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Temperature Effect on the Refinement of *Jatropha* Oil Biodiesel Upper-Rich Phase

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Abstract

Biodiesels obtained from renewable energy sources are considered to be good alternatives to traditional fuel sources due to their environmental friendliness. Purification of the biodiesel upper-rich phase composition after transesterification is often influenced by some parameters. This study investigated the influence of temperature and time interval on the purification of biodiesel upper-rich phase mixture composition of *Jatropha* oil biodiesel system consisting of *Jatropha* oil biodiesel, methanol, glycerol at (20°C, 25°C, 30°C, 35°C, 40°C, 45°C, 50°C, 55°C, 60°C) and (2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32) minutes respectively. The results were obtained by cloud point titration method under isothermal conditions at the different temperatures and time intervals and further analyzed using GC to provide the phase composition in mass fractions of the sample containing the mixture component. The analysis indicated increased mass composition of *Jatropha* oil biodiesel from 20°C to 60°C at intervals of 5°C attaining maximum value of 97.2% at 20°C, 97.4% at 40°C and 97.2% at 55°C for time intervals of 2 minutes in each case. This implied that temperature and time had minimal influence on the purification of the components of the *Jatropha* oil biodiesel upper-rich phase.

Keywords: *Jatropha* oil; Biodiesel; Temperature; Upper-rich phase; Purification; Mixture

Introduction

Due to the world's depletion of crude oil reserves, there has being greater awareness on renewable alternatives in most developed and industrialized countries of the world [1-8]. The purity level of any biodiesel is essential to its use as a fuel and invariably its fuel properties. Hence, the purification step after transesterification is very important and highly essential [9-11]. More recently, there has been laws permitting and regulating the addition of biodiesel into fossil fuels in many countries of the world and this has increased it usage tremendously [2,11-13].

The production of biodiesel is normally by the transesterification of vegetable oils or animal fats which is usually by alkaline, acid or enzyme catalyzed processes or non-catalyzed processes [5-8]. However, Meneghetti et al. [14] observed that alkaline catalysis is the most effective and widely applied method prevalent today. The use of NaOH or KOH forms soaps as a by-product which is the major disadvantage of alkaline catalysis. In the same manner, the reaction mixture after transesterification contains fatty acid methyl esters, triglycerides, diglycerides, monoglycerides, glycerol, methanol, soaps and minor amounts of other substances [6,15-17]. Thus, the separation of the resultant product mixture by sedimentation into the biodiesel phase and the glycerol phase is a very important step in the biodiesel production and purification process. At the completion of biodiesel production reaction, a heterogeneous liquid mixture is formed. Thus, the knowledge of liquid-liquid equilibrium is useful for understanding the steps in purification and separation of biodiesel-rich phases from glycerol-rich phases. Limited studies and researches on equilibrium data for biodiesel or fatty acid methyl esters+alcohol+glycerol systems have been reported by Authors [18-26]. Liquid-liquid equilibrium data on biodiesel transesterification using ethanol and the distribution of alcohol in biodiesel systems were reported by other researchers [27,28] studied the solubility curve systems of soybeans oil and castor oil biodiesel+ethanol+glycerol at different temperatures though the tie lines and LLE data were not determined.

Since the production and purification of biodiesel is normally characterized by multiple objectives, quantitative prediction of the system behavior from basic physical and chemical principles is often inadequate and sometimes difficult. By varying the proportions of each component in the mixture, it would be expected that the properties of the final product obtained could be well controlled. Liquid-liquid equilibrium of ternary mixtures involves a lot of challenges which includes chemical reaction of the liquid-liquid systems, phase separation of the products, complex two-phase flows, mass transfer from reaction and diffusion [10,16,21,29-31]. Equilibrium data for liquid-liquid ternary systems are needed to properly situate the reaction and purification process [4,19,20,24,32]. Adequate knowledge about the phase equilibrium which involves the determination of the solubility or binodal curve data or composition, and tie lines data or 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 [8,18,28,33,34]. Understanding the limits of biodiesel purification methods and selecting appropriate combinations of feedstock, parameters and purification steps are important steps required to achieve consistent quality of fuel [11,35-38].

In order to enhance the efficiency and effectiveness of the process, accurate phase equilibrium data for the interactions of the reaction products are required. Accurate phase data parameters, adequate

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equilibrium data-base and resource information are essential in biodiesel ternary phase development and purification processes; hence the need to develop phase diagrams representing the co-existing phases and those of stability regions when equilibrium is to be established among the phases in the biodiesel mixture [21,24,39-41]. Importantly, this would require the determination and development of ternary phase diagrams of fatty acid methyl ester (FAME)-biodiesel, methanol and glycerol which are the fundamental information for biodiesel purification [8,14,33].

The limited knowledge and information data-base of the influence of temperature and time interval on the purification of *Jatropha* oil biodiesel upper-rich phase equilibrium in the ternary mixture of *Jatropha* oil biodiesel/glycerol/methanol system and the limited-availability of equilibrium data-base on the ternary mixture essential for better understanding of the actual purification process, improvement in the reaction process, selectivity of the desired product and purification processes for the product mixture necessitated this research.

Materials and Methods

The experimental procedures involved the procurement of materials and equipment; pretreatment of the *Jatropha* non-edible oil bearing seeds; extraction of the oil from the non-edible oil bearing seed; characterization of the oil obtained for physicochemical properties; production of the biodiesel from the oil using transesterification reaction process; separation and purification of the upper biodiesel layer from the lower glycerol layer; investigating the properties of the ternary phase behavior of the purified upper biodiesel layer which consisted of biodiesel, methanol and glycerol respect to the temperature and time influences and development and construction of ternary phase diagram for the biodiesel phase mixture.

Materials

The *Jatropha* curcas oil was obtained by grinding the *Jatropha* seeds obtained from *Jatropha* curcas L. tree. The oil was extracted using hydraulic pressing machine and thereafter purified by filtering solid impurities with NaOH and activated earth. The chemicals used in the research were distilled water; fatty acid methyl esters (FAME) produced in the laboratory from *Jatropha* curcas; Glycerol >99% and methanol >99% both sourced from Sigma-Aldrich, Germany. The equipment used included burette, mechanical agitator-stirrer, pipette, analytical balance, water-bath (for temperature control), conical flasks, stop watch, beakers and GC/MS FID.

