The Effects of Diethyl Carbonate in Light Naphtha Blending to Utilize New Energy Resource

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Abstract. Light naphtha is not reliable used as automotive fuel because of its low octane number (RON) and high vapor pressure. To utilize light naphtha as fuel, blending process may be used to obtain usable gasoline fuel. Diethyl carbonate (DEC) can be used as blending agent with light naphtha because its high octane number and low vapor pressure. Therefore in this work, the vapor pressure and octane number (RON) of DEC–light naphtha blends were measured to study the effect of DEC in light naphtha blending. The vapor pressure measurements show that vapor pressure of DEC–light naphtha blends decreased while the DEC fraction increased. The Wilson and nonrandom two-liquid (NRTL) model are giving good correlation and prediction result with average absolute deviation (AAD) less than 1.3% meanwhile the Hildebrand & Scatchard model give quiet poor result with AAD value of 4.4%. The RON measurements show that the RON values of the blends increased while the DEC fraction increased. The DEC is successfully used as blending agent into light naphtha with 30% v/v optimum fraction.

1. Introduction
Light naphtha is a fraction of crude oil which has C5 – C6 hydrocarbons mixture and normal boiling temperature from 303.15 K to 363.15 K [1]. In general, the product of crude oil distillation gives light naphtha yield of 10% [2] and it is usually used as industrial solvent [3]. Light naphtha is not reliable if directly used as gasoline fuel without any additional treatments because of its low research octane number (RON) and high vapor pressure. Many industries have converted light naphtha become usable gasoline fuel with reforming and isomerization processes [2]. However, these processes are complicated and cost-consuming. To utilize light naphtha as fuel, blending process may be used to obtain usable gasoline fuel with an easy and low-cost process. Oxygenate compounds are the most promising blending agent in gasoline to increase the combustion performance and increase octane number since the prohibition of tetraethyl lead [4]. Methyl tert-butyl ether (MTBE) and ethanol are widely used as blending agent in gasoline because of their high octane number [5] and high production from biomass [6]. On the other hand, MTBE and ethanol cannot be used to blend with light naphtha because these compounds are increasing the vapor pressure significantly when mixed with hydrocarbons [5]. Diethyl carbonate (DEC), an oxygenate, may be used as blending agent with light naphtha because its high octane number and low vapor pressure [7]. The DEC is also known as biochemical compound because of its production from ethanol [7]. Therefore, the blended light naphtha + DEC may be categorized as biofuel which the usage of biofuel become a...
concern in energy research [8]. Thus, in order to apply DEC as blending agent, the knowledge of vapor pressure and octane number of the mixture are necessary. There are some publications about DEC as blending agent in open literature. Li et al. [9] were studying the volatility and flash point of typical aviation fuel + DMC/DEC mixture and found that DMC/DEC increase the volatility of aviation fuel. Rodríguez et al. [10] were studying the boiling temperature of DEC + (n-hexane, n-heptane, n-octane and cyclohexane) mixture and found that DEC increase the boiling temperature of the mixture. Anugraha et al. [11] were studying the vapor pressure of DEC + (n-heptane, isooctane and toluene) mixtures and showed that DEC successfully decrease the vapor pressure of the mixtures.

Based on our knowledge, there are no vapor pressure and octane number for DEC + light naphtha published in open literature. Therefore, in this work, the vapor pressure and RON of DEC–light naphtha blends were measured. The vapor pressure data of the mixtures are used to study the DEC as vapor pressure reducer agent in light naphtha. The RON data of the mixtures are used to study the DEC as octane booster in light naphtha.

2. Experimental methods

2.1. Materials

The light naphtha used in this study was obtained from PT. Trans Pacific Petrochemical Indotama (TPPI) Tuban, Indonesia. The diethyl carbonate (DEC) was purchased from Wuhan Fortuna Chemical Co. Ltd., China. Table 1 shows the specification of the materials used in this work. All materials in this work were used directly without any additional purification process.

| Component        | Supplier                          | Molecular weight (g/mol) | Vapor pressure at 303.15 K (kPa) | Purity  |
|------------------|-----------------------------------|--------------------------|---------------------------------|---------|
| Light naphtha    | PT. Trans Pacific Petrochemical   | 81.88                    | 44.96                           | –       |
|                  | Indotama                          |                          |                                 |         |
| Diethyl carbonate| Wuhan Fortuna Chemical Co. Ltd.   | 118.13                   | 1.95                            | 0.995   |

2.2. Measurement of vapor pressure

The apparatus and procedure for measuring vapor pressure used in this work were developed by Oktavian et al. (2013). The schematic diagram of the apparatus was shown in Figure 1.

