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A Comparative Azeotropic Research on Combustion of Common Ternary Systems

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Abstract: Methyl Tertiary Butyl Ether (MTBE) and Methanol are effective fuel oxygenate that boost octane number, improve fuel performance, combustion behavior and minimize environmental pollutant emissions. In the petroleum business, however, their high-water solubility restricts their use in terms of fuel homogeneity loss. This work presents a full investigation map for the status of the phase diagram for the tertiary system of MTBE-methanol-water at different temperatures; 0, 40, and 70oC, and different pressures; 1.0 and 3.0 atm, based on different compositions. Furthermore, the thermodynamic coefficient, UNIFAC-LL, was linked to the Aspen plus Version 9. After validation of the software by the real experimental data, the software was used to complete the full map at all missing conditions. Pressure does not influence the occurrence of phase transitions, but the temperature has a minor effect on the LLE. The methanol concentration at which phase separation occurred dropped from 43% to 31.2% when the temperature was lowered from 70 to 40°C. With the use of simulation, the compositions at which phase separation occurs were also discovered. Last but not least, it was observed that the thermodynamic model (UNIFAC-LL) properly predicted the behavior of the methanol-water–MTBE ternary system with less than 3% inaccuracy in the binodal curve points. Consequently, a validated phase diagram is developed to accurately predict the physical state of the MTBE-methanol-water system at ant temperature, pressure, and mole fraction of each component. Hence, it guarantees the feasibility of using this tertiary system, as an effective octane booster additive, under severe working conditions.

Keywords: Liquid-Liquid Separation; Azeotrope Equilibria; Pressure-Temperature Optimization; High-Octane Ternary Systems; Gasoline Oxygenates.

1. Introduction

When ignition occurs within gasoline engines, harmful pollutants; CO_2, CO, and CxHy are released into the atmosphere. Fossil fuel burning, while a necessary energy source is clearly to blame for the huge rise in pollution caused by the pollutants from that fuel's burning. These emissions may serve as a tipping point for hazardous climate changes brought on by human-caused global warming [1]. As a result, the need for additional petroleum fuels is unavoidable, notwithstanding the environmental consequences. Demand for petroleum fossil fuels is rising drastically due to an expanding global population, despite global rules encouraging limiting usage [2]. It's anticipated that the worldwide demand for gasoline would climb by 40% by 2040 [3]. Fuel demand cannot be fulfilled only through

