Adsorption of fatty acid methyl ester derived from squid liver lipid onto silica gel adsorbent

Hideo MARUYAMA[1*], Akito FURUKAWA[2], Hideshi SEKI[1],

1. Division of Marine Biosciences, Graduate School of Fisheries Sciences, Hokkaido University, Minato 3-1-1, Hakodate JAPAN, 041-8611

2. Mitsubishi Chemical Corporation, 1-1 Marunouchi 1, Chiyoda-ku, Tokyo Japan, 100-8251

Telephone: +81-138-40-8813, Facsimile: +81-138-40-5048, E-mail: maruyama@fish.hokudai.ac.jp

* corresponding to the author

Abstract

The purpose of this study is the effective utilization of fisheries waste, squid liver, as a raw material of biodiesel. To obtain the biodiesel from squid liver, fatty acids extracted are esterified with methyl alcohol. As the product of the esterification contains many by-products, the target product, fatty acid methyl ester of squid liver (SFAME) must be recovered from the products. SFAME was divided into three groups, they are, saturated (SF), monounsaturated (MF), and polyunsaturated (PF) fatty acid methyl esters (FAME) based on the number of the double bond. In this study, the recovery of SFAME from the product of esterification through adsorption (dry washing) was investigated. Especially, the effect of solvents, toluene, and methyl alcohol, on the recovery efficiency of SFAME using silica gel as an adsorbent was focused on. The competitive adsorption model successfully explained the present adsorption system, and the equilibrium adsorption constants and the saturated adsorption density could be determined by the model analysis. The equilibrium adsorption constant of PF was the largest among SFAME (PF > MF > SF), and this order could correspond to the values of their dielectric constants. Methanol greatly affected to the adsorption behavior of SFAME due to its hydrophilicity.

KEYWORDS: Fatty acid methyl ester; silica gel; biodiesel; squid liver; adsorption

1. Introduction

The recent movement of the Sustainable Development Goals (SDGs) is interesting for several reasons, including the requirement of reproductive energy, proceeding carbon neutrality, and the effective utilization of unused biomass. To address these issues, in the past decade, the utilization and the production of biodiesel have been greatly focused on. At first, edible oil has been employed for biodiesel production, however, it gradually shifted to non-edible oil, waste cooking oil, and oils derived from terrestrial or aquatic plants and animals [1]. For the viewpoint of effective utilization of bio-resources, we have been proceeding with the use of fisheries waste for biodiesel [2]. Biodiesel is chemically a fatty acid methyl ester (FAME), which can be obtained from transesterification reaction of triglyceride (TG). Many types of lipid resources have been used and produced to make biodiesel. Among them, one of the most important resources is recognized vegetable oils such as canola oil, rapeseed oil, palm oil, olive oil, and so on. They were mainly used from waste oil used in frying cooking oil for biodiesel.

On the other hand, fisheries wastes, that is, viscera of fishes or shells, have been known to contain proteins and lipids (TG). TGs derived from squid liver contain particulaly docosahexaenoic acid (C22:6, DHA) and eicosapentaenoic acid (C20:5, EPA) [3], which are well known to be health-promoting substances, leading to their use in pharmaceuticals and health supplements. The other fatty acids which are less available can be used as a source for biodiesel if EPA and DHA can be separated from them by some methods. However, fatty acids from fish waste have rarely been used as a source of biodiesel fuel. Little research has been published in the last two decades. Although there have not been many attempts to use marine wastes as biodiesel feedstock, we have developed a model [4] for the distribution of FAME in the solid phase (urea-FAME complex) using the urea inclusion method, which has

long been used for the separation of FAME, and in particular We have also developed a model for the distribution of FAME in the solid phase (urea-FAME complex), and have divided FAME into three major categories (saturated, monounsaturated, and polyunsaturated) for modeling.

Recently the wet washing method was widely used as a purification way of biodiesel [5]. This process can process large quantities of crude biodiesel, which is one of its advantages, but it has several disadvantages such as increased cost and generation of high effluents, including high chemical oxygen demand (COD). On the other hand, dry washing with adsorption has also been attempted to remove contaminants or recover biodiesel (fatty acid alkyl esters).

Adsorptive separation is well known and has been used in various processes to remove/recover hazardous/available substances, and so on. There have been some reports used as adsorbents such as chemical products of adsorbent [6,7], biomaterial adsorbent [7], and activated carbon [8]. However, from the viewpoint of biodiesel fuel recovery, research on the adsorption behavior and properties of fatty acid alkyl ester on adsorbents has rarely been reported. Clarification of the adsorption behavior and properties should be important for the design and operation of the separation apparatus from practical and chemical engineering aspects.

In addition, the extracted lipids are not always soluble in all types of organic solvents, so the difference in polarity between the lipids (TG) and these organic solvents causes the lipid oil droplets to be dispersed in the organic solvent. To solve this problem, a relatively highly polar solvent, such as toluene or benzene, must be added to the system. Lipids could be dissolved in the organic solvent to enhance the esterification reaction rate. When using the adsorption method (dry washing method) to recover FAME, it is necessary to understand the effect of these coexisting substances on the adsorption properties of the target material, i.e.,

FAME (biodiesel).

In the previous study [9], we investigated the influences of coexisting substances (methanol and toluene) on the adsorption behavior of methyl palmitate on silica gel and proposed a competitive adsorption model based on Langmuir type adsorption equilibrium. The proposed competitive adsorption model, which is also treated in this study, is very different from the conventional competitive adsorption model for more than two adsorption target substances, which are solutes. Most of the previous competitive adsorption models are based on and extend the Langmuir type to systems with more than two components, and many of the studies have dealt with metal ions and dyes as adsorption target substances [10-12]. The proposed competitive adsorption model differs from other competitive adsorption models in that it treats the adsorbate as a solute and the solvent as its medium. Such a treatment has rarely been used in the treatment of both aqueous adsorption and non-aqueous adsorption systems. It is well known that lipid-derived from fishery products should contain many polyunsaturated fatty acids (PUFA). The adsorbent used in this study was silica gel, which is commonly used for general analytical pretreatment and is relatively inexpensive and readily available. In previous studies, molecular sieve, 13X [6,8], an activated carbon from macaúba fruit kernel [8], and rise hull ash [7] have been used as adsorbents for FAME adsorption, in addition, a silver-exchanged zeolite Y has been used for separation of cis and trans geometric isomers of mono- and polyunsaturated fatty acid methyl esters [13].

For dry washing with silica gel, it is important to know the adsorption behavior and properties of these polyunsaturated fatty acid methyl esters (PUFAMEs) for dry washing with silica gel and the influence of coexisting organic solvents on the adsorption behavior and properties of PUFAMEs for dry washing with silica gel. For this purpose, it is necessary to verify whether the proposed competitive adsorption model can be extended to multi-component systems. FAME obtained from TG derived from natural products is

expected to be complicated due to its wide variety of components. For this reason, we decided to treat FAME derived from squid liver in the same way as in the modeling of FAME derived from fishery wastes by the urea inclusion method, i.e., by dividing FAME into three major categories: saturated, monounsaturated, and polyunsaturated. In this study, based on the obtained experimental results, we discussed the influence of the coexisting substances on the adsorption behavior of FAME-derived squid liver by applying