Experimental procedure

Reaction mechanism/biodiesel production: *Jatropha* seed oil was used in the production of the biodiesel. Cold-pressed *Jatropha* seed oil was obtained from the oil-bearing seed plant using hydraulic pressing machine with temperature controller having maximum load and pressure capacities of 400 g and 69 MPa respectively with piston diameter of 140 mm. The reaction mechanism employed in the production of the biodiesel was transesterification which was a reaction between triglycerides and alcohols to produce biodiesel in the presence of catalyst. *Jatropha* biodiesel was prepared in a batch glass reactor (500 ml) from the *Jatropha* oil with a molar ratio of 6:1 for methanol and oil respectively. The amount of catalyst used was 5% w/v at a temperature of 60°C for 1 hour. The *Jatropha* biodiesel was prepared in the laboratory by transesterification of the *Jatropha* oil with methanol and potassium hydroxide as the catalyst with constant agitation achieved at stirrer speed set of 1200 rpm. This was maintained throughout the reaction. Cold-pressed filtrated *Jatropha* seed oil with acid value of 0.988 mgKOH/g, free fatty acid as oleic of 0.454, density of 0.887 kg/m^3 and moisture content of 0.196% g/g Oil produced in the laboratory was used in the transesterification with methanol. When the reaction was completed, the contents of the reaction chamber was drained into a separating funnel and the mixture allowed to separate into two layers with the biodiesel layer on top and the lower layer consisted of mixtures of glycerol and methanol. Thereafter, the lower layer was drained off. The biodiesel top layer was then washed with one litre of acidified water (0.01 M H_2SO_4) to neutralize any catalyst remaining and washed with one litre of distilled water to remove glycerol and soaps. Furthermore, the biodiesel sample was centrifuged in a centrifuge (Mark IV, Auto Bench, Baird and Tatlock Ltd, London, UK) at 5°C for ten minutes at 5000 rpm to remove water, traces of impurities and any remaining soaps The biodiesel obtained after separation was thereafter dried in a Thermotech TIC-4000E oven with temperature controller to remove the remaining water and any methanol still present by evaporation. Samples of the biodiesel were subsequently stored in small containers with septum covers and refrigerated. The biodiesel was subsequently analyzed using PerkinElimer® Clarus®600 gas chromatography connected to a flame detector.

***Jatropha* biodiesel and oil characterization:** The content of the *Jatropha* oil and *Jatropha* biodiesel were determined by GC method using FAME norm in accordance with EN14214, EN14103 and EN14105. The instrument used was a Perkin Elmer® Clarus® 600 GC connected to a flame ionization detector (FID). The criterion which was both qualitative and quantitative for the analysis of the biodiesel produced was specified in EN14214 and EN14103 for fatty acid methyl ester (FAME) and linolenic acid methyl esters content respectively. These methods were also used to profile the oil feedstock used in the biodiesel production. Calibration was made of all FAME components by relative response to a single component; methylheptadecanoate and this required the measurement of accurate weights of the sample and addition of an internal standard. The range of FAME, for which the method was applicable, fell within the range of C14: 0 and C24:1. Quantification was done with the aid of Chem Station Data handling software.

The biodiesel analysis was carried out with a split injection onto an analytical column with a polar stationary phase and a flame ionization detector (FID). The analytical column was the PerkinElmer Elite-Famewax column (Crossbond®polyethylene glycol). The inlet temperature was maintained at 250°C with a column flow rate of 1 ml/min, split flow of 50 mL/min and injection volume of 0.5 µL. The initial and final temperature of the oven program was set at 210°C and 230°C respectively with a hold time 1 and hold time 2 of 13.00 min and 15.00 min respectively while the equilibration time was 0.0 min. The ramp 1 was set at 5 C/min while Elite-Famewax, 30 m × 320 µm × 0.25 µm film column was used. Helium was used as the carrier gas while the flame ionization temperature (FID) was set as 250°C, hydrogen and air flow rates of 45 mL/min and 450 mL/min respectively with a range and attenuation of 1 and -5 respectively.

The analysis undertaken made use of FAME mixture at known concentration and determined the response and retention time of each component experimentally. The results for the fatty acid methyl ester content was expressed as mass fraction using commercial mix of FAME as calibration-check internal standard. Total FAME content was greater than 90% while internal standard was greater than 1% but less than 15%. The internal standard was a mixture containing methyl palmitate, methyl oleate, methyl linoleate, methyl stearate and methyl heptadecanoate. A known weight (5 g) of oil or biodiesel sample was placed inside the sample holder. The sample holder was vigorously agitated for five minutes. Thereafter, excess sodium methoxide (15 ml) was added into the sample holder containing the oil or biodiesel sample. The phases were then allowed to stabilize for ten minutes and from the stabilized phase, 1 μL of the upper layer of the mixture was then injected into the GC for the analysis and quantification.

Determination of phase diagram of biodiesel+Methanol+Glycerol (binodal or solubility curve composition and tie line composition): The tie-line and binodal or solubility curve composition for the *Jatropha* oil ternary system at the different temperatures and time intervals was determined by the cloud-point method using titration procedure under isothermal conditions employed by several researchers [3,4,7,19,23,24,26]. This entailed the determination of the biodiesel-rich phase composition data, binodal or solubility curve composition data and tie-lines composition data at the different temperlatures of (20°C, 25°C, 30°C, 35°C, 40°C, 45°C, 50°C, 55°C and 60°C) and at time intervals of (2, 4, 6, 8, 10, 12, 14,16,18, 20, 22, 24, 26, 28, 30 and 32) minutes. The objective in creating the *Jatropha* oil biodiesel/glycerol/methanol ternary mixture phase diagram was to determine compositions along the binodal or solubility curve corresponding to the tie lines. Each component (biodiesel, methanol and glycerol) was weighed using AG200 analytical balance with precision of ± 0.00006 g. Mixing of components was done at approximately 1200 rpm and vigorously agitated with a Fisatom 752 A magnetic stirrer for four (4) hours at the specific temperature to allow for good and intimate contact between the phases. Equilibrium was achieved by letting the mixture rest or settle for twenty four (24) hours until complete separation into two clear liquid phases were clearly observed. Preliminary experiments conducted showed that the agitation and separation time was adequate for the system to reach equilibrium.

