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Experimental and Modelling Analysis of Liquid-Liquid Formation in Alcohol-mixed Gasoline Fuel

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To tackle the environmental and sustainability problems, substituting gasoline, partially or solitary with bio-based alcohols becomes global practice. Bioethanol and biomethanol are being blended with gasoline in the ratio between 5-100 % by volume varying on the region. Various studies show positive impact of utilizing the blended fuel environmentally, while the others report the adequate efficiency of the blended fuel compare to the conventional gasoline; however, there were nearly no report on the failure or the shorten lifespan of the engine parts such as a high pressure pump (HPP) or an injector. It has been reported that water residue in the blended-bioethanol and biomethanol could cause the formation of the second liquid phase, leading to the chemical ageing reaction, which resulted in the corrosion of the HPP. To understand and prevent the damage, a quaternary behaviour of the blended gasoline-ethanol-methanol-water at the HPP operating condition is needed. In this work, an experimental study of the quaternary behaviour of the blended fuels has been conducted, the experimental data have been matching with the simulated results for better predictive of the mixture behaviour at different conditions. These results could potentially lead to limit or eliminate the HPP-corrosive problem.

1. Introduction

To tackle the environmental and sustainability problems, substituting gasoline partially or solitary with bio-based alcohols becomes global practice. Bioethanol can be used as gasoline blends for conventional gasoline engine, or gasoline substitute for flexible fuel vehicles (FFVs) (Wyman, 2018). Similarly, biomethanol can also be used as gasoline blends, gasoline substitute, or mixed with ethanol and used as gasoline substitute as well (Jangi et al., 2017; Zhen, 2018). Bioethanol and/or biomethanol are being blended with gasoline in the ratio between 5-100 % by volume varying on the region (Manochio et al., 2017). Likewise, in bio based-alcohol can also be used as substitute fuel in diesel engine (Geng et al., 2017). There are various reports confirming the environmental benefits of the utilization of bio-based alcohol in transportation such as carbon monoxide and oxides of nitrogen reduction (Sodré et al., 2014); carbon dioxide and Sulphur reductions (Hashim et al., 2017); toxicity reduction (Manzetti and Andersen, 2015); and particulate matters reduction (Nabi et al., 2017; Praptijanto et al., 2015). Moreover, the efficiencies of the blended-fuel in both gasoline and diesel engine are acceptable; in term of energy consumption the efficiencies of blended-fuels drop less than 10 % comparing to the conventional gasoline (Iodice et al., 2018) and less than 2 % in diesel engine (Tan et al., 2017).
However, blending alcohols with fuel introduces new problems like the failure or shorten lifespan of the crucial engine parts such as a high-pressure pump (HPP) and/or an injector. Alcohols, especially ethanol and methanol, have tendencies to absorb water from humid atmosphere (Awad et al., 2018) causing the formation of aqueous surface layer (Figure 1, Type 3), or the partition of heterogeneous phase (Figure 1, Type 2). The ions, most importantly chloride ion, condense on the aqueous surface layer at moderate water concentration as displayed in Figure 1 (Abel and Virtanen, 2015). These condensed ions formation is the origin of both deteriorate of gasoline by chemical ageing reaction and the corrosion engine parts.
To understand and prevent these problems, a quaternary behavior of the blended gasoline-ethanol-methanol-water at the HPP operating condition is needed. Moreover, the water absorption rate of blended gasoline is also required in order to predict the shelf-life of blended gasoline at different alcohol concentration. In this work, an experimental study of the quaternary behavior of the blended fuels at 70 °C has been conducted, the

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experimental data have been matching with the simulated results for better predictive of the mixture behavior at different conditions. The water absorption rate into gasoline blended in Thailand has also been collected and explained through simple rate-base model for the prediction of the optimum shelf-life of blended gasoline.

