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Liquid-Liquid Equilibria Study for a Common Azeotropic Ternary System

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Abstract

Methyl-tert-butyl ether (MTBE) and Methanol (MeOH) have been known as effective fuel oxygenates to increase the octane number, improve fuel performance, and cut the environmental pollutants. However, their high solubility in water limits their usage in the petroleum industry field regarding the loss of fuel homogeneity. In this work, the liquid-liquid phase equilibrium of the ternary system of MTBE – Methanol –Water. Experiments have been studied at different mole fractions, various temperatures; 0°C, 25°C, and 50°C, and at several pressures; 1.0 atm, 1.5 atm, and 2.0 atm. This work represents a combination of practical laboratory experimental results and simulation sets utilizing Aspen HYSYS software version 7.2. The results show that Aspen HYSYS simulation data are proficient with the output data developed from the laboratory experimental laboratory measurements and thus it is capable to correlate software simulation with practical data for the studied systems with realistic accuracy. This protocol aims to optimize the oxygenate composition, pressure, and temperature during the usage of MTBE – MeOH as a common fuel oxygenate additive.

Keywords: Liquid-Liquid Equilibrium•Methyl tert-butyl ether (MTBE)• Water -Methanol-MTBE mixtures• Fuel Oxygenates• High-Octane Gasoline Blends

Introduction

Spark ignition combustion that took place inside engines using gasoline releases some dangerous pollutant emissions, such as CO2, CO, hydrocarbons, and nitrogen oxides. Undeniably, the combustion of fossil fuels, as an essential source of energy, is responsible for the dramatic increase in environmental pollution due to their combustion emissions. These emissions could be considered as the pivot for dangerous climate change due to the global warming crisis in our world [1-4]. However, the need for more feed of petroleum fuels becomes inevitable despite its severe negative impact on the environment. Despite the global policies worldwide to encourage the limited consumption of petroleum fossil fuels, the demand is increasing dramatically regarding the global population growth which is accompanied by the increase in fuel exploitation and commercial activities in daily life [5-7]. It is expected that the global gasoline demand growth could be estimated to be around 40% until 2040 [8,9]. As a result, renewable energy sources, such as biofuel, solar cells, electric cars, natural gases, dimethyl ether (DME), and fuel cells powered by hydrogen, become incapable to meet the fuel demand. Hence, the usage of fossil fuels together with renewable energy sources becomes a must [10-18].

Petroleum products, especially gasoline blends, are very complex organic materials composed of a wide range of hydrocarbons. These hydrocarbons could be divided into four main categories; olefins, aromatics, paraffins, and naphthenes. However, some contaminants including nitrogen, sulfur, oxygen, and some inorganic metal particles are involved in these gasoline blends. For that reason, the gasoline blends ignition quality, and their flammability should be assessed accurately [19-21]. Petroleum fuel quality could be fundamentally evaluated through the octane number value. Basically, the octane number value is equivalent to the percentage ratio of isooctane (2,2,4-trimethylpentane) to n-heptane in the fuel mixture. Octane number is the major parameter utilized regarding gasoline performance evaluation for automobile engines. It gives direct information about motor efficiency, power loss, and emissions. Also, it represents the motor ability to resist the knocking phenomenon which reduces the engine efficiency. Knocking occurs when the burning process took place uncontrollably causing an early ignition before the spark ignites the fuel blend as designed [22-25]. Avoiding the undesirable knocking offers optimal operation conditions of the engine, thus improves the engine compression ratio, enables the high-load operations, and maximizes the engine performance along with both high speeds and heavy loads applied [8,26].

Increasing the octane number of gasoline fuels attracts many researchers to investigate in this field. For that reason, several additives have been used given the commercial name of "octane boosters". These additives are mainly oxygenating, such as methanol, ethanol, methyl tert-butyl ether (MTBE), 2,2,4-Trimethylpentane (iso-octane), dimethoxymethane (DMM), ethyl tert-butyl ether (ETBE) [7], and di-isopropyl ether (DIPE). Adding oxygenates to gasoline blends improves the combustion reaction, increases the fuel quality, and decreases the pollution [19, 27-37]. Nowadays, additives became an essential component of gasoline fuel. This could be attributed to their significant impact on fuel quality and characteristics. Additives also have a great influence on fuel economics by introducing new desired properties enhancing the fuel performance, increasing its storage life with maintaining its cost as minimum as possible. Additives could be used in refineries or with direct-use by the costumer. Beside improving the performance, fuel additives are dedicated for several other functions such as lubrication, anti-knocking, anti-icing, metal deactivators, anti-rust and could be act as detergents [16,38,39].