The mixture (*Jatropha* oil biodiesel or methanol against glycerol and glycerol and methanol against *Jatropha* oil biodiesel) was titrated under constant stirring using a magnetic stirrer (Fisatom 752A) until phase transition on the ternary mixture was observed (i.e., change from transparent to turbid). The temperature was regulated by a thermostatic water bath (Tecnal TE-184) with an accuracy of ± 0.001 K. A thermometer was also used to monitor the temperature. The cloud point was considered to be the binodal curve point. Initial and final components were always weighed on an analytical balance (Shimadzu) with an accuracy of 0.0001 g to determine mass of the components. The mixture system homogenization was enhanced by using a magnetic stirrer for four (4) hours. The ternary mixture was then left to rest for twenty four (24) hours in a thermostatic water bath at the desired temperature, until two separate, transparent liquid phases were clearly observed. After the time needed for stabilization, phase separation was visually observed with well-defined interface. The phases were then separated. After separation of the biodiesel-rich and glycerol-rich phases, 5 ml sample each of both separate phases in equilibrium was carefully collected from each phase using disposable syringe at two minutes interval at the specific temperature and analyzed to determine their composition by GC analysis. The mass fraction of biodiesel, methanol and glycerol in both phases was determined by GC methodology.

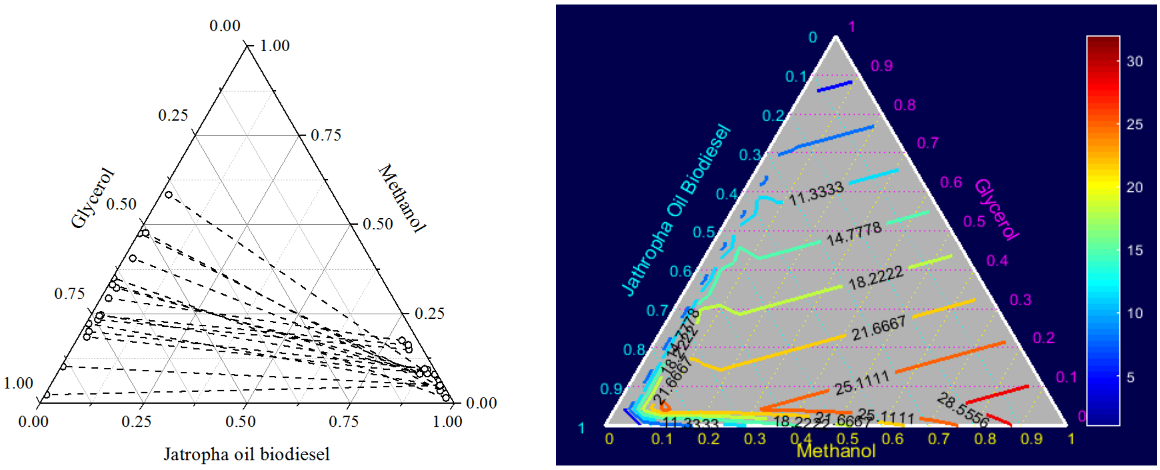
The quantitative determination of the phase composition was carried out using calibration curves (external calibration) obtained using standard solutions for each component. The experimental data for each tie line at the different time intervals and temperatures was replicated three times.

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. Phase composition in mass fraction was determined using calibration curves. Calibration curves were obtained by gas chromatography (GC) coupled with flame ionization detector (FID).

Results and Discussion

The results of the analysis of the influence of temperature and time interval of the tie line data and plots on the *Jatropha* oil biodiesel upper-rich phase at the investigated temperatures and time intervals are shown in Figures 1-9.

From the results shown in Figures 1-9, it could be seen that there



A

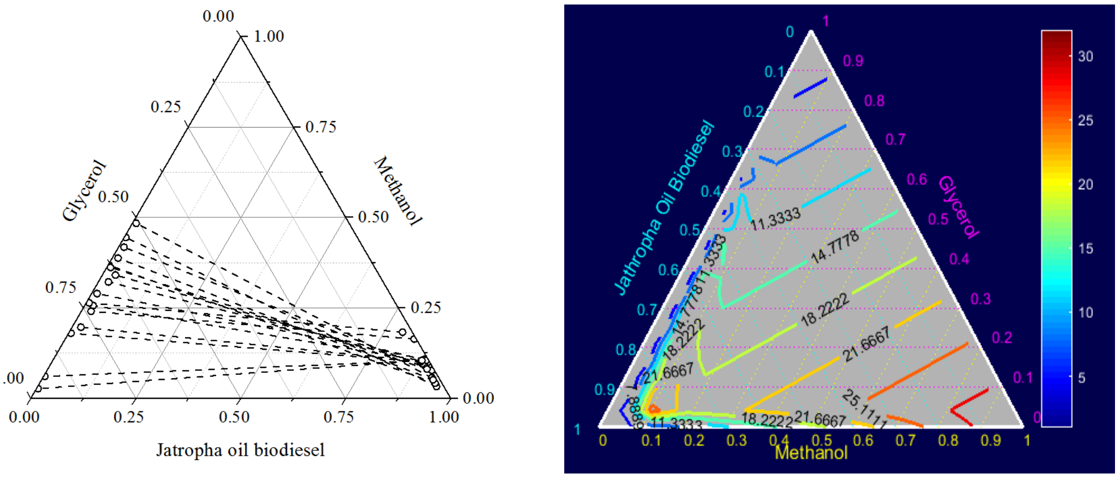
B

Figure 1: (A) Tie Line Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 20°C; **(B)** Biodiesel-rich Phase Ternary Plot of Mass Fraction at Different Withdrawal Time Interval for 20°C.

