glycerol in both phases was determined by GC methodology. The quantitative determination of the phase composition was carried out using calibration curves (external calibration) obtained using standard solutions for each component. The experimental data for each tie line at the different time intervals and temperatures was replicated three times and the values reported in this work are the average ones. The mass fraction of biodiesel, methanol and glycerol were determined from the areas of the corresponding GC chromatographic peaks, adjusted by the response factors obtained by previous calibrations.

The distribution coefficient K, and the solvent selectivity S, were calculated using experimental compositions of both phases according to the following expressions as used by several researchers (Franca et al., 2009; Mesquita et al., 2012; Machado et al., 2012; Ardila et al., 2013; Rostami et al., 2013):

$$K = \frac{\text{mass fraction of methanol in the biodiesel-rich phase}}{\text{mass fraction of methanol in the glycerol-rich phase}} \quad (1)$$

$$= \frac{\text{mass fraction of glycerol in the biodiesel-rich phase}}{\text{mass fraction of glycerol in the glycerol-rich phase}} \quad (2)$$

$$S = \frac{\text{distribution coefficient of methanol}}{\text{distribution coefficient of glycerol}} \quad (3)$$

$$= \frac{K_{\text{methanol}}}{K_{\text{glycerol}}} \quad (4)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. Fatty Acid Profile of Biodiesel

Table 1 presents results of the fatty acid profile of castor oil biodiesel FAME. From the table, it could be seen that methyl ricinoleate (ricinoleic acid) had the highest percentage of fatty acid methyl ester at 40.06%. This was followed by methyl linoleate ester at 30.180%. Others were methyl laurate ester (4.9495), methyl palmitate ester (5.822%), methyl arachidate (4.771%), methyl stearate ester (3.589%) and methyl heptadecanoate (1.729%). It could be observed from Table 1 that the main character of the castor oil biodiesel (FAME) was defined by the high concentration of the methyl ricinoleate ester which agreed with what was obtained in the fatty acid composition of the corresponding castor seed oil. Ramos et al., 2009 observed that the fatty acid composition of oils and their corresponding biodiesels remained the same even after the oil had undergone transesterification process. This behavior was observed for the castor seed oil and the castor oil biodiesel FAME.

Table 1: Fatty acid profile of castor oil biodiesel

Parameters	Results (%)
Methyl laurate (lauric) (C <sub>12:0</sub> )	4.949
Methyl heptadecanoate (heptadecanoic) (C <sub>17:0</sub> )	1.729
Methyl myristate (myristic) (C <sub>14:0</sub> )	3.228
Methyl arachidate (arachidic) (C <sub>20:0</sub> )	4.771
Methyl linoleate (linoleic) (C <sub>18:2</sub> )	30.180
Methyl ricinoleate (ricinoleic) (C <sub>18:1</sub> OH)	40.060
Methyl stearate (stearic) (C <sub>18:0</sub> )	3.589
Methyl palmitate (palmitic) (C <sub>16:0</sub> )	5.822

#### 3.2. Castor Oil Biodiesel/Glycerol/Methanol Ternary Phase Mixture Composition

The analysis of the tie line data and plots for the castor oil biodiesel mixture composition at temperatures of 20°C and 30°C and time intervals of 2 mins to 32 mins at 2 mins interval for the overall phase mixture composition before phase separation are given in Figures 1 and 2 respectively. Figures 1 and 2 shows the tie line plots for the overall mixture composition before separation at 20°C and 30°C, tie lines data at the various withdrawal time intervals at 20°C and 30°C, ternary contour plots of the mass fraction at the different withdrawal time intervals at 20°C and 30°C and ternary surface plot of mass fraction at the different withdrawal time interval at 20°C and 30°C. From Figures 1A and 2A, it could be seen that the tie line data plot predicts and shows the distribution of castor oil biodiesel, methanol and glycerol in the phase overall composition before separation at 20°C and 30°C respectively. From Figures 1A, B, C and D respectively at 20°C, it could be seen that the components of the mixture were uniformly distributed and concentrated in the feed composition at the various time intervals. This is observable from the position of the data point mostly located at the center of the ternary phase diagram. Each data point in the phase diagram represented the component composition of castor oil biodiesel, methanol and glycerol at the various time intervals investigated at 20°C. The trend was also seen in Figures 2A, B, C and D respectively at 30°C. Figures 1B, 2B, 1C, 2C and 1D, 2D respectively present the tie lines, ternary contour plots and ternary surface plots of the mass composition at 20°C and 30°C at the different withdrawal time intervals of 2 mins to 32 mins at 2 mins intervals. The colour bars represented each of the components withdrawn at the different withdrawal time intervals. The range of colour bar and time interval was a demonstration of the major component

withdrawn at the particular period though each withdrawal time interval indicated three components present at the particular time and at temperature of 20°C and 30°C respectively.