Methyl tert-butyl ether (MTBE) is a well-known material in the petrochemical industries field. MTBE is colorless, transparent, and low viscous oxygenate that significantly increases the gasoline octane number and hinders the undesirable knocking [40-47]. It could be synthesized through the exothermic reaction between Methanol and Isobutylene in an acidic medium, however, an efficient separation technique is crucial for the azeotropic methanol-MTBE mixture [48-51]. One of the serious problems that hindered the usage of MTBE as an efficient fuel additive is its relatively high solubility in water. The high solubility of MTBE in water resulted in permanent contamination of the underground aquifers [5, 52-55]. This problem was discovered primarily in 1995 where thousands of water wells were found contaminated with MTBE [8]. Then, a series of similar contamination accidents took place in Harford County, Maryland in 2004 and Jacksonville, Maryland in 2005 [56-58]. These accidents encourage the USA government to prohibit the usage of MTBE in 2002 [18,59,60]. This problem has been multiplied when using the highly water-soluble methanol as a co-additive together with MTBE.

Methanol is commonly used for the synthesis of several chemicals such as MTBE [61,62]. Also, it is a promising candidate to purify MTBE and decreases its groundwater contamination problem [1,62]. Besides, it has been used as a transportation fuel and as racing vehicles fuel a long time ago. Interestingly, methanol is used in the petrochemical and fuel industry as an octane booster

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regarding its high research octane number (RON) [30]. Nowadays, a great interest was focused on methanol regarding the shortage of petroleum resources concerning the continually increasing demand. Being easily made from available sources, such as biomass and natural gas magnified the importance of methanol in the energy field. Methanol was used as an energy source either in its pure state or mixed in a variety of gasoline blends. One of the most common gasoline blends is a methanol-MTBE mixture. This mixture was famous for its high-octane number and its relatively lower percentage of pollutant emissions. However, the methanol-MTBE blends faced the serious problem of the possible phase separation in the presence of water, which is a major disadvantage that hindered the use of this blend on several occasions [30,63,64]. This paper represents a full-range study of the liquid-liquid phase transitions for the MTBE– Methanol –Water ternary system. This study covers a wide range of temperatures; 0°C, 25°C and 50 °C, and pressures; 1 atm, 1.5 atm, and 2 atm. Different mole fractions of MTBE, water, and methanol were used to prepare sample mixtures for analysis. The experimental results combined with the modeling output data of the liquid-liquid phase equilibrium using Aspen HYSIS software version 7.2 were utilized to optimizing the use of MTBE– Methanol blend as an octane booster efficiently without suffering from the phase separation in presence of water in the surroundings.

Materials and Methods

Materials

Methanol 99.8% (HPLC Gradient grade) and Methyl tert-butyl Ether (MTBE) 99.5% were purchased from LOBA CHEMIE PVT. LTD (Mumbai, India). All reagents were used as supplied without any auxiliary purification where gas chromatography (GC) confirms their high purity. The specifications of the used chemicals reagents are given in Table 1. The densities of methanol and MTBE were measured onsite using an ordinary densimeter inserted in a measuring cylinder filled with a tested sample. The sample was left to settle then the reading was recorded from the densimeter.

Apparatus and Procedure

The liquid-liquid phase transitions for the MTBE– Methanol –Water ternary system was studied using a modified LLE device [65,66]. Firstly, the required water mole fraction was added to an adjusted amount of MTBE. Finally, the methanol amount was added to the mixture to control its volatility. Once methanol was added, the mixture was subjected to a good and continuous agitation for 30 min, using an AKM LAB High-Quality magnetic stirrer, at a constant temperature and pressure in a thermostated water bath. Then, the mixture was left overnight for 24 h to guarantee the achievement of the equilibrium state under the adjusted temperature and pressure. After 24 h, the mixture was either separated into a two-layer solution or still in the homogenous state. In both cases, samples were collected and analyzed using the HZGC-1212 gas chromatography (GC-2014C) analyzer to ensure the identity and purity of the product. In the case of the two-layer solution, the lower layer was collected from the device bottom, while the upper layer was collected from the top to avoid any contamination.