were gradual increases in mass fraction composition of *Jatropha* oil biodiesel from 20°C to 60°C at intervals of 5°C and time intervals of 2 minutes each at the investigated parameters. In the ternary phase diagram plot of Figures 1A-9A, it could be seen that the compositions between the equilibrium biodiesel-rich phase and the glycerol-rich phase was represented by the tie lines. The biodiesel-rich phase and the glycerol-rich phase that were in equilibrium are the conjugate phases. From the figures, it could be seen that the tie lines were not horizontal at the investigated compositions. It could also be observed that the solubility of methanol was lower in the biodiesel-rich phase as seen by the size of the two phase region bordering methanol and glycerol and the gradient of the tie lines. 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 temperatures of 20°C to 60°C. 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 the same 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 were evenly distributed approaching global composition at some points and deviating from equilibrium global composition at some other points due to dispersive forces. The results showed that the mass composition of *Jatropha* oil biodiesel increased from 20°C to 60°C for temperature interval of 5°C attaining maximum value of 97.2 mg/ml% at 20°C, 97.4 mg/ml% at 40°C and 97.2 mg/ml% at 55°C for time interval of 2 minutes in each case. At other temperatures of 25°C, 30°C, 35°C, 45°C, 50°C and 60°C, the mass composition was observed to be 95.0 mg/ml%, 96.4 mg/ml%, 95.5 mg/ml% 96.7 mg/ml%, 95.9 mg/ml% and 95.6 mg/ml% respectively. It was also observed that the influence of time interval on the *Jatropha* oil biodiesel upper-rich purification was such that the mass composition was relatively constant from 2 minutes to 12 minutes reducing marginally from 14 minutes to 26 minutes time interval and maintained a gradual increase between 28 minutes to 32 minutes. This could be observed from the slope of the tie lines of Figures 1A-9A. The same pattern was observed for the methanol and glycerol components of the *Jatropha* oil biodiesel upper-rich phase. Across the different temperatures from 20°C to 60°C, it could be seen from Figures 1A-9A that the gradient of the tie lines were relatively horizontal and parallel at similar angles except for 20°C, 40°C, and 55°C. It was also observed that the mass composition of *Jatropha* oil biodiesel, methanol and glycerol in the upper-rich phase was relatively constant from 25°C to 35°C, 45°C to 50°C and 60°C at average values of 95.6 mg/ml%, 96.3 mg/ml% and 95.6 mg/ml% respectively. Figures 1B-9B shows the biodiesel-rich phase ternary plot of mass fraction at the different time intervals and at the different temperatures. From the Figures, it could be seen that the influence of temperature and time interval on the purification of the *Jatropha* oil biodiesel upper-rich phase was such that the mass composition of *Jatropha* oil biodiesel decreased with increasing time interval from 2 minutes to 26 minutes with a slight increase from 28 minutes to 32 minutes at 20°C and with similar trend at the other temperatures. The colored bar indicated that between 2 minutes to 26 minutes, more of the *Jatropha* oil biodiesel in the ternary mixture was withdrawn and analyzed from the upper-rich phase composition. Each analysis gave a mass composition of the three components and as the time increased, more of the biodiesel component was withdrawn for analysis with less of glycerol and methanol. The was also observed and shown in the tie line plots of Figures 1A-9A.

The results of the analysis of the binodal or solubility curve data and plots on the influence of temperatures and time intervals on the purification of *Jatropha* oil biodiesel upper-rich phase composition are shown in Figures 10-18.

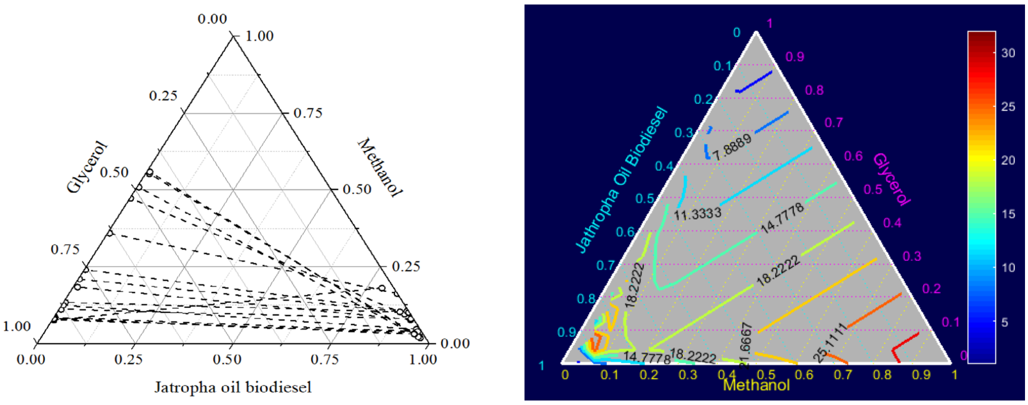
Figures 10A-18A shows the binodal or solubility curve plots for *Jatropha* oil biodiesel, glycerol and methanol systems at the different temperatures and time intervals on the purification of *Jatropha* oil biodiesel upper-rich phase. Similarly, Figures 10B-18B shows the ternary composition plot at the different withdrawal time intervals for the different temperatures. From the experimental analysis, it was



A

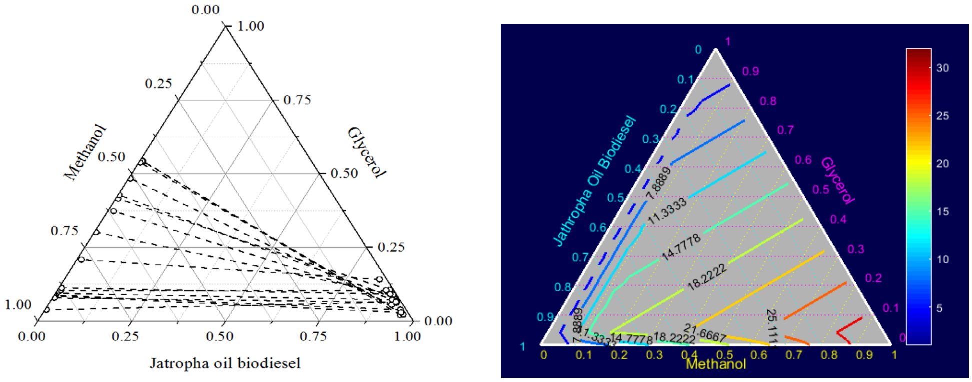
B

Figure 2: (A) Tie Line Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 25°C; **(B)** Biodiesel-rich Phase Ternary Plot of Mass Fraction at Different Withdrawal Time Interval for 25°C.



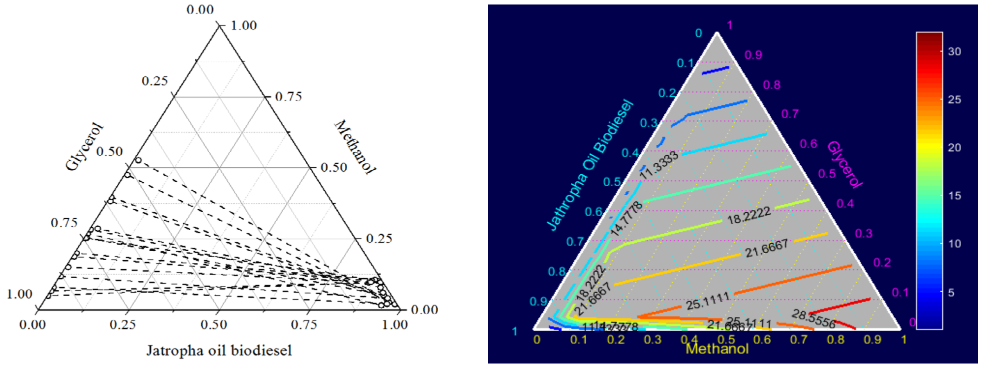
A **B**

Figure 3: (A) Tie Line Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 30°C; **(B)** Biodiesel-rich Phase Ternary Plot of Mass Fraction at Different Withdrawal Time Interval for 30°C.