renewable sources such as biofuels, solar cell automobiles, electric vehicles, natural gas, dimethyl ether (DME), and hydrogen fuel cells. This needs a combination of fossil fuels and renewable energy sources [4]. Hydrocarbons make up the vast majority of petroleum products, including gasoline mixtures. Paraffin, aromatics, olefins, and naphthenes are the basic groups of hydrocarbons. Also they have several applications in the field of energetic materials [5-7]. There may also be certain inorganic metal particles in the formation of gasoline blends, such as sulfur dioxide, nitrogen, and oxygen. The ignition quality and flammability of gasoline mixes must be carefully examined as a result [8]. The octane number can be used to determine the quality of petroleum gasoline. The percentage of 2,2,4-trimethylpentane (isooctane) is comparable to the octane number value. It is the octane number that determines the performance of a car's gasoline. It provides specifics on motor efficiency, power loss, and pollution levels directly from the motor. When the engine's knocking efficiency is low, this is a telltale sign that something has to be done about it. Uncontrollable burning can lead to knocking, which happens when the fuel blend is ignited before a proper spark [9]. To avoid the undesired knocking, ideal operating conditions for the engine are achieved [10]. As octane numbers in gasoline fuels rose, numerous experts were interested in investigating this subject matter several substances marketed as "octane boosters" were put to the test in this regard. These are mostly oxygenated molecules, such as Methyl Tertiary Butyl Ether (MTBE), isooctane, DMM (dimethoxymethane), ETBE, and DIPE (di-isopropyl ether) [11]. Enhancing the combustion process, enhancing fuel quality, and reducing pollutants are all benefits of adding oxygenates to gasoline mixes [12]. These days, gasoline fuel formulas would not be complete without the addition of additives. Fuel quality and qualities have a considerable influence on this. As an added benefit, the introduction of new desirable qualities into the gasoline results in improved performance and longer storage life, all while keeping the cost of the fuel low. In refineries or directly by the customer, additives might be utilized. There are several more roles that gasoline additives serve, including lubrication and anti-knocking as well as metal deactivation and anti-rusting [13]. The petrochemical industry is well-versed in the use of MTBE, a substance with a long history of use. Octane number and knocking are greatly improved by using MTBE as a colorless, clear, low viscosity oxygenate [14]. However, an efficient separation method is required for the Azeotropic combination of methanol and MTBE to synthesize in an acidic medium [15]. Due to MTBE's relatively high-water solubility, it is not widely used as an efficient fuel additive. Because of the high-water solubility of MTBE, the subterranean aquifers were permanently contaminated [16]. In 1995, thousands of water wells in the United States were found to be polluted with MTBE [3]. As a result of these incidents, the US government banned the use of MTBE in 2002. MTBE is one of the many compounds that may be synthesized using methanol. Even more promising, it might cleanse and reduce the groundwater pollution of MTBE. Furthermore, it has been utilized as a fuel for transportation and racing vehicles for a long time. Due to its high research octane number (RON), methanol is utilized as an octane booster in the petrochemical and gasoline industries [17]. In the energy sector, methanol's relevance is amplified by its easy production from readily available sources like biomass and natural gas, which might compensate for the scarcity of petroleum supplies caused by rising demand. As a source of energy, methanol was employed either in its pure form or in a variety of gasoline mixtures. When it comes to gasoline, methanol-MTBE mixes are among the most frequent. Octane number and pollutant emissions are the main characteristics of this blend. The phase separation issue with methanol-MTBE blends in the presence of water is a key drawback that has prevented this mixture from being used on several occasions [18]. In this research, the liquid-liquid phase transitions of the MTBE-Methanol-Water ternary system have been extensively studied. The study covers a wide variety of temperatures and pressures, including 0, 40, and 70 degrees Celsius, and 1.0 and 3.0 atm. A variety of MTBE, water, and methanol mixes were employed to make up twenty distinct analytical sample mixtures. A new version of Aspen Plus, version 9, was used to link the experimental results to the activity coefficient model (UNIFAC-LL). Calculating the absolute errors and % relative errors in the compositions of the points on the binodal curve allowed us to assess the model's forecasting accuracy. As part of our investigation, we'll be looking at the conditions under which a MeOH-MTBE mix preserves its homogenous composition while water is present.

2. Experimental Procedure

Methanol; 99.8% and MTBE; 99.5% were purchased from LOBA CHEMIE PVT. LTD (Mumbai, India). A modified LLE device was used to study the liquid-liquid phase transitions [19]. At first, the correct mole fraction of water was added to the MTBE solution. After then, methanol was added to the mixture to keep it from becoming too volatile. The mixture was agitated for 30 minutes in a water bath after the addition of methanol. As a result, a 24-hour rest period was required to ensure a stable equilibrium was established under the correct temperature and pressure conditions. A clear, hazy, or two-phase solution was seen to emerge after 24 hours of mixing. The HZGC-1212 gas chromatography analyzer (GC-2014C) was used to identify the compositions of the organic and aqueous phases in the latter scenario. At least two dozen unique samples were made for the investigation. As seen in Figure 1, shows each sample's ternary phase diagram location, as well as its code. Three distinct temperatures (0, 40, and 70 °C) and three different pressures (1.0 and 3.0 atm) were used in the tests to examine the impact of temperature and pressure on the phase transition of the ternary mixture. Several mole fractions of the three components were used, as given in Table 1 and Figure 1, to develop a full map for the investigated tertiary system.