The liquid-liquid phase equilibrium data for the ternary system of MTBE–Methanol –Water was investigated at 1.0 atm and a range of different temperatures; 0°C, 25°C, and 50°C, as shown in Figure 1. The results of these experiments are summarized in Table 2. The equilibrium tie-line data was then investigated at the same range of temperatures; 0°C, 25°C, and 50°C, but under the pressure of 1.5 atm as shown in Figure 2 and tabulated in Table 3. Finally, the phase equilibrium of the ternary system of MTBE – Methanol –Water was investigated under the pressure of 2.0 atm and at the same set of temperatures (0oC, 25oC, and 50oC). The equilibrium data of the ternary system at 2.0 atm is given in Table 4 and represented in Figure 3. A set of 20 "MTBE – Methanol –Water" samples were studied, as reported in Table 5, at a range of temperatures 0°C, 25°C, and 50°C, and pressures, 1.0 atm, 1.5 atm, and 2.0 atm. Each sample was repetitive three times to ensure the exactness of the results. The results of the experiments have been used to feed the Aspen HYSIS software to develop a full-range liquid-liquid equilibrium data for the MTBE–Methanol–Water blends. Afterward, the verified Aspen HYSYS code was used to perform a full-range comparative study for the liquid-liquid phase equilibria among the three proposed ternary systems.

Simulations

Aspen HYSIS software version 7.2 was utilized to optimize the liquid-liquid phase equilibrium data for the ternary system of MTBE – Methanol – Water at a wide range of temperatures, pressures, and mole fractions. Firstly, experimental measurements have been performed practically at the laboratory as a validation protocol to verify the simulation data-driven from Aspen HYSIS. Secondly, practical results have been fed to the Aspen HYSYS software to validate the simulation study of the same ternary system developed by the software at the same conditions as inputs. Finally, set simulation processes have been performed to develop an extended study of the liquid-liquid phase behavior regarding the MTBE – Methanol –Water ternary system as a common azeotropic mixture. This protocol helps to accurately study the effect of temperature, pressure, and composition mole fraction individually on the phase behavior of that system. Thus, optimizing the usage of MTBE – MeOH blend as a fuel oxygenate additive to enhance the fuel efficiently without suffering from the phase separation that took place in the presence of water.

Table 1. Raw materials used in the experimental part.

Material Name	Source	Density, (g/cm^3)	Purity, %	Molar mass, (g/mole)	Boiling point, °C
Methanol (CH3OH)	LOBA CHEMIE	0.815	99.80%	32.04	64
Methyl tert-butyl Ether (MTBE)	LOBA CHEMIE	0.739	99.50%	88.15	55

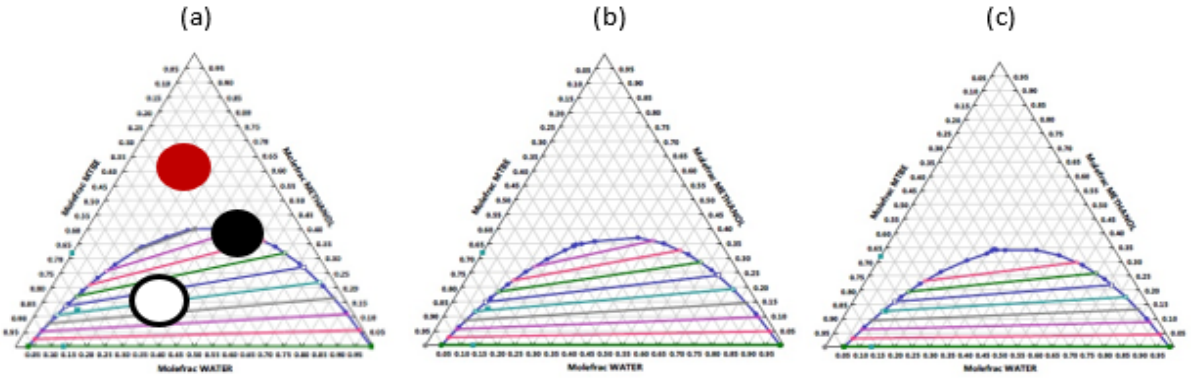

Figure 1. Liquid-liquid equilibrium data for the Water-MTBE-Methanol ternary system at 1.0 atm; (a) 0°C, (b) 25°C, and (C) 50°C.