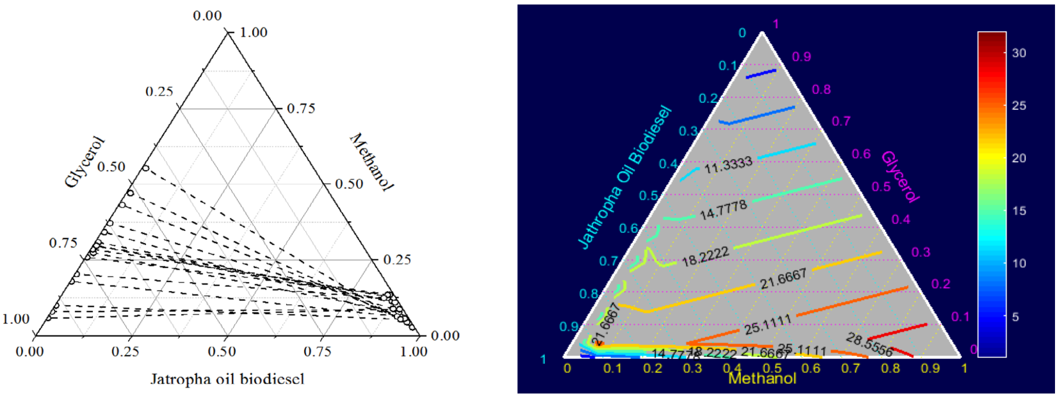
A **B**

Figure 4: (A) Tie Line Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 35°C; **(B)** Biodiesel-rich Phase Ternary Plot of Mass Fraction at Different Withdrawal Time Interval for 35°C.



A **B**

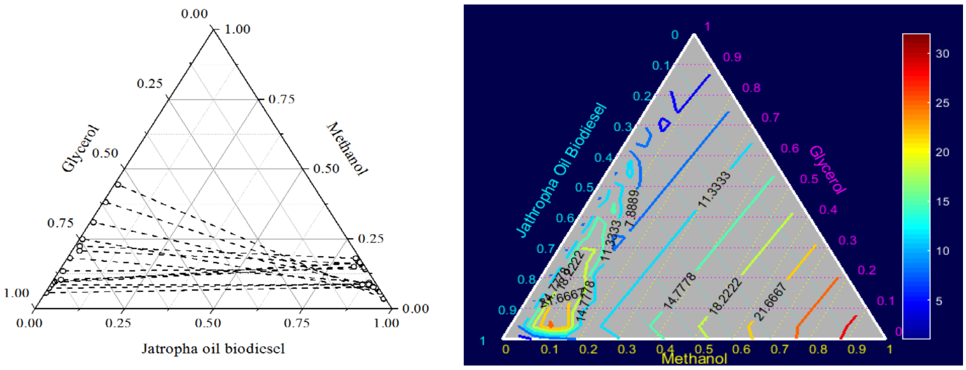
Figure 5: (A) Tie Line Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 40°C; **(B)** Biodiesel-rich Phase Ternary Plot of Mass Fraction at Different Withdrawal Time Interval for 40°C.



A

B

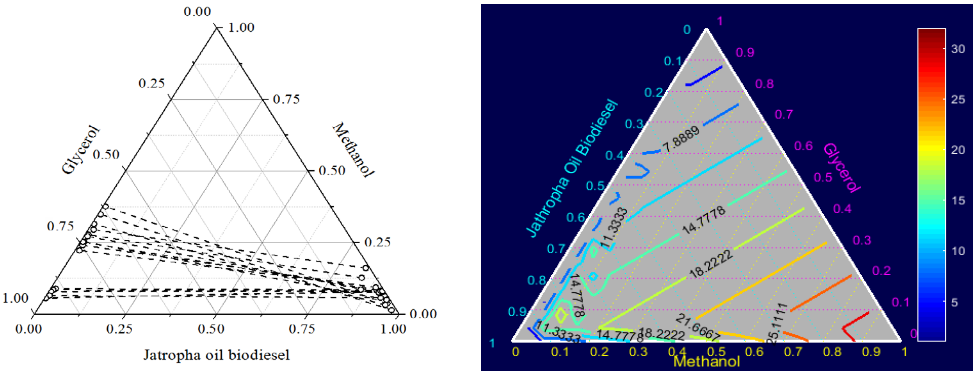
Figure 6: (A) Tie Line Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 45°C; **(B)** Biodiesel-rich Phase Ternary Plot of Mass Fraction at Different Withdrawal Time Interval for 45°C.



A

B

Figure 7: (A) Tie Line Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 50°C; **(B)** Biodiesel-rich Phase Ternary Plot of Mass Fraction at Different Withdrawal Time Interval for 50°C.



A

B

Figure 8: (A) Tie Line Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 55°C; **(B)** Biodiesel-rich Phase Ternary Plot of Mass Fraction at Different Withdrawal Time Interval for 55°C.

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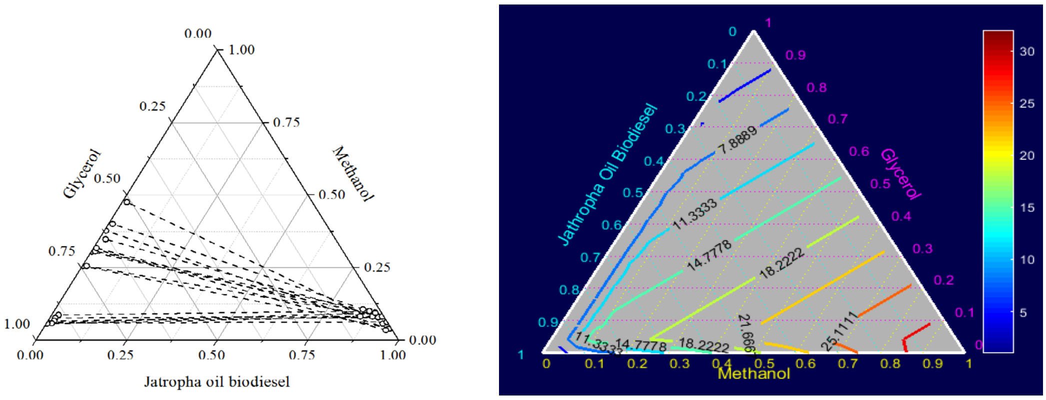
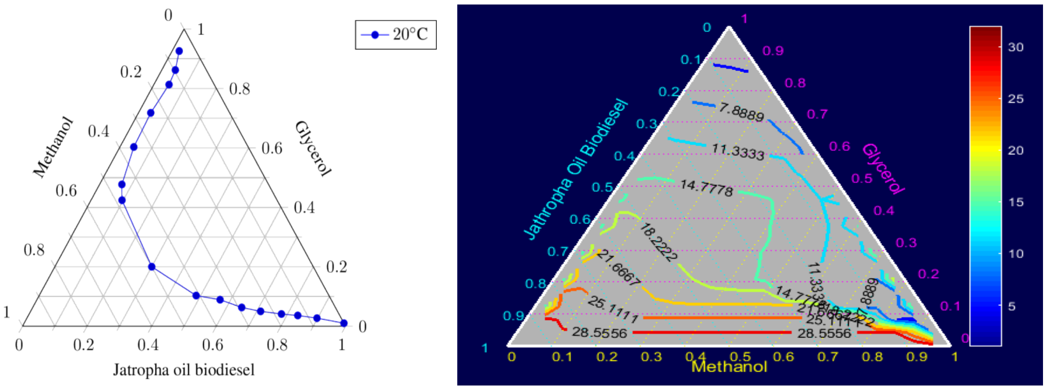