Table 1. The mole fraction of each investigated sample of the MTBE-Methanol-Water Mixture.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
X_{MTBE}	0.9	0.45	0.95	0.85	0.4	0.7	0.75	0.3	0.5	0.65	0.2	0.3	0.55	0.1	0.26	0.45	0.0	0.15	0.05	0.07
X_{MeOH}	0.05	0.5	0.0	0.05	0.5	0.2	0.05	0.5	0.3	0.05	0.5	0.4	0.05	0.5	0.34	0.05	0.5	0.35	0.25	0.23
X_{H2O}	0.05	0.05	0.05	0.1	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.7	0.7
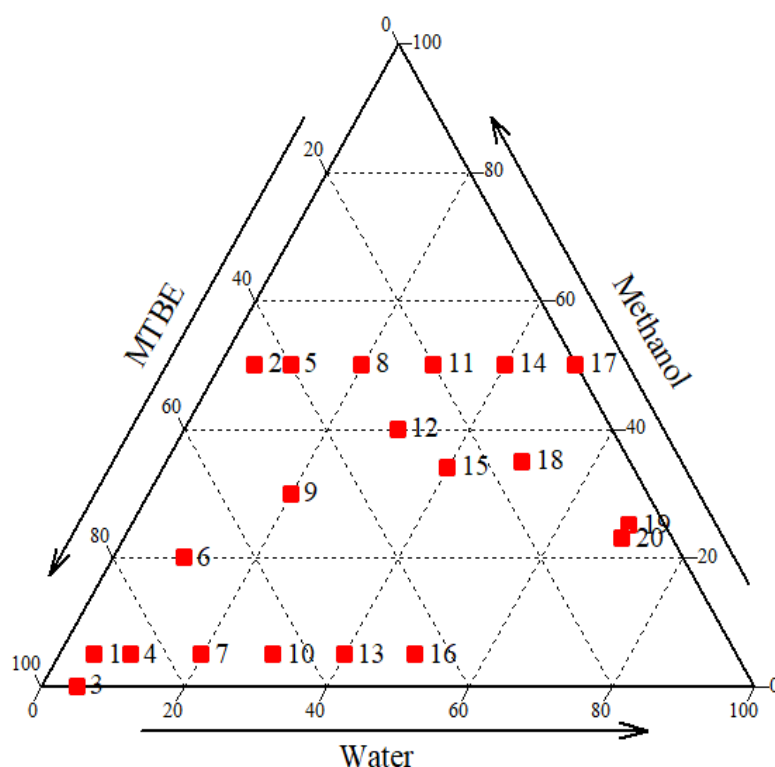
Figure 1: The ternary phase diagram positions and codes of the prepared

3. Simulation

A thermodynamic activity coefficient model named UNIFAC-LL was used to connect the experimental data with group interaction parameters acquired from the LLE data bank provided in the software program using Aspen Plus version 9. Analyzing MTBE-Methanol-Water system behavior, the model's accuracy was evaluated by measuring the relative errors and percent relative errors for each of the points on the binodal curve.

The UNIFAC-LL approach is a quantum chemical-based thermodynamic modelling technique that combines a precise statistical thermodynamic approach with an electrostatic theory of locally interacting molecule surface descriptors. As UNIFAC-LL is a quantum-chemical-based thermodynamic model, it does not require experimental values for group parametrization like conventional activity coefficient approaches do. To estimate activity coefficients, UNIFAC-quantum-chemical LL's foundation is applied.

4. Results and Discussion

The appearance of the twenty samples at three different temperatures 0, 40, and 70 °C, and under different pressures; 1.0 and 3.0 atm were presented. The ternary mixture forms either one phase, two-phase or hazy (cloudy) solution. Observation of one-phase means no phase separation occurs at these conditions, while the appearance of a hazy solution means that equilibrium exists at these conditions (pressure, temperature, and composition). However, the appearance of a two-phase solution means that the mixture is apparently separated at this point. These experimental results correctly fit into the regions of the ternary phase diagram simulated by Aspen Plus software as shown in Figures 2 and 4.

Table 2. Observed liquid-liquid equilibrium (LLE) for the investigated samples at 1.0 atm.

		1	2	3	4	5	6	7	8	9	10
X_{MTBE}		0.9	0.45	0.95	0.85	0.4	0.7	0.75	0.3	0.5	0.65
X_{MeOH}		0.05	0.5	0.0	0.05	0.5	0.2	0.05	0.5	0.3	0.05
X_{H2O}		0.05	0.05	0.05	0.1	0.1	0.1	0.2	0.2	0.2	0.3
(1 atm)	0°C	Haze	One-phase	Two-phase	Two-phase	One-phase	Haze	Two-phase	One-phase	Two-phase	Two-phase
	40°C	One-phase	One-phase	Haze	Two-phase	One-phase	One-phase	Two-phase	One-phase	Haze	Two-phase
	70°C	One-phase	One-phase	Haze	Two-phase	One-phase	One-phase	Two-phase	One-phase	One-phase	Two-phase