Table 2. Liquid-liquid equilibrium data for MTBE – Methanol –Water samples at 1.0 atm.

Sample No.	Water (mole fraction)	Methanol (mole fraction)	MTBE (mole fraction)	Appearance (1.0 atm)		
				0°C	25°C	50°C
1	0.05	0.05	0.9	Haze	One-phase	One-phase
2	0.05	0.5	0.45	One-phase	One-phase	One-phase
3	0.05	0	0.95	Two-phase	Haze	Haze
4	0.1	0.05	0.85	Two-phase	Two-phase	Two-phase
5	0.1	0.5	0.4	One-phase	One-phase	One-phase
6	0.1	0.2	0.7	Haze	One-phase	One-phase
7	0.2	0.05	0.75	Two-phase	Two-phase	Two-phase
8	0.2	0.5	0.3	One-phase	One-phase	One-phase
9	0.2	0.3	0.5	Two-phase	Haze	One-phase
10	0.3	0.05	0.65	Two-phase	Two-phase	Two-phase
11	0.3	0.5	0.2	One-phase	One-phase	One-phase
12	0.3	0.4	0.3	Haze	One-phase	One-phase
13	0.4	0.05	0.55	Two-phase	Two-phase	Two-phase
14	0.4	0.5	0.1	One-phase	One-phase	One-phase
15	0.4	0.34	0.26	Two-phase	Two-phase	Haze
16	0.5	0.05	0.45	Two-phase	Two-phase	Two-phase
17	0.5	0.5	0	One-phase	One-phase	One-phase
18	0.5	0.35	0.15	Two-phase	Haze	One-phase
19	0.7	0.25	0.05	Haze	One-phase	One-phase
20	0.7	0.23	0.07	Two-phase	Haze	Haze

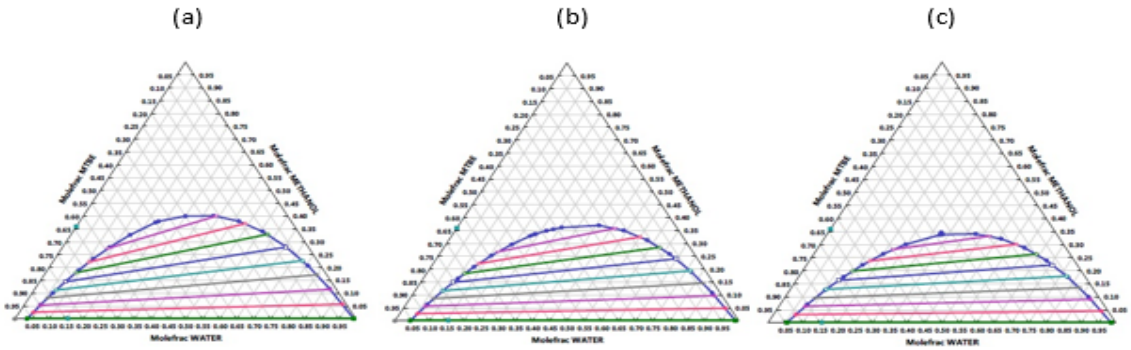

Figure 2. Liquid-liquid equilibrium data for the Water-MTBE-Methanol ternary system at 1.5 atm; (a) 0°C, (b) 25°C, and (C) 50°C.

Table 3. Liquid-liquid equilibrium data for MTBE–Methanol–Water samples at 1.5 atm.