A

B

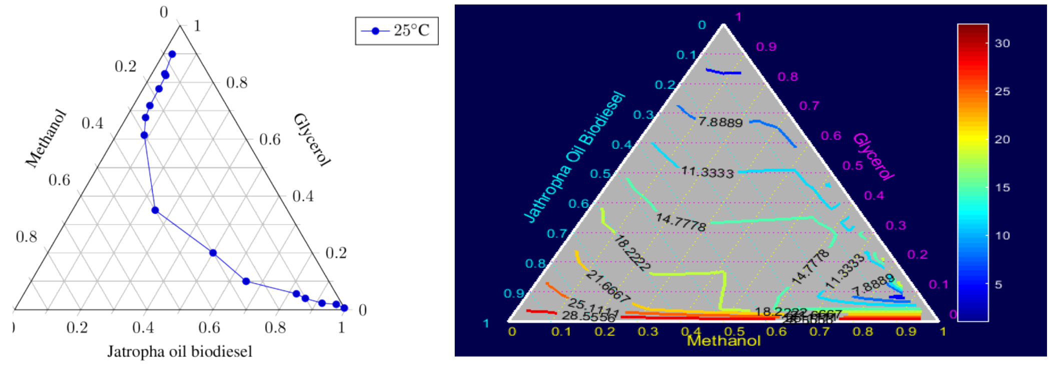
Figure 9: (A) Tie Line Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 60°C; **(B)** Biodiesel-rich Phase Ternary Plot of Mass Fraction at Different Withdrawal Time Interval for 60°C.



A

B

Figure 10: (A) Binodal Curve Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 20°C; **(B)** Ternary Composition Plot at Different Withdrawal Time Interval for 20°C.



A

B

Figure 11: (A) Binodal Curve Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 25°C; **(B)** Ternary Composition Plot at Different Withdrawal Time Interval for 25°C.

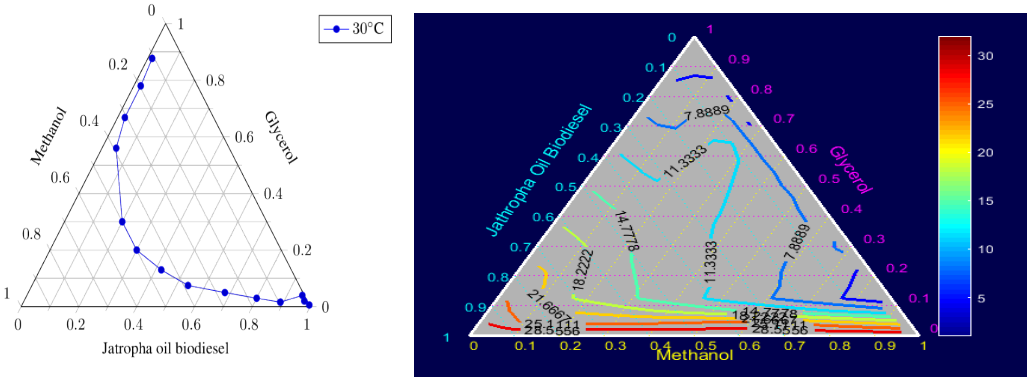
observed that *Jatropha* oil biodiesel and methanol as well as glycerol and methanol were completely miscible and soluble in each other. However, glycerol and *Jatropha* oil biodiesel were completely immiscible but partially soluble in each other. This was observed from the binodal or solubility ternary phase diagrams at the different temperatures and times investigated as shown in Figures 10-18. The results of the data analysis and plots of the binodal or solubility curve showed that the solubility of the ternary mixture was insignificantly affected by changes in both temperature and time intervals within the range of 20°C to 60°C temperature range and 2 minutes to 32 minutes time interval. At higher time interval of 28-32 minutes, the ternary phase composition was observed to be uniform at all the temperatures investigated meaning that any further increase in the time interval would virtually have minimal effect on the solubility of the constituent of the phases. At initial time intervals, it could be seen that the composition of the phases were uniform between 2 minutes to 8 minutes and thereafter, there were increases and decreases in phase composition at the different time intervals. This trend was observed at all temperatures investigated until a stable and uniform/consistent mixture composition was attained in which any further increase in time interval had no effect on the phase composition. A steady and constant concentration of methanol was observed to be maintained at higher operating time interval in the biodiesel-rich phase. In the biodiesel-rich phase, it was observed that the biodiesel concentration decreased with increasing temperature and time intervals. At 20°C, the concentration of biodiesel in the biodiesel-rich phase was 2.20 wt%. This was at a time interval of 2 minutes. At time interval of 32 minutes, the biodiesel concentration was 99.0 wt%. There was a consistent composition or concentration of biodiesel with increasing time intervals from 2 minutes to 32 minutes across all the temperatures investigated. It could be seen from the binodal plots of Figures 10-18 that at higher time interval of between 26 minutes to 32 minutes, more of the biodiesel was withdrawn from the upper-rich phase with less of glycerol and methanol present in the mixture phase. However, it was observed that the effect of temperature on the purification process was insignificant as the mass composition at the optimum time of 32 minutes was observed to be averagely 99.1 wt% at all the temperatures. This trend could be ascribed to the fact that at longer periods, the biodiesel tended to solubilize the methanol in the biodiesel rich-phase due to its affinity for methanol. Hence, higher time interval adversely affected the solubility of biodiesel in the ternary mixture. Across the different temperatures, the influence and effect of temperature increases was slightly significant. Hence, temperature influence or effect was observed to be generally minimal. Figures 10B-18B shows the biodiesel-rich phase ternary composition plots at different withdrawal time intervals at the different temperatures investigated. From the plots, it could be seen that the influence of temperature and time interval on the purification of the *Jatropha* oil biodiesel upper-rich phase was such that the mass composition of *Jatropha* oil biodiesel increased with increasing time interval from 2 minutes to 32 minutes at 20°C. The color bars indicated the levels of biodiesel, glycerol and methanol withdrawals with time interval from 2 minutes to 32 minutes at the different temperatures. The range of colour bar and time interval was a representation of the major component withdrawn at the particular period though each withdrawal time interval showed the three components present at the particular withdrawal time interval and temperature. From Figure 10B, at 20°C, it could be observed that more of *Jatropha* oil biodiesel was withdrawn between 16 minutes to 32 minutes, more of methanol was withdrawn between 8 minutes to 24 minutes and between 2 minutes to 16 minutes, more of glycerol was withdrawn from the *Jatropha* oil biodiesel upper-rich phase mixture composition. This pattern was observable at all other temperatures investigated.

