

# Hydrogen solubility in triolein, and propane solubility in oleic acid for second generation BDF synthesis by use of hydrodeoxygenation reaction



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## ARTICLE INFO

### Article history:

Received 29 July 2013

Received in revised form 30 October 2013

Accepted 2 November 2013

Available online 11 November 2013

### Keywords:

Biodiesel fuels

Hydrodeoxygenation reaction

Gas solubility

Equation of state

Mixing rule

## ABSTRACT

The hydrogen solubility in triolein and propane solubility in oleic acid were measured up to 20 MPa at the temperature around 353.2, 413.2, and 473.2 K. The hydrogen solubility in triolein was slightly larger than the linear pressure dependence like Henry's law, and it was increased with the temperature. On the contrary, propane solubility in oleic acid was decreased with the temperature. The experimental data were correlated with Peng–Robinson (PR) equation of state. Though the usage of conventional mixing rule showed a good reproducibility just for the propane solubility in oleic acid, the Wong–Sandler type mixing rule, combined with Flory–Huggins equation, was required to evaluate the hydrogen solubility in triolein. The correlated phase behavior well described for the temperature dependence of hydrodeoxygenation rate observed in our previous study.

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## 1. Introduction

The first generation biodiesel fuels (BDFs) have been synthesized from triglyceride of fatty acid by addition of methanol and basic catalyst. The BDF is easily obtained by a transesterification of fatty acid under the atmospheric pressure at the room temperature. However, the byproduct, glycerol, is not always useful. So, the second generation BDF is now paid much attention as a new method.

Fig. 1 shows the reaction scheme for a new method of new synthesis [1]. The production is so-called the second generation BDF. As shown in the figure, the BDF is obtained by a hydrodeoxygenation reaction for triglyceride, and the triglyceride is converted to propane and some alkanes, having 16–18 carbon atoms in the molecule, via the following chemical transformations; unsaturated free fatty acid, saturated fatty acid, fatty alcohol, and alkane. The advantage of the reaction is utilization of a desulfurization reactor in conventional petroleum refinery. In our previous study [1], trap grease was considered as a feedstock for the BDF. The trap

grease is free-floating grease in waste water reservoir of restaurant, food courts, food industry and so on, and mainly composed of triglyceride of fatty acids. The conventional hydrodesulfurization catalysts were effective for the hydrodeoxygenation reaction in the pressure range from 5 to 20 MPa, and the temperature from 473.2 to 573.2 K. Especially, the reaction rate was drastically increased in the higher temperature range. Though the phase equilibrium and the reaction rate are essential for designing the hydrodeoxygenation reaction process, there are few available data. In this study, a new apparatus was designed for the measurement up to 473.2 K. Though the experimental data should be obtained at the temperature up to 573.2 K, the data were up to 473.2 K owing to the maximum working temperature of equipments. Obtaining several isotherm, the solubility will be evaluated by an assumption of the temperature dependence. So, in this study, ensuring the reliability of the experimental data, hydrogen solubility in decane at 343.20, 413.17, and 473.18 K, and propane solubility in decane at 410.94 and 477.55 K. After ensuring the reliability, hydrogen solubility in triolein, and propane solubility in oleic acid, as the reactant and the product at the first reaction step, were measured up to 20 MPa at the temperature around 353.2, 413.2, and 473.2 K. The experimental data were correlated with Peng–Robinson (PR) equation of state [2].

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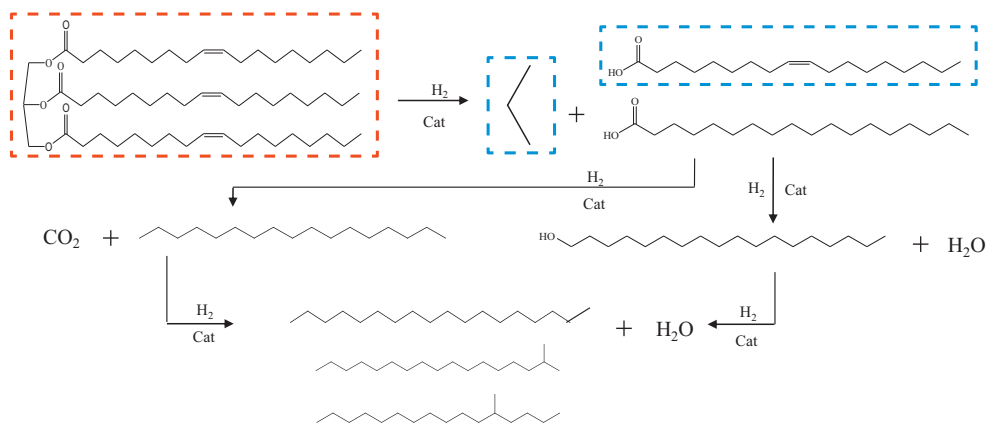
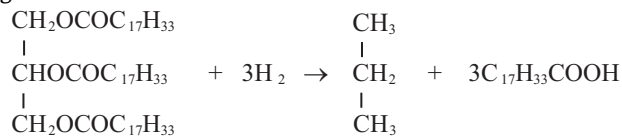


Fig. 1. Reaction scheme to obtain second generation BDF.