Sample No.	Water (mole fraction)	Methanol (mole fraction)	MTBE (mole fraction)	Appearance (1.5 atm)		
				0°C	25°C	50°C
1	0.05	0.05	0.9	Haze	One-phase	One-phase
2	0.05	0.5	0.45	One-phase	One-phase	One-phase
3	0.05	0	0.95	Two-phase	Haze	One-phase
4	0.1	0.05	0.85	Two-phase	Two-phase	Two-phase
5	0.1	0.5	0.4	One-phase	One-phase	One-phase
6	0.1	0.2	0.7	Haze	One-phase	One-phase
7	0.2	0.05	0.75	Two-phase	Two-phase	Two-phase
8	0.2	0.5	0.3	One-phase	One-phase	One-phase
9	0.2	0.3	0.5	Two-phase	Haze	One-phase
10	0.3	0.05	0.65	Two-phase	Two-phase	Two-phase
11	0.3	0.5	0.2	One-phase	One-phase	One-phase
12	0.3	0.4	0.3	Haze	One-phase	One-phase
13	0.4	0.05	0.55	Two-phase	Two-phase	Two-phase
14	0.4	0.5	0.1	One-phase	One-phase	One-phase
15	0.4	0.34	0.26	Two-phase	Two-phase	Haze
16	0.5	0.05	0.45	Two-phase	Two-phase	Two-phase
17	0.5	0.5	0	One-phase	One-phase	One-phase
18	0.5	0.35	0.15	Two-phase	Haze	One-phase
19	0.7	0.25	0.05	Haze	One-phase	One-phase
20	0.7	0.23	0.07	Two-phase	Haze	Haze

Table 4. Liquid-liquid equilibrium data for MTBE–Methanol–Water samples at 2.0 atm.

Sample No.	Water (mole fraction)	Methanol (mole fraction)	MTBE (mole fraction)	Appearance (2.0 atm)		
				0°C	25°C	50°C
1	0.05	0.05	0.9	Haze	One-phase	One-phase
2	0.05	0.5	0.45	One-phase	One-phase	One-phase
3	0.05	0	0.95	Two-phase	One-phase	One-phase
4	0.1	0.05	0.85	Two-phase	Two-phase	Two-phase
5	0.1	0.5	0.4	One-phase	One-phase	One-phase
6	0.1	0.2	0.7	Haze	One-phase	One-phase
7	0.2	0.05	0.75	Two-phase	Two-phase	Two-phase
8	0.2	0.5	0.3	One-phase	One-phase	One-phase
9	0.2	0.3	0.5	Two-phase	Haze	One-phase
10	0.3	0.05	0.65	Two-phase	Two-phase	Two-phase
11	0.3	0.5	0.2	One-phase	One-phase	One-phase
12	0.3	0.4	0.3	Haze	One-phase	One-phase
13	0.4	0.05	0.55	Two-phase	Two-phase	Two-phase
14	0.4	0.5	0.1	One-phase	One-phase	One-phase
15	0.4	0.34	0.26	Two-phase	Two-phase	Haze
16	0.5	0.05	0.45	Two-phase	Two-phase	Two-phase
17	0.5	0.5	0	One-phase	One-phase	One-phase
18	0.5	0.35	0.15	Two-phase	Haze	One-phase
19	0.7	0.25	0.05	Haze	One-phase	One-phase
20	0.7	0.23	0.07	Two-phase	Haze	One-phase