Conclusions

The study of the influence of temperature and time interval on the purification of *Jatropha* oil biodiesel upper-rich phase mixture composition revealed the following:

There were gradual increases in mass fraction composition of *Jatropha* oil biodiesel from 20°C to 60°C at intervals of 5°C and time intervals of 2 minutes each at the investigated parameters. The solubility of methanol was lower in the biodiesel-rich phase as seen by the size of the two phase region bordering methanol and glycerol and the gradient of the tie lines. The glycerol concentration in the biodiesel-rich phase was observed to be 0.01 wt% at 20°C and optimum time interval of 32 minutes. This trend was observed to be prevalent at all the time intervals investigated at temperatures of 20°C to 60°C.

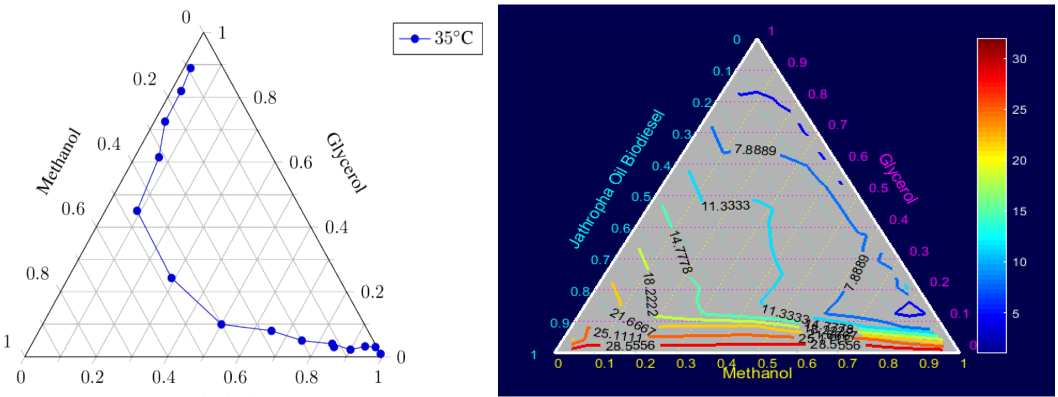
The mass composition of *Jatropha* oil biodiesel increased from 20°C to 60°C for temperature interval of 5°C attaining maximum value of 97.2 mg/ml% at 20°C, 97.4 mg/ml% at 40°C and 97.2 mg/ml% at 55°C for time interval of 2 minutes in each case. The mass composition of *Jatropha* oil biodiesel, methanol and glycerol in the upper-rich phase



A

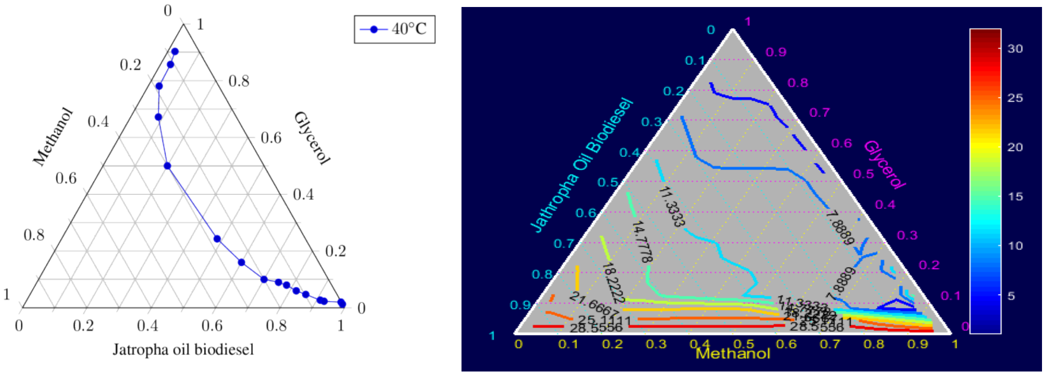
B

Figure 12: (A) Binodal Curve Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 30°C; **(B)** Ternary Composition Plot at Different Withdrawal Time Interval for 30°C.



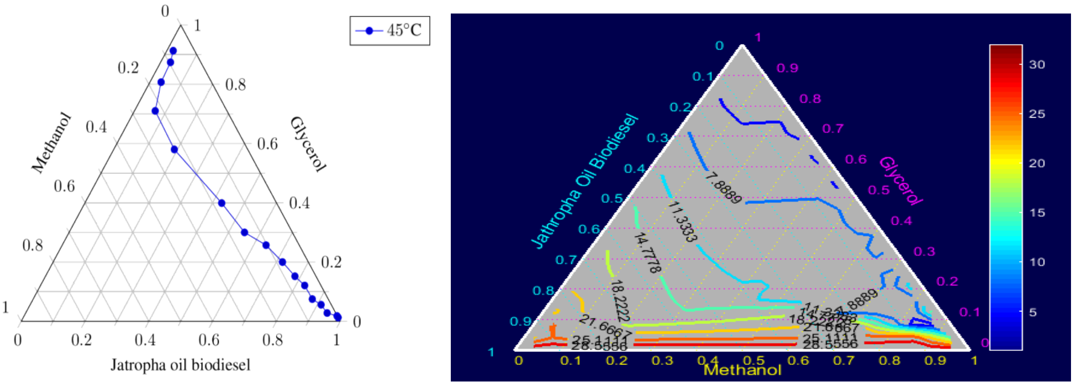
A **B**

Figure 13: (A) Binodal Curve Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 35°C; **(B)** Ternary Composition Plot at Different Withdrawal Time Interval for 35°C.