The analysis of the tie line data and plots for castor oil biodiesel upper-rich and glycerol lower-rich phases' mixture composition after separation at the studied temperature and time intervals is presented in Figures 3 and 4. In the ternary phase diagram plot of Figures 3 and 4, it could be seen that the compositions between the equilibrium biodiesel-rich phase and the glycerol-rich phase was represented by the tie lines (Figures 3A and 4A). The biodiesel-rich phase and the glycerol-rich phase that were in equilibrium were the conjugate phases. Castor oil biodiesel and glycerol were partially miscible and soluble in methanol. However, castor oil biodiesel and glycerol were totally immiscible in each other.

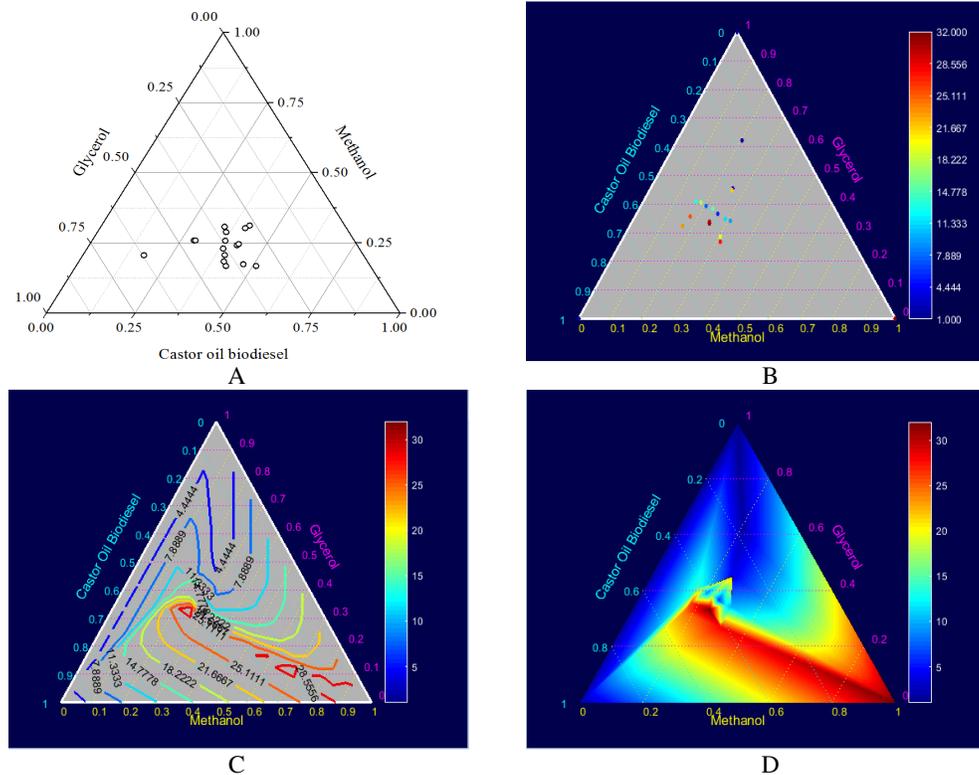


Figure 1: A) Tie line for overall composition at 20°C, B) Tie lines with withdrawal time intervals at 20°C, C) Ternary contour plot of mass fraction at different withdrawal time interval for 20°C, D) Ternary surface plot of mass fraction at different withdrawal time interval for 20°C