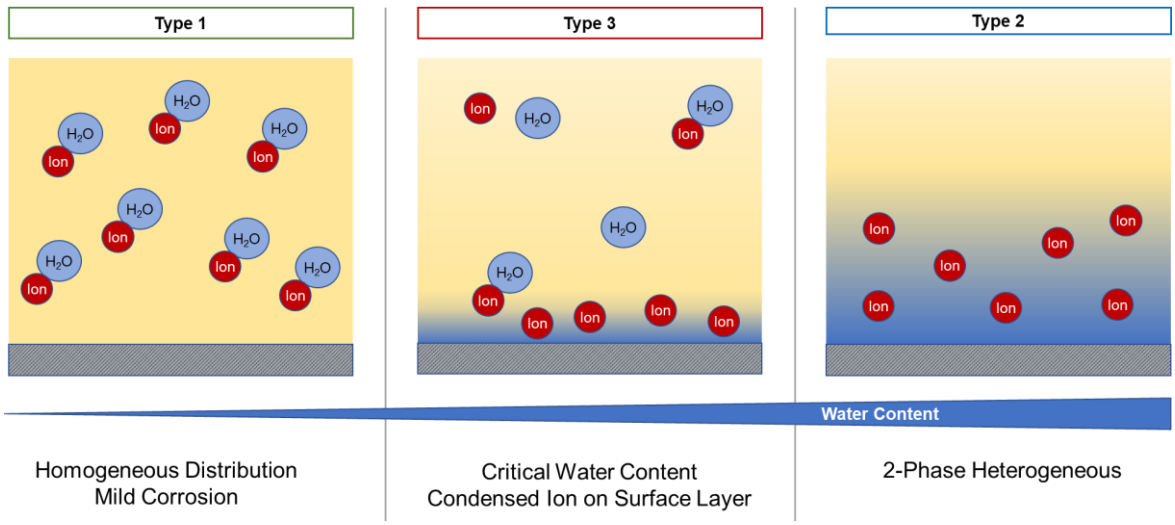

Figure 1: Effect of water content to the partition of ions (Abel and Virtanen, 2015)

2. Experimental and modelling setups

2.1 Phase partition experiment

Gasoline sample, named as CEC-X following the non-disclosure agreement, is supplied by the partner company; analytical-grade ethanol (99.5 %) and analytical-grade methanol (100 %) are supplied by Apex Chemicals (Thailand); de-ionized water is produced in-house via reverse osmosis. The experiments have been conducted in an ultrasonic bath at controlled temperature of 25 °C and 70 °C. 100 ml of gasoline-alcohol mixtures have been prepared as state in Table 1; 17 samples (1-17) have been conducted on ethanol-gasoline mixtures, 12 samples (18-29) for methanol-gasoline mixtures, and 21 samples (30-50) for ternary methanol-ethanol-gasoline mixtures. Water is dropped to the sample, then the sample is shaken for 1 minute, the dropping continues until the sample become cloudy. Each concentration has been re-verified twice.

2.2 Water absorption rate data collection

In Thailand, there are 4 levels of ethanol-blended gasoline (commercial name: Gasohol), E5, E10, E20, and E85, at which the letter E denotes ethanol and the following number denotes percent by volume of ethanol blended into the gasoline fuel. The water absorption rates in ethanol-blended fuels in Thailand have been collect by the partner company. The data are collected from the petrol station type A, B, and D where the fuels are stored in underground tanks with the tank sizes varying between 30k-180k liters.

2.3 Modelling setup

Liquid-liquid equilibrium description

UNIFAC model (Fredenslund et al., 1975) is selected to describe liquid-liquid equilibrium (LLE) of this system; the expressions for activity coefficient can be found in various publications (Abildskov et al., 1996; Gonzàlez et al., 2007; Kang et al., 2011) and details will not be discussed here. The expression for an average volume parameter follows an un-modified UNIFAC as expressed in Eq(1)

$$\phi_i = \frac{r_i}{\sum_j x_j r_j} \tag{1}$$

where r_i is the volume and x_i is the mole fraction among all subgroups composing the mixture of the *i*-th structural subgroup.