		11	12	13	14	15	16	17	18	19	20
X_{MTBE}		0.2	0.3	0.55	0.1	0.26	0.45	0.0	0.15	0.05	0.07
X_{MeOH}		0.5	0.4	0.05	0.5	0.34	0.05	0.5	0.35	0.25	0.23
X_{H2O}		0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.7	0.7
(1 atm)	0°C	One-phase	Haze	Two-phase	One-phase	Two-phase	Two-phase	One-phase	Two-phase	Haze	Two-phase
	40°C	One-phase	One-phase	Two-phase	One-phase	Two-phase	Two-phase	One-phase	Haze	One-phase	Haze
	70°C	One-phase	One-phase	Two-phase	One-phase	Haze	Two-phase	One-phase	One-phase	One-phase	Haze
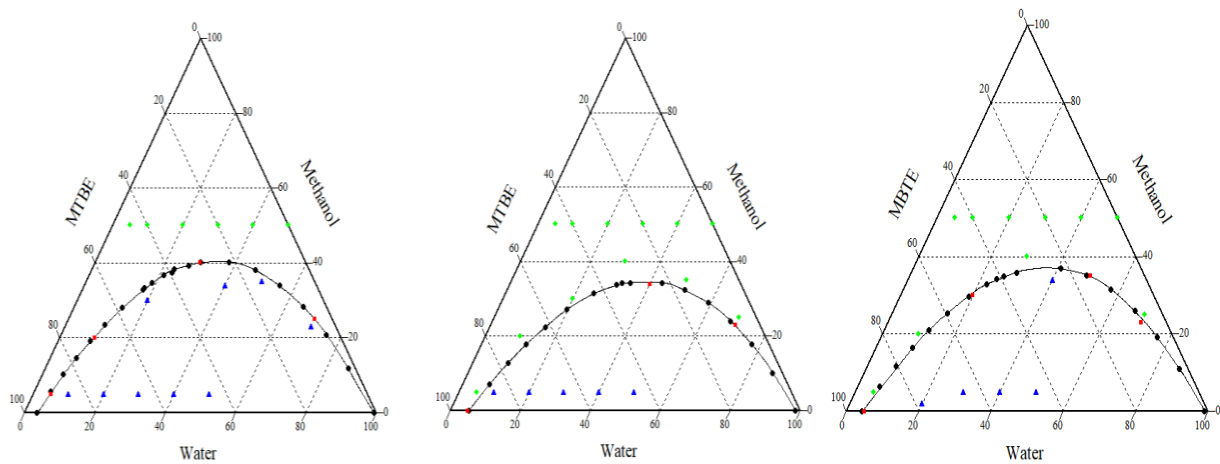
Figure. 2: Water, MTBE, and methanol ternary system equilibrium data at 1.0 atm; 0°C, (b) 40°C, and (C) 70°C. Codes: ▲ two-phase; ◆ one-phase; ■ Haze (cloud point); and simulated results.
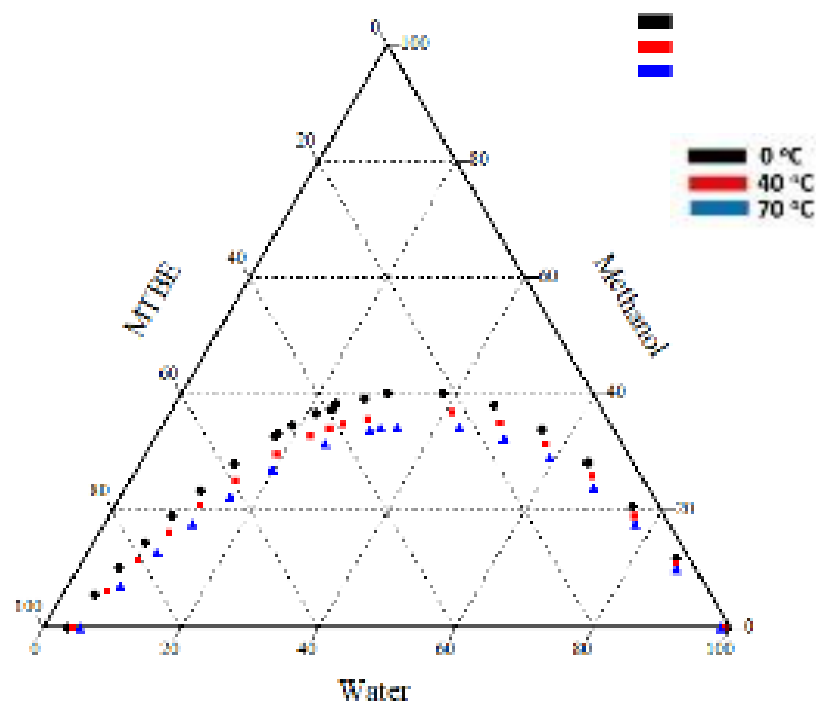
**Figure 3.** Effect of temperature on the phase transitions of used ternary system at 1.0 atm.