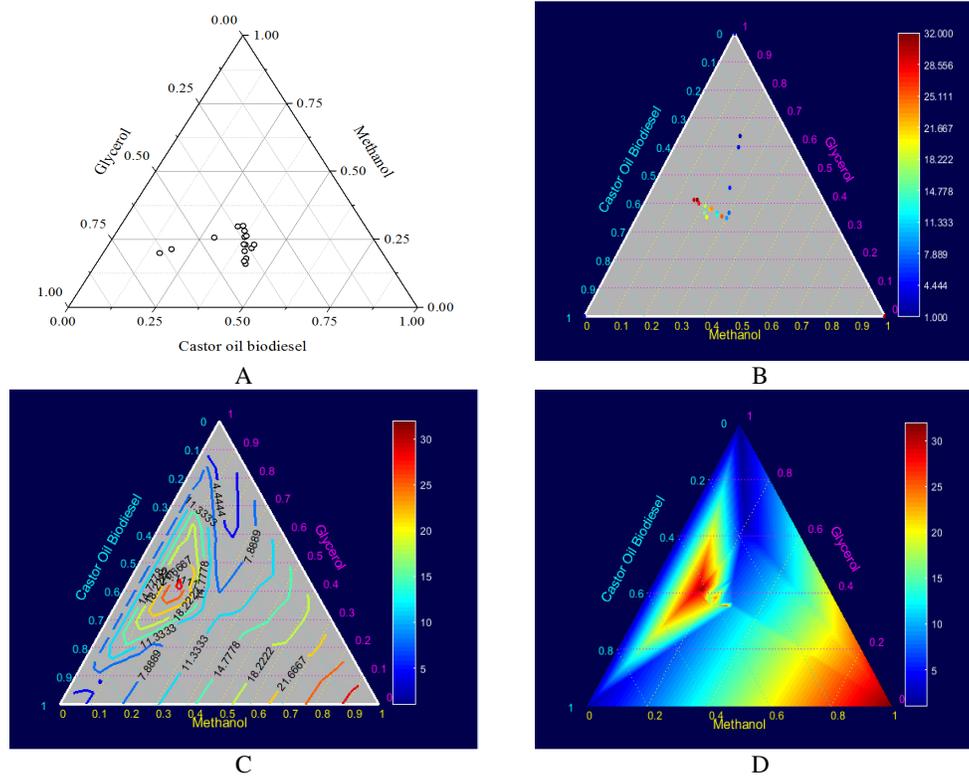


Figure 2: A) Tie line for overall composition at 30°C, B) Tie lines with withdrawal time intervals at 30°C, C) Ternary contour plot of mass fraction at different withdrawal time interval for 30°C, D) Ternary surface plot of mass fraction at different withdrawal time interval for 30°C

From Figures 3A and 4A, it could be observed that the tie lines were not horizontal at the investigated compositions. It could also be detected that the solubility of methanol in the glycerol-rich phase was greater and higher than in the biodiesel-rich phase as indicated by the size of the phase region bordering methanol and glycerol and the gradient of the tie lines. The solubility of methanol in the glycerol-rich phase was greater and higher than in the biodiesel-rich phase. This could be seen from the gradient of the tie lines. At the investigated temperatures of 20°C and 30°C, it could be observed that the two-phase region remained consistent. This implied that the distributions of the components in the phases were not affected by temperature changes which implied that lower temperatures would give higher concentration of biodiesel in the biodiesel-rich phase. The glycerol concentration in the biodiesel-rich phase was observed to be 0.01 wt% at 20°C while that of biodiesel at the same 20°C in the glycerol-rich phase was observed to be 0.002 wt% at the optimum time of 32 minutes. This trend was observed to be prevalent at all the time intervals investigated at temperature of 20°C. This was also observed to be similar for the phase composition at 30°C as shown Figure 4A. On the other hand, the methanol concentration in the glycerol-rich phase at 20°C was observed to be 0.15 wt% while that in the biodiesel-rich phase was 0.069 wt% at the same 20°C. This was at the optimum operating time of 32 minutes. On the average, the methanol concentration in the glycerol-rich phase at 20°C was 38.2 wt% while that of the biodiesel-rich phase was about 7.8 wt% at 20°C. From the plots of the tie line data at 20°C temperature and time intervals, it was observed that the composition of the equilibrium phase was evenly distributed approaching global composition at some points and deviating from equilibrium global composition at some other points due to dispersive forces.