The CEC-X gasoline is treated as an unknown group where its' properties are estimated by API standard methods (1988); its' van der Waal volume and area are approximated numerically (Petitjean, 1994).

Table 1: Mixture composition in the experiments

Experiment	Alcohol (% v/v)	Experiment	Methanol (% v/v)	Ethanol (% v/v)
1	5	30	2.5	95
2	10	31	72.5	25
3	18	32	12.5	80
4	20	33	82.5	10
5	22	34	42.5	45
6	24	35	62.5	25
7	26	36	32.5	50
8	28	37	77.5	5
9	30	38	47.5	30
10	40	39	22.5	50
11	50	40	37.5	30
12	60	41	52.5	15
13	82	42	27.5	35
14	85	43	7.5	50
15	86	44	57.5	1
16	93	45	17.5	35
17	95	46	32.5	15
18	10	47	42.5	0
19	13	48	2.5	35
20	15	49	7.5	20
21	17	50	12.5	10
22	20			
23	25			
24	40			
25	50			
26	60			
27	83			
28	85			
29	87			

The interaction parameter is expressed as the first order form used in KT-UNIFAC (Abildskov et al., 1999) as displayed in Eq(2)

$$\Delta u_{mk} = a_{mk,1} + a_{mk,2}(T - T_0) \tag{2}$$

where $a_{mk,1}$ and $a_{mk,2}$ are temperature independent and dependent coefficients of parameter for the *m*–*k* group interaction.

The objective function for the parameter regression of UNIFAC parameters in this work focuses only to the LLE data set, the function is a least square of a summation of errors as displayed in Eq(3)

$$A_{LLE} = \frac{1}{N}\sum_{k}\left(\frac{x_k^{\exp} - x_k^{cal}}{x_k^{\exp}}\right)^2 \tag{3}$$

where A_{LLE} is the objective function, N is number of experiments, $x_k^{\exp}$ and x_k^{cal} are experiment and calculated value of the equilibrated fraction of alcohols. A combination of maximum likelihood (Anderson et al., 1978) and simplex method (Nelder and Mead, 1965) is used for the fitting of groups interaction parameters.

Water absorption rate

The absorption model is built based on the assumption that there is an equilibrium of water content in blended-fuel mixtures depending on the alcohol compositions and the rate of absorption is limited by mass transfer. The absorption occurs at the liquid surface of the fuels. The liquid phase is a well-mixed system; therefore, any absorbed water is instantly and directly affecting the concentration of water in the liquid phase. The model is contracted as a first order simple reaction as displayed in Eq(4)

$$\frac{dc_W}{dt} = k_{EW}\left(c_W^* - \frac{c_W}{K_E c_E}\right) \tag{4}$$

where k_{EW} is the absorption rate constant of water to the alcohol, K_E is the equilibrium constant of water composition based alcohol content, c_E, c_W and c_W^* are the concentration of ethanol in the mixture and water in the liquid mixture and ambient respectively.
The lack of data for the soil and air humidity leads to the assumption that the ambient water content is constant, using average air and soil humidity in Bangkok, Thailand as a reference (Phosri et al., 2019; Pollution Control Department, 2019, 2015).
The model is linearized for fitting the rate and equilibrium constants with the maximum likelihood method.

3. Results and discussions

Liquid-liquid equilibrium

The experiment LLE results are displayed in Figure 2; both figures 2A and 2B show good agreement between the experiments and UNIFAC model calculations. Least square error (A_{LLE}) of the ethanol-blended system is 0.02 and the methanol-blended system is 0.08. It's appeared that the 2 liquid phases region of the methanol-