![Figure 1](image-url)  
Figure 1. The schematic diagram of the apparatus for measuring vapor pressure

The specification of main components of the apparatus was explained in our previous works [12,13]. Initially, the mixture of light naphtha and DEC with certain volume fraction was prepared using 100 mL measuring glass by measuring the required volume of each component. The prepared mixture was
poured into equilibrium cell and stirred using a magnetic stirrer. Then, the vacuum pump was used to eliminate air and impurities from the equilibrium cell and the line package. The temperature condition in the ebulliometer cell was set and maintained by an electric heater equipped with a controller. The vapor pressure value of the mixture was recorded when the pressure reached a constant value at a certain temperature. The liquid composition in the ebulliometer cell was assumed to be same as initial composition because the change amount of the liquids caused by vaporization could be negligible. This procedure was repeated for other liquid mixtures and temperature conditions as listed in Table 2. The reliability of the apparatus for measuring vapor pressure of similar liquids was shown in our previous works [11,14].

2.3. Measurement of research octane number (RON)

The research octane number (RON) of a mixture was measured using portable octane analyzer KOEHLER K88600 developed by Koehler Instrument Company, Inc. This apparatus was claimed to give performance as same as ASTM D-2699 standard [15] which developed by ASTM International. Firstly, the pure isooctane was analyzed and the result was used as reference octane number. The mixture of light naphtha and DEC with certain volume fraction was prepared by measuring the required volume of each component. The prepared mixture was made with amount of 300 mL for each fraction. Then, it was inserted into the apparatus and to measure the RON value. The printed RON value was treated using reference octane number which obtained from pure isooctane to give the acceptable RON value.

3. Results and discussion

3.1. Vapor pressure data of light naphtha + DEC mixtures

The vapor pressure data of Light Naphtha + DEC mixtures were measured at temperature ranging from 303.15 K to 318.15 K as listed in Table 2. The P-T diagram of light naphtha + DEC for various compositions is presented in Figure 2. Figure 2 shows that the vapor pressure of mixtures was increasing while the temperature was increased. The temperature is increasing the vapor pressure because the vapor from the liquid is more produced due to vaporization. DEC was decreasing the vapor pressure of light naphtha mixture with the increase of DEC composition. This is happen because the DEC has very low vapor pressure and DEC make no azeotropic phenomenon with several hydrocarbon [10,11].

Table 2. Vapor pressure experimental data of light naphtha (1) + DEC (2) mixtures at 303.15 K – 318.15 K

| \( v_1 \) | 303.15 K | 308.15 K | 313.15 K | 318.15 K |
|---|---|---|---|---|
| 1 | 44.96 | 54.09 | 63.44 | 74.91 |
| 0.9 | 44.07 | 53.31 | 62.12 | 73.46 |
| 0.8 | 42.84 | 51.21 | 60.91 | 72.09 |
| 0.7 | 41.44 | 49.12 | 59.15 | 70.25 |
| 0.6 | 39.65 | 46.91 | 56.79 | 66.94 |
| 0.5 | 36.35 | 43.91 | 51.74 | 65.18 |
| 0 | 1.95 | 2.61 | 3.43 | 4.46 |

where \( v_1 \) is volumetric fraction of light naphtha

At 30% v/v DEC composition, the vapor pressure of the mixture was reached the maximum vapor pressure specification of gasoline with value of 60 kPa at 310.95 K [16]. With 50% v/v DEC composition added to the mixture, the vapor pressure could be reduce to 20% compared with pure light naphtha.
Therefore, DEC is successfully to become vapor pressure reducer agent in light naphtha. Based on the vapor pressure specification of gasoline, the blended LN + DEC fuel may be used as alternative fuel resource without additional processes at the DEC composition value of 30% v/v.