The ternary equilibrium data for distribution coefficients of glycerol ( $K_{\text{glycerol}}$ ), methanol ( $K_{\text{methanol}}$ ) and selectivity ( $S$ ) at temperature of (20°C and 30°C) and time intervals of (2 to 32 minutes) for castor oil biodiesel/methanol/glycerol phase compositions are presented in Tables 2 and 3. Tables 2 and 3 present the results of the distribution coefficient ( $K$ ) and selectivity ( $S$ ) for castor oil biodiesel/methanol/glycerol ternary phase composition at 20°C and 30°C. From Tables 2 and 3, it could be observed that the glycerol distribution coefficient had slight increases and decreases with time reaching values of 0.012 and 0.010 respectively at 32 minutes. On the other hand, the methanol distribution coefficient was observed to have slight increases and decreases with time attaining values of 0.460 and 0.283 respectively at the optimum time investigated. At both temperatures investigated, as the distribution coefficients either decreased or increased slightly with time, the selectivity ( $S$ ) was observed to gradually increase attaining maximum value at the optimum time of the analysis. This behaviour was due to the presence of phase interaction components between the two phases and components present in each phase and also attributed to the polar nature of the methyl ricinoleate molecule which had a hydroxyl group attached to its structure thereby influencing the distribution of the equally polar molecule (methanol and glycerol) in both phases of the mixture composition (Franca et al., 2009; Ardila et al., 2013; Nangbes et al., 2013; Mosquera et al., 2016).

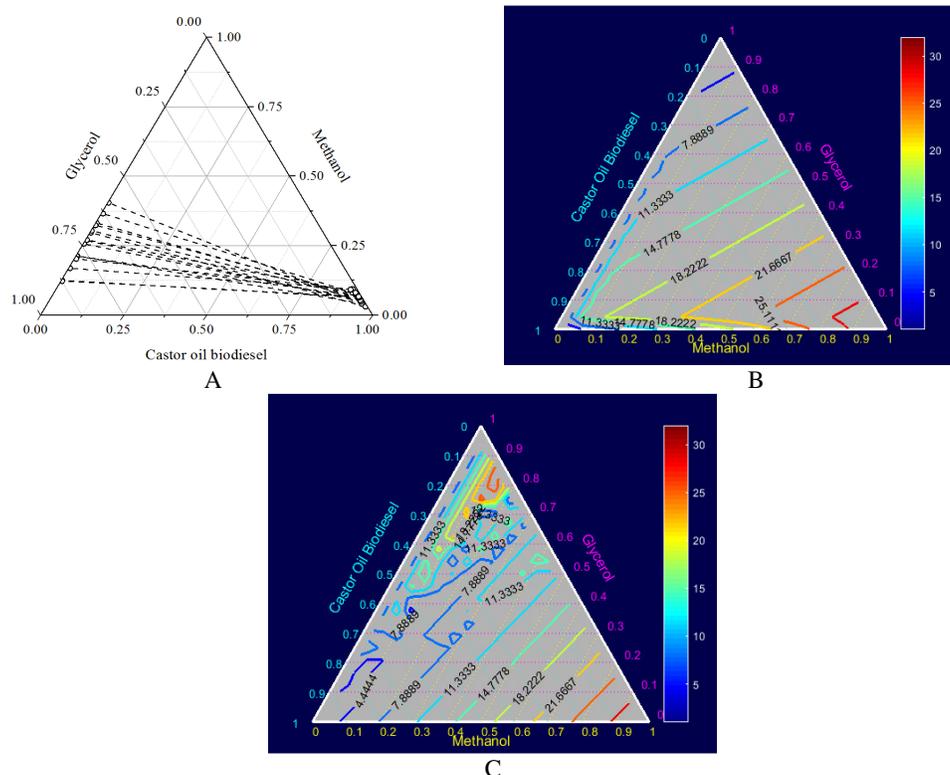


Figure 3: A) Tie line plot for castor oil biodiesel/glycerol/methanol system at 20°C, B) Biodiesel-rich phase ternary contour plot of mass fraction at different withdrawal time interval for 20°C, C) Glycerol-rich phase ternary contour plot of mass fraction at different withdrawal time interval for 20°C