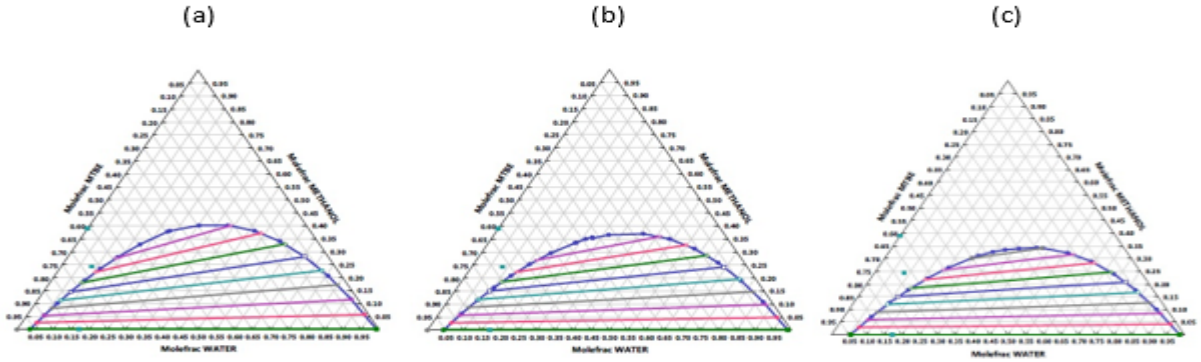

Figure 3. Liquid-liquid equilibrium data for the Water-MTBE-Methanol ternary system at 2.0 atm; (a) 0°C, (b) 25°C, and (C) 50°C.

Table 5. Mole fractions of MTBE–Methanol–Water samples.

Sample No.	Water mole fraction	Methanol mole fraction	MTBE mole fraction
1	0.05	0.05	0.9
2	0.05	0.5	0.45
3	0.05	0	0.95
4	0.1	0.05	0.85
5	0.1	0.5	0.4
6	0.1	0.2	0.7
7	0.2	0.05	0.75
8	0.2	0.5	0.3
9	0.2	0.3	0.5
10	0.3	0.05	0.65
11	0.3	0.5	0.2
12	0.3	0.4	0.3
13	0.4	0.05	0.55
14	0.4	0.5	0.1
15	0.4	0.34	0.26
16	0.5	0.05	0.45
17	0.5	0.5	0
18	0.5	0.35	0.15
19	0.7	0.25	0.05
20	0.7	0.23	0.07

Results and Discussion

Results showed that MTBE – Methanol –Water ternary system forms at some points clear mixtures; as represented by the white circle in Figure 1(a), two-layer mixtures, which represent the two-phase region. In this region, methanol dissolves in water and thus is separated from MTBE. This could lead to serious problems in the engines using gasoline blends containing MTBE and methanol as an octane booster additive. Thus, this hindered the wide usage of these blends despite their high ability to increase the octane number and improve gasoline performance and consumption. On the other hand, an azeotropic mixture was formed at which only one homogenous phase is shaped; as denoted by the red circle in Figure 1(a). In this region, the addition of water to the mixture of MTBE – Methanol is not able to separate methanol from the main oxygenate mixture. Therefore, gasoline blends containing these additives would conserve their properties and could act properly in the automobile engines. However, in some cases such as represented in Figure 1(a) by the black circle, the formed homogenous phase was accompanied by a hazy appearance. These points represent the boundary points that critically separate the one-phase region and the two-phase region.

Also, it was found that temperature has a significant impact on the phase equilibrium of MTBE–Methanol–Water ternary system. For the composition of MTBE:Methanol:Water of 0.2:0.3:0.5 respectively by mole fraction, at 1.0 atm and 0°C the mixture forms a two-layer solution while increasing the temperature to 25°C turns the system into a hazy one phase solution that represents the boundary at equilibrium between the one-phase and two-phase mixtures. In addition, increasing the temperature from 25°C to 50oC turns the mixture into a clear one-phase solution without any noticeable barriers. On the other hand, it was found that changing the pressure among 1 atm, 1.5 atm, and 2.0 atm showed no significant impact on the liquid-liquid phase equilibrium of the investigated ternary system.

Conclusion

Herein, the liquid-liquid phase equilibrium of the ternary system of the MTBE–Methanol–Watermixture was successfully investigated over a wide range of mole fractions of individual compositions and at different temperatures; 0°C, 25°C, and 50°C, and various pressures; 1 atm, 1.5 atm, and 2.0 atm. Then, Aspen HYSYS software was utilized and compared with the experimental results to verify code. Subsequently, the verified software was then used to perform a full-range liquid-liquid equilibrium study for the common azeotropic mixture of MTBE–Methanol–Water ternary system. It was confirmed that both composition and temperature have a significant impact on the mixture homogeneity. However, the pressure was found to have relatively little impact on the phase equilibrium. This study helped to develop, for the first time ever, an accurate phase diagram chart for the MTBE–Methanol –Water ternary system. Using these data could help to optimize practical In-situ conditions to avoid separation challenges while developing the chance to utilize the abilities of methanol and MTBE to improve fuel characteristics.

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