From the figures, we can conclude the followings:

   i)   Under the conditions of 0 °C and 1 atm, phase separation occurs for all mixtures whose methanol concentration is less than 38% and water concentration is greater than 3%.

   ii) Under the conditions of 50°C and 1 atm, phase separation occurs for all mixtures whose methanol concentration is less than 35% and water concentration is greater than 4.2%.

   iii) Under the conditions of 70 °C and 1 atm, phase separation occurs for all mixtures whose methanol concentration is less than 32.6% and water concentration is greater than 7%.

Table 3. Observed liquid-liquid equilibrium (LLE) for the investigated samples at 3.0 atm.

		1	2	3	4	5	6	7	8	9	10
X_{MTBE}		0.9	0.45	0.95	0.85	0.4	0.7	0.75	0.3	0.5	0.65
X_{MeOH}		0.05	0.5	0.0	0.05	0.5	0.2	0.05	0.5	0.3	0.05
X_{H2O}		0.05	0.05	0.05	0.1	0.1	0.1	0.2	0.2	0.2	0.3
(1 atm)	Haze	One-phase	Two-phase	Two-phase	One-phase	Haze	Two-phase	One-phase	Two-phase	Two-phase	Two-phase
	One-phase	One-phase	One-phase	Two-phase	One-phase	One-phase	Two-phase	One-phase	Haze	Two-phase	Two-phase
	One-phase	One-phase	One-phase	Two-phase	One-phase	One-phase	Two-phase	One-phase	One-phase	Two-phase	Two-phase

		11	12	13	14	15	16	17	18	19	20
X_{MTBE}		0.2	0.3	0.55	0.1	0.26	0.45	0.0	0.15	0.05	0.07
X_{MeOH}		0.5	0.4	0.05	0.5	0.34	0.05	0.5	0.35	0.25	0.23
X_{H2O}		0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.7	0.7
(1 atm)	One-phase	Haze	Two-phase	One-phase	Two-phase	Two-phase	One-phase	Two-phase	Haze	Two-phase	Two-phase
	One-phase	One-phase	Two-phase	One-phase	Two-phase	Two-phase	One-phase	Haze	One-phase	Haze	Haze
	One-phase	One-phase	Two-phase	One-phase	Haze	Two-phase	One-phase	One-phase	One-phase	One-phase	Haze
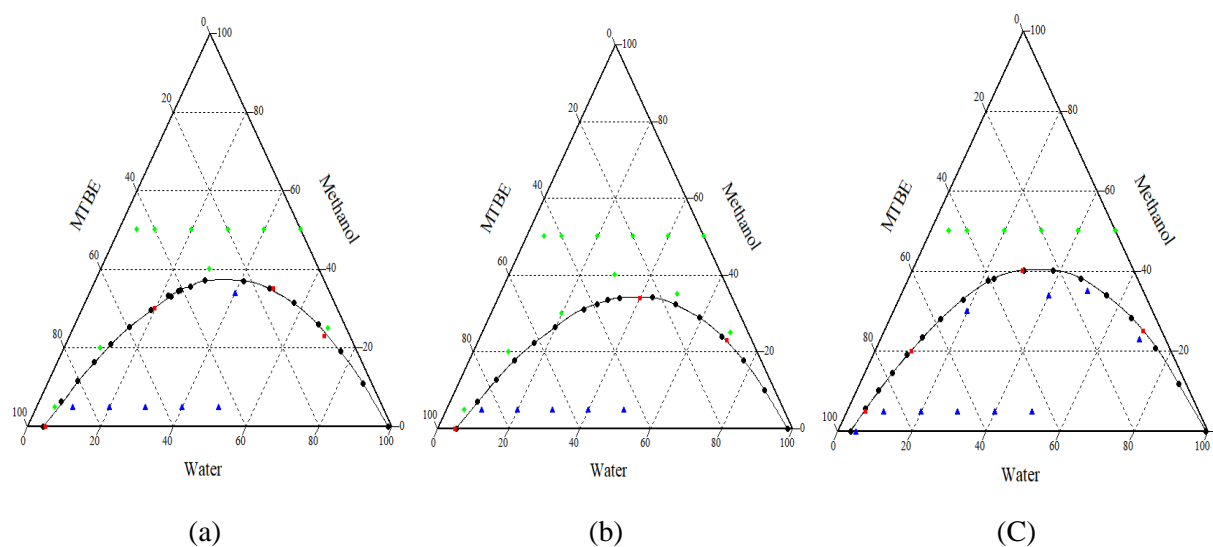
Figure 4. Liquid-liquid equilibrium data for the Water-MTBE-Methanol ternary system at 3.0 atm; (a) 0 °C, (b) 40 °C, and (C) 70 °C. Codes: ▲ two-phase; ◆ one-phase; ■ Haze (cloud point); and ● simulated results.
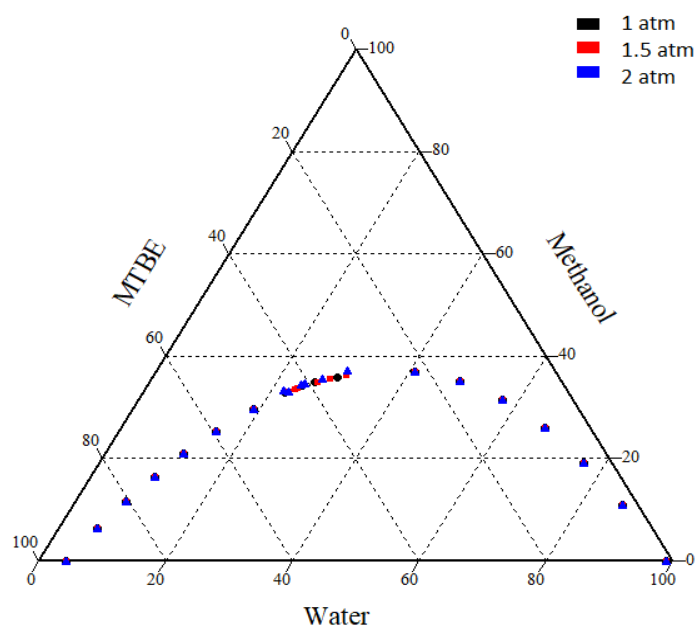
Figure 5. The ternary MTB-Methanol-Water system's phase transitions at 3 atm.