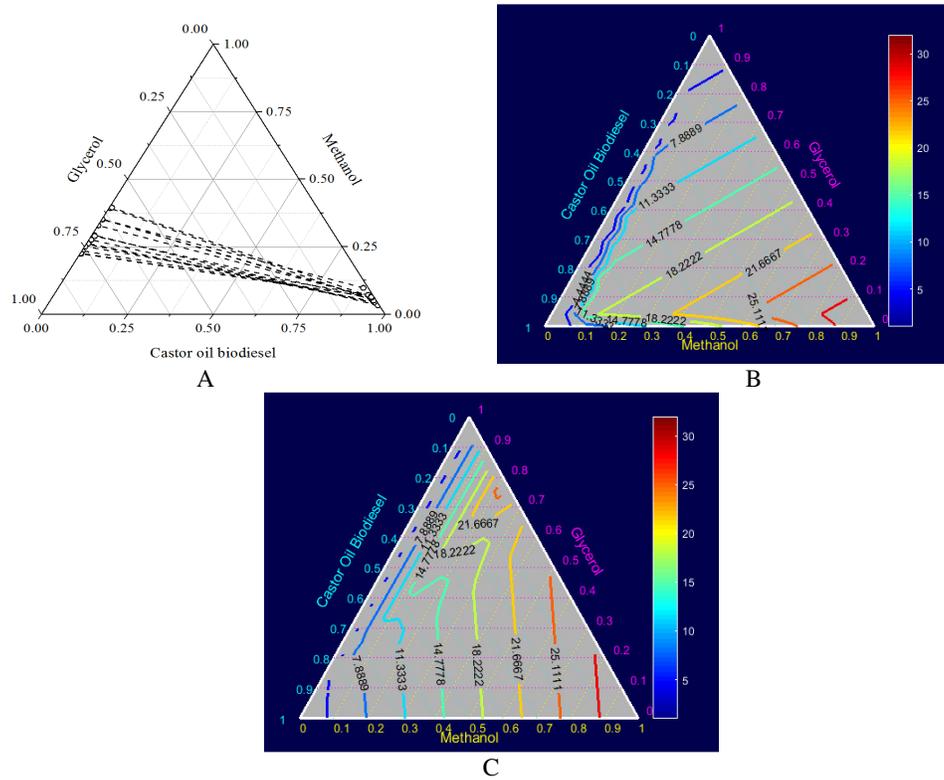


Figure 4: A) Tie line plot for castor oil biodiesel/glycerol/methanol system at 30°C, B) Biodiesel-rich phase ternary contour plot of mass fraction at different withdrawal time interval for 30°C, C) Glycerol-rich phase ternary contour plot of mass fraction at different withdrawal time interval for 30°C

Table 2: Distribution coefficient (K) and selectivity (S) at T= 20°C

Time (mins)	$K_{\text{glycerol}}$	$K_{\text{methanol}}$	S
2.00	0.016	0.341	21.313
4.00	0.014	0.313	22.357
6.00	0.013	0.214	16.462
8.00	0.016	0.177	11.063
10.00	0.022	0.134	6.091
12.00	0.011	0.267	24.273
14.00	0.033	0.230	6.970
16.00	0.055	0.148	2.691
18.00	0.036	0.210	5.833
20.00	0.020	0.221	11.050
22.00	0.014	0.261	18.643
24.00	0.011	0.330	30.000
26.00	0.013	0.369	28.385
28.00	0.023	0.659	28.652
30.00	0.012	0.448	37.333
32.00	0.012	0.460	38.333

Table 3: Distribution coefficient (K) and selectivity (S) at T= 30°C

Time (mins)	K <sub>glycerol</sub>	K <sub>methanol</sub>	S
2.00	0.011	0.165	11.786
4.00	0.014	0.179	12.786
6.00	0.016	0.272	17.000
8.00	0.017	0.287	16.882
10.00	0.008	0.149	18.625
12.00	0.014	0.205	14.643
14.00	0.006	0.113	18.833
16.00	0.012	0.195	16.250
18.00	0.022	0.278	16.636
20.00	0.014	0.197	14.071
22.00	0.013	0.130	10.000
24.00	0.013	0.165	12.692
26.00	0.012	0.176	14.667
28.00	0.010	0.286	28.600
30.00	0.010	0.283	28.300
32.00	0.010	0.283	28.300