A **B**

Figure 14: (A) Binodal Curve Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 40°C; **(B)** Ternary Composition Plot at Different Withdrawal Time Interval for 40°C.



A **B**

Figure 15: (A) Binodal Curve Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 45°C; **(B)** Ternary Composition Plot at Different Withdrawal Time Interval for 45°C.

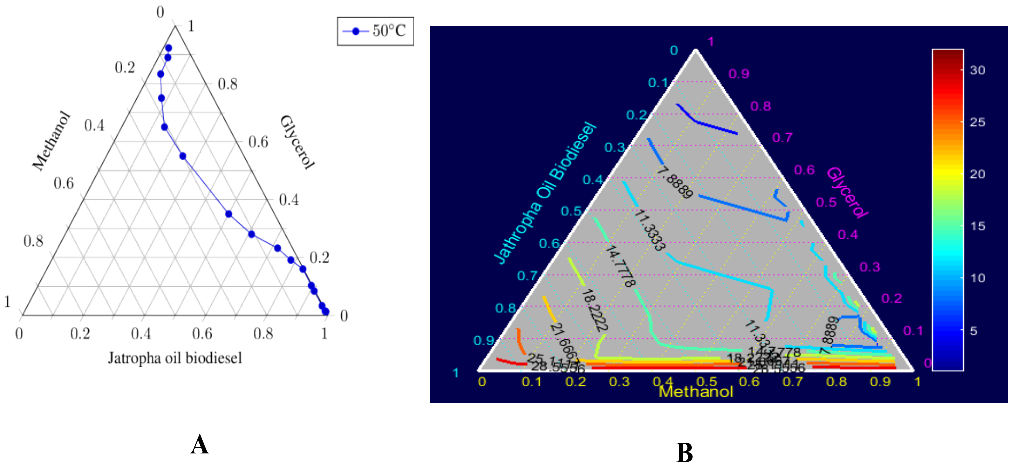


Figure 16: (A) Binodal Curve Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 50°C; **(B)** Ternary Composition Plot at Different Withdrawal Time Interval for 50°C.

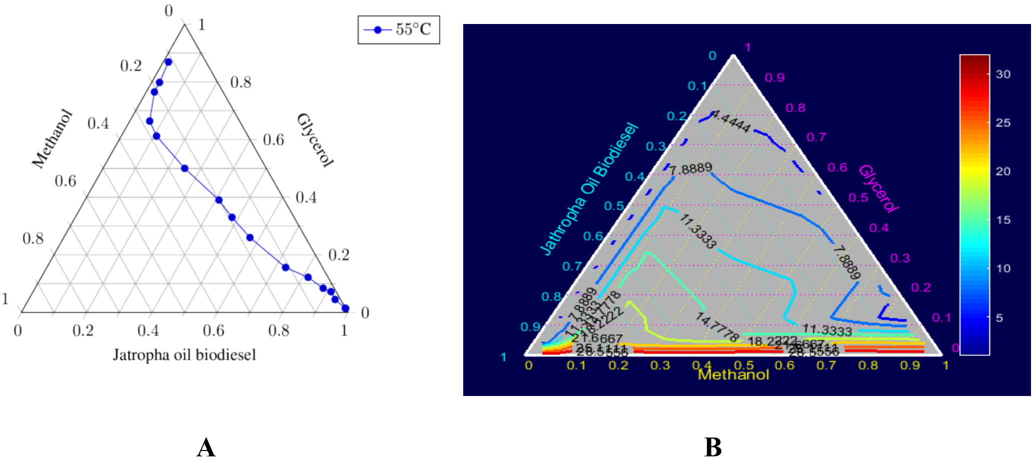


Figure 17: (A) Binodal Curve Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 55°C; **(B)** Ternary Composition Plot at Different Withdrawal Time Interval for 55°C.

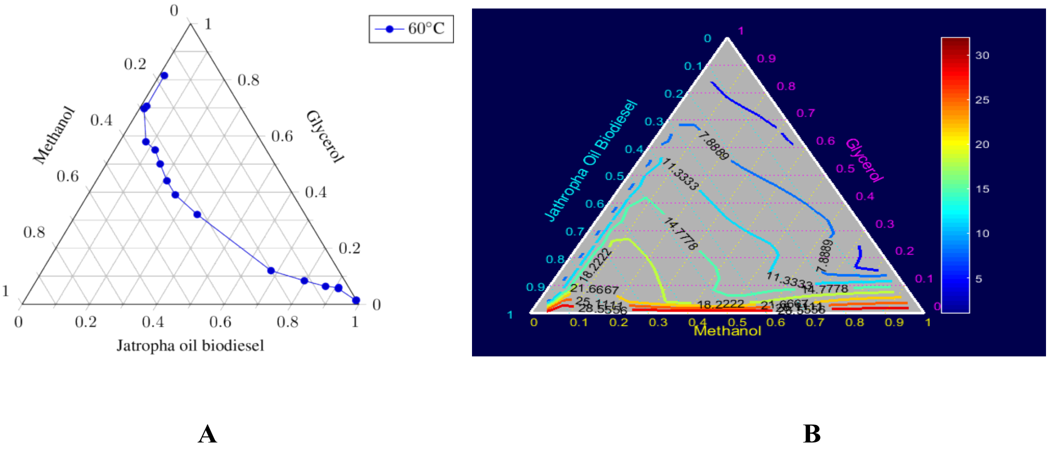


Figure 18: (A) Binodal Curve Plot for *Jatropha* Oil Biodiesel/Glycerol/Methanol System at 60°C; **(B)** Ternary Composition Plot at Different Withdrawal Time Interval for 60°C.

was relatively constant from 25°C to 35°C, 45°C to 50°C and 60°C at average values of 95.6 mg/ml%, 96.3 mg/ml% and 95.6 mg/ml% respectively. The effect of temperature on the purification process was minimal as the mass composition at the optimum time of 32 minutes was observed to be averagely 96.1 wt% at all the temperatures. The solubility of the ternary mixture was minimally affected by changes in both temperature and time intervals within the range of 20°C to 60°C temperature and 2 minutes to 32 minutes time interval.

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