At constant pressure of 1.0 atm, we found that increasing the temperature from 40 °C to 70 °C decreased the methanol concentration at which phase separation occurs from 43% to 31.2 percent while increasing the water concentration from 3 percent to 7 percent, as previously shown. There are three alternative phase diagrams of the ternary system in Figure (2) that were simulated at different temperatures and pressures of 1.0 atm. Phase separation happens more often at lower methanol concentrations as the temperature rises, according to the results of this experiment. However, the computed phase diagrams in Figure 3 shows these experimental results. We may conclude that phase separation happens in any mixes that fulfill one of the following characteristics from these figures: (at 0 °C, 1.0 atm, methanol concentration is less than 40.3 percent; at 0 °C, 1.0 at methanol concentration is less than 37.1 percent; at 40 °C, 1.0 atm, methanol concentration is less than 37.1 percent; at 70 °C, 1.0 at methanol concentration is less than 37.1 percent). We can see from past research that pressure has a minor effect on phase transitions. We used three ternary phase diagrams simulated at 25 °C and at various pressures (1.0 and 3.0 atm, as shown in Figures) to overlay this factor for our research findings. Pressure does not influence the phase transitions of our ternary system, as can be seen from Figures 3 and 5 where the binodal curves of the three diagrams closely overlap.

5. Conclusion

The research attempts to determine what pressures, temperatures, and compositions of MeOH-MTBE mix maintain homogeneity in the presence of water, among other things. Experiments have been conducted at various temperatures, pressures, and compositions; 0, 40, and 70 °C, and 1.0 and 3.0 atm respectively. A thermodynamic activity coefficient model, UNIFAC-LL, was used to correlate the experimental results using Aspen Plus Version 9. Phase transitions of the MTBE-Methanol-water system are not affected by pressure, whereas temperature has little influence on the established LLE. The methanol concentration at which phase separation occurred dropped from 43% to 31.2 percent when the temperature was lowered from 70°C to 40°C. With the use of simulation, the compositions at which phase separation occurs were also discovered. It was also confirmed that the thermodynamic model UNIFAC-LL can accurately forecast the composition of the binodal curve's points with relative errors less than 3 percent. Using these data, the oxidation advantage of MTBE together with the methanol even in the presence of water content might be implemented without the risk of the

separation of the contents. These results could help to boost the valuable usage of this tertiary mixture as an Octane enhancer without the risk of being separated at any working conditions.

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