3.2. Pseudo binary analysis

The experimental data of light naphtha + DEC vapor pressures were approached using pseudo binary analysis which the light naphtha was assumed as pure compound. With the pseudo binary approachment, the experimental data were treated based on isofugacity criterion and give the calculated vapor pressure of mixtures ($P_{cal}$) which expressed in following equation:

$$P_{cal} = \sum_{i=1}^{m} x_i \gamma_i P_{i,sat}$$

where $m$ is the number of component in the mixture, $x_i$ is the mole fraction of component $i$, $\gamma_i$ is the activity coefficient of component $i$ and $P_{i,sat}$ is the pure vapor pressure of component $i$.

The activity coefficient of each component was correlated using Hildebrand & Scatchard [17], Wilson [18] and nonrandom two-liquid (NRTL) [19] models. The Hildebrand & Scatchard model was ever used to correlate the vapor pressure experimental data of typical fuel [9]. The Wilson and NRTL model were widely used to correlate the vapor pressure experimental data of nonelectrolyte liquid binary systems [10,11]. The parameters of the models were optimized using Barker’s method [20] by minimizing the following objective function (OF):

$$OF = \sum_{i=1}^{n} \left( P_{i,cal} - P_{i,exp} \right)^2$$

where $n$ is the number of data points and the subscript cal and exp refer to calculated and experimental values, respectively.

The parameters of each model were evaluated using average absolute deviation (AAD) between experimental and calculated values which showed in following equation:

$$AAD = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{P_{i,cal} - P_{i,exp}}{P_{i,exp}} \right| \times 100\%$$

The best fitted parameters for each model are listed in Table 3. Figure 3 show the vapor pressure of light naphtha + DEC mixtures and the comparison of prediction each model.
Table 3. The best fitted parameters for light naphtha (1) + DEC (2) mixtures and their performance in AAD

| Model      | Parameter | AAD  |
|------------|-----------|------|
| Wilson     | $a_{12}$  = 131.50 J/mol | 0.9 % |
|            | $a_{21}$  = 7745.00 J/mol |      |
| NRTL       | $b_{12}$  = 8026.62 J/mol | 1.2 % |
|            | $b_{21}$  = -1428.23 J/mol |      |
|            | $\alpha$  = 0.30 |      |
| Hildebrand & Scatchard | $l_0$ = 0.046 | 4.4 % |
|            | $\alpha_0$ = 6050.535 |      |
|            | $\alpha_1$ = 0.796 |      |
|            | $\alpha_2$ = 0.007 |      |

As shown in Table 3 and Figure 3, Wilson and NRTL model are giving good correlation and prediction result with AAD less than 1.3%. The Hildebrand-Scatchard model give quietly poor result with AAD value of 4.4%. Therefore, Wilson and NRTL models may be used to predict the vapor pressure of light naphtha and DEC mixture accurately.

3.3. Research octane number (RON) of light naphtha + DEC blends

The research octane number (RON) data of light naphtha + DEC mixtures were measured as showed in Figure 4. Figure 4 is also showing the effect of DEC addition in the RON of the mixtures. From the figure, it shows that DEC is increasing the RON value in the light naphtha + DEC mixture with the increase of DEC composition. DEC could increase the RON value in light naphtha blending because DEC itself has high RON value [7].
Figure 4. The research octane number (RON) data of light naphtha + DEC mixtures.
DEC, one of the oxygenated compounds, could influence the pre-flame combusting reaction with preventing undesired reaction at low temperature [5]. DEC also has branched molecule structure which give difficulties to breaking the bond and make it more resistance to pre-ignition caused by engine compression. Therefore, DEC may be used as octane booster in light naphtha blending to create the alternative fuel resources.

4. Conclusion
The vapor pressure and research octane number (RON) of DEC–light naphtha blends were measured to study the effect of DEC in light naphtha blending. The vapor pressure measurements show the vapor pressure of DEC–light naphtha blends decreased while the DEC fraction increased. The pseudo binary analysis approach was used to correlate the vapor pressure experimental data and predict the vapor pressure of light naphtha + DEC blends. The Wilson and NRTL model are giving good correlation and prediction result with AAD less than 1.3% meanwhile the Hildebrand & Scatchard model give quietly poor result with AAD value of 4.4%. The RON measurements show that the RON values of the blends increased while the DEC fraction increased. The DEC is successfully used as blending agent into light naphtha with 30% v/v optimum fraction.

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