The experimental data will be useful for considering the following reactions:



For example, the equilibrium constant of the reaction will be calculated by the following relation.

$$K = \frac{[\text{C}_3\text{H}_8][\text{Oleic acid}]^3}{[\text{Triolein}][\text{H}_2]^3} \approx \frac{(x_{\text{C}_3\text{H}_8}/v_L)(x_{\text{Oleic acid}}/v_L)^3}{(x_{\text{Triolein}}/v_L)(x_{\text{H}_2}/v_L)^3}$$

Though the estimation was not carried out, the experimental data will be utilized for a design of the reaction process.

## 2. Experimental

### 2.1. Materials

Hydrogen was obtained from Takachiho Trading Co. Ltd., Tokyo, and the purity is no less than 99.99%. Propane was also obtained from Takachiho Trading Co. Ltd., Tokyo, and the purity is no less than 99.9%. Decane was a special grade reagent obtained from Wako Pure Chemical Ltd., Osaka, Japan, and the purity higher than 99.0%. Triolein was purchased from Kanto Chemical Co. Inc, Tokyo. Oleic acid from Sigma–Aldrich Co. Ltd., St. Louise, U. S. The stated purity of these chemicals was higher than 60 and 90%, respectively. Their purity seems to not be high, the impurities were not investigated. However, they were thought to be reagents with the highest purity obtained from natural products. According to the supplier, the impurities seem to be other fatty acid or their groups. All chemicals were used without further purification.

### 2.2. Equipments and procedure

Fig. 2 shows a schematic diagram of an apparatus. The apparatus was designed for this study, and based on a recirculation method. The cell was made of stainless steel with the inner volume about 145 cm<sup>3</sup>. A pressure resistance windows was equipped with the cell to observe the phase behavior. The maximum working pressure was estimated to be 15 MPa at 523 K. The cell was held in an oil bath with the volume about 90 L, and it was filled with silicone oil (Momentum Performance Materials TSF433, New York). To agitate viscous fluids, an agitator was equipped with the cell. Two magnetic driven recirculating pumps were also equipped. One was for vapor phase, the other for liquid phase. In the recirculating line of the liquid phase, a liquid sampler, with volume about 150 cm<sup>3</sup>,

were equipped. The inlet and the outlet of the sampler have VCR assemblies (Swagelok SS-4-VCR-2-GR). So, the liquid sample was picked up repeatedly. The experimental temperature was measured by a platinum resistance thermometer (ASL F250 MkII, Miton Keynes, U.K.), calibrated with a standard thermometer based on ITS90. The resolution and the precision was estimated to be within 0.001 and 0.03 K, respectively. The pressure was measured by a pressure transducer (Kyowa PHS-300KB, Tokyo) calibrated with a dead weight tester (Nagano Keiki PD22, Tokyo) up to 0.001 MPa. The procedure of the measurement was described below:

At first, sample gas, hydrogen or propane was fed into the evacuated cell, and successively liquid sample, triolein or oleic acid, into the cell by HPLC pump (GL Science PU 716, Tokyo). Up to the desired pressure, the sample gas was reloaded again by using a pressure generator. After attaining the constant temperature and pressure, a portion of the liquid phase was picked up by using the liquid sampler. Removing the sampler from the recirculating line, the mass was measured by a direct reading balance (Shimadzu BX3200H, Kyoto, Japan) with maximum capacity of 3.2 kg and the minimum 10 mg. Successively, the sampler was connected with a gas expansion system. In Fig. 2, the gas expansion system was also shown. It was mainly composed of a constant temperature bath, two buffering vessels made of glass with each volume about 10 L, a condenser made of stainless tube with the inner diameter 4.9 mm, and the length about 500 mm, and a wet test gas meter (Shinagawa W-NK-0.5, Tokyo). The minimum capacity of the meter is 1 cm<sup>3</sup>. After the mass of the picked up sample was measured by the direct reading balance, the cell was connected with the gas expansion system. The dissolved gas was expanded under the atmospheric pressure, then the gas was exchanged with the air in the two vessels with volume of 20 L. The volume was measured by the gas meter. From the vacant mass of the sampler and the expanded gas volume, the composition was determined.

## 3. Results and discussion

### 3.1. Hydrogen solubility in triolein and propane solubility in oleic acid

Ensuring the reliability of the experimental data, hydrogen solubility in decane at 343.20, 413.17, and 473.18 K, and propane solubility in decane at 410.94, and 477.55 K were measured.

Figs. 3 and 4 show the experimental results. Table 1 lists the data. In the figure, those of Connolly et al. [3] and Reamer et al. [4]. As shown in the figures, hydrogen solubility was increase with the temperature. On the contrary, propane solubility was decreased with the temperature. These temperature dependences agreed well with the those of literature.

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