Also, from Tables 2 and 3, it was observed that both the distribution coefficient (K) and selectivity (S) were relatively high for the castor oil biodiesel mixture compositions at 20°C and 30°C and at the various times (Franca et al., 2009; Ardila et al., 2013). This trend is desirable because large values of K would mean that less of the solvent (methanol) would be needed for effective separation and purification and also for the glycerol extraction. The value of K, the distribution coefficient is a defining parameter in establishing the minimum solvent-to-feed ratio in any liquid-liquid extraction process. Thus, the relatively high values of solvent selectivity, S, exhibited was found to influence and cause significant increases in the capacity of methanol (the solvent) to retain the glycerol in the glycerol-rich phase and thereby minimizing its presence in the biodiesel-rich phase. The high solvent selectivity (S), was in agreement with several authors (Franca et al., 2009; Machado et al., 2012; Rostami et al., 2013; Noriega et al., 2016) who insisted that for all useful liquid-liquid extraction processes, the solvent selectivity must be greater than one and the further the selectivity value from one, the better the extraction process. Also, it was observed that the methanol distribution between the biodiesel-rich phase and the glycerol-rich phase was temperature-insensitive. This was due to the fact that at both temperatures, the K- values remained below one implying that methanol solubilized preferentially at both temperatures in the glycerol-rich phase which agreed with many research studies (Zhou et al., 2006; Andreatta et al., 2008; Franca et al., 2009). This showed that the effect of temperature increase had little or no effect on the methanol distribution coefficient during the investigated temperatures and times. The selectivity of castor oil biodiesel was observed to be such that it preferentially solubilized methanol or glycerol at all the temperatures investigated. Also, as seen from Tables 2 and 3, increasing values of methanol mass fraction in the glycerol-rich phase resulted in increased biodiesel or glycerol selectivity for methanol. Again, this phenomenon was observed to be due to the ability of the glycerol-rich phase to readily solubilize the methanol which in turn, solubilizes an equal value of glycerol and methanol in the biodiesel-rich phase. Also, it could be observed from Tables 2 and 3 that at individually investigated temperatures for castor oil biodiesel phase mixture composition, the selectivity gradually increased with time attaining the highest values for 'S' (38.33 at 32 minutes for 20°C and 28.30 at 32 minutes for 30°C) at the highest time. For instance, at temperature of 20°C, the selectivity was observed to be 21.313 at 2minutes time interval while at 32minutes time interval, the selectivity was observed to be 38.383. In all cases, as the distribution coefficient (K) either decreased or increased slightly with time, the selectivity (S) was observed to gradually increase attaining maximum value at the optimum time of the analysis. This relationship was observed to be replicated at all times and temperatures of the investigation. This behavior could be assumed to be due to the presence of phase interaction components amongst the two-phases and components present in each of the biodiesel-rich and glycerol-rich phases (Franca et al., 2009; Ardila et al.,

2013; Nangbes et al., 2013; Mosquera et al., 2016). Biodiesel, methanol and glycerol mixture systems are polar mixtures and highly non-ideal systems. They are mixtures of components with substantially different solubility parameters and as such, their activity coefficients were observed to be much greater than unity. Since the solubility parameter was sufficiently different, immiscibility was found to be prevalent and this confirmed the general trend that polar molecules like methanol and glycerol tend to have high solubility parameters while non-polar molecule like biodiesel, have low solubility parameters. Snyder and Kirkland (1979), postulated that the solubility parameter was related to the solvent polarity parameter. This parameter was a measure of the molecule's ability to participate in dispersion forces, dipole-dipole interactions, hydrogen bonding and dielectric interactions. In the present study, the ternary mixture of castor oil biodiesel, glycerol and methanol generally separated into two liquid phases. The biodiesel in this study was composed primarily of six different methyl esters with close solubility parameters.

#### 4. CONCLUSION

Ternary phase diagrams for castor oil biodiesel, methanol and glycerol system was developed at 20°C and 30°C temperature and for 2 mins to 32 minutes at 2 minutes time interval. The optimum areas for the castor oil biodiesel, methanol and glycerol at 20°C and 30°C were located using the ternary phase diagrams from the tie line data analysis. Hence, a ternary phase diagram could be easily used to locate the optimum area of influence in biodiesel purification. The phase mixture composition of the castor oil biodiesel ternary system was adequately described using the phase diagram which showed the mixture components at the coexistence regions or location when equilibrium was established amongst the components. The ternary diagram showed that the components of the phases was a representation of the equilibrium composition of the components in the mixture with methanol residing more towards the glycerol-rich phase due to its strong affinity for glycerol. The fundamental data inherent in the ternary phase development were the tie line data, distribution coefficient (K) and selectivity (S). These parameters are needed to properly define the ternary phase diagram and behavior of the castor oil biodiesel, methanol and glycerol mixture composition. Ternary phase diagrams elucidating on the phase composition of the castor oil biodiesel mixture composition was generated which would be useful in optimizing the purification process and in simulating model behavior for analyzing future biodiesel systems. The influence of temperature and time on the ternary phase process was minimal as a result of the strong affinity of methanol for glycerol which readily solubilizes in the glycerol-rich phase. The knowledge of the ternary phase equilibrium behavior in the castor oil biodiesel ternary mixture phase composition would create better understanding of the purification process, improvement in the reaction rate, selectivity of the desired product and enhancement of the purification process for the final product mixture.

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#### 6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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