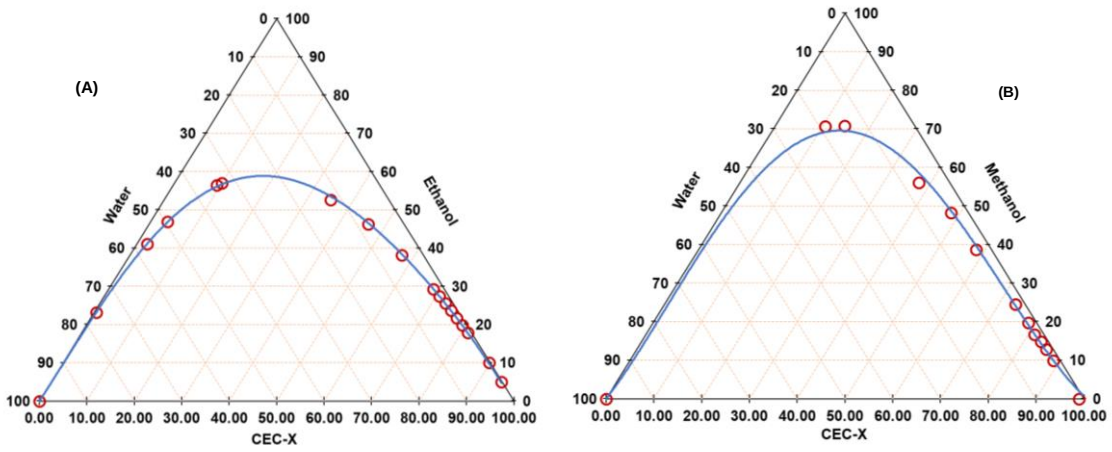

Figure 2: Ternary diagrams at 70 °C of (A) ethanol-water-gasoline; (B) methanol-water-gasoline with dots denote experiments and lines denote model calculations

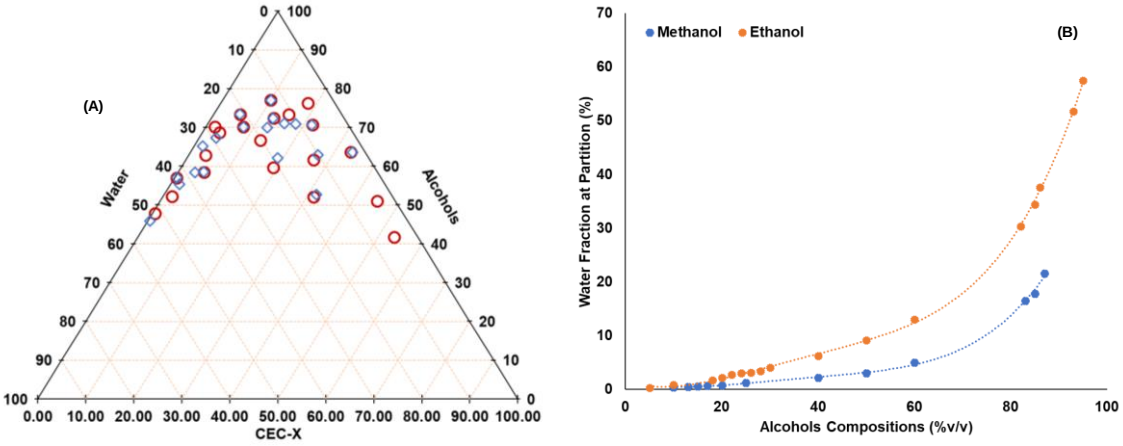

Figure 3: (A) Ternary diagrams at 70 °C of ethanol-methanol-water-gasoline, dots (o) denote experiments, rhombi (◊) denote model calculations; (B) water tolerance of difference alcohol mixture at 70 °C with dots denote experiments and lines denote model calculations.

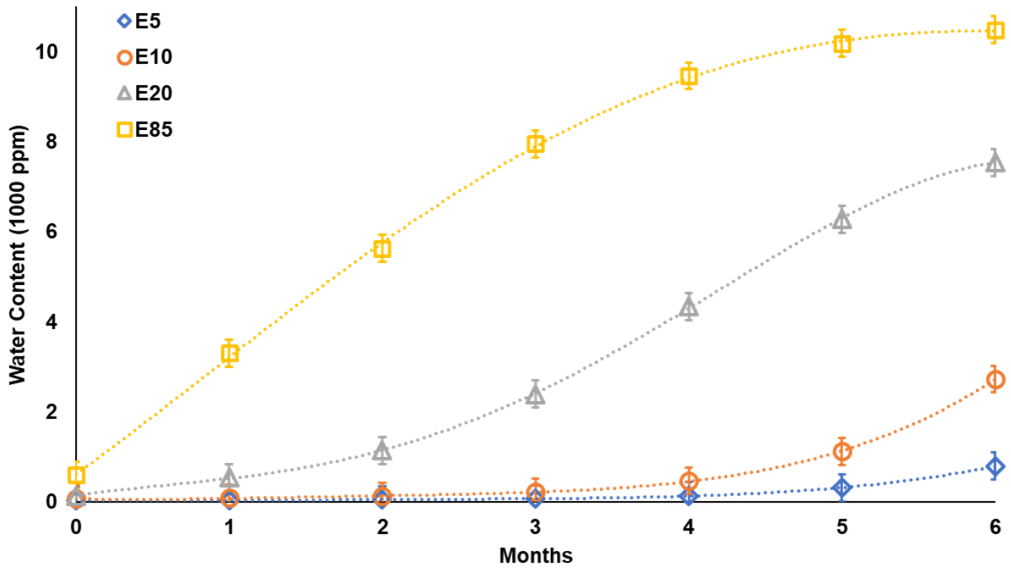

Figure 4: Average water content in gasohols with different ethanol percentage during 6 months of storage

gasoline mixture is far larger than that of ethanol-gasoline mixture; however, it's also observed that at high alcohol contents, the system becomes aqueous-based system with soluble oil, which could cause a slight corrosion to the engine parts (similar to Figure 1, type 2).

Figure 3A presents the extended comparison between experiments and model calculations of the quaternary water-ethanol-methanol-gasoline system. The alcohol fractions appeared on the right-hand side of the ternary diagram is the combined ethanol-methanol fractions. These calculations utilize the regressed interaction parameter from the ternary experiments for quaternary calculations, the least square error of this system is slightly higher at 0.29.

Water tolerances of both ethanol and methanol blended systems before they are partitioned into 2 phases are displayed in Figure 3B. The water tolerance increases with alcohol composition. It is, as already mentioned, appeared that the ethanol-blended fuel will less likely partition into 2 phases.

Water absorption and maximum storage period

Water contents in the stored gasohols (E5-E85), as displayed in Figure 4, were measured by the partner company. It is worth mentioned that the raw measured data are fluctuating among size and type of the storages; therefore, error bars of each data point are included in the figure. It is appeared that the rate of absorption is largely depended the alcohol concentration; as well as, there are absorption limit as seen in the E85 gasohol case. Combining these results with the LLE data, it seems highly likely that there are second phase formed in E10 and E20 gasohols during the 6 months of storage.

The maximum storage period for E20, considering the formation of the 2nd phase is around 4.5 months; while water concentration reaches critical point at 6 months for E10. E85 gasohol would never absorb enough water to partition; however, it is alcohol-based with soluble gasoline, adding water could cause it to behave like aqueous phase inducing a slight corrosion. For E5, extrapolation of the rate model shows that the critical water concentration could be reached after 9.4 months; however, it is a very rare case for fuel to be stored for more than 6 months in general practice.

4. Conclusions

The experiments on the liquid-liquid equilibriums of water-alcohols-gasoline have been conducted; the results have been used for fitting the model parameters to include the predictive capability for this and similar systems. The model has been validated with different set of experiment successfully. The equilibrium results combining with the predictive rate-based model of water absorption can be used to predict the maximum storage period to prevent the formation of unwanted water-rich second phase.

The results, especially rate-based absorption, are still measured under uncontrolled condition, with various unknown and unmeasured controlled parameters. Therefore, the future will be focused on the inclusion of these uncertainties in order to broaden the applicability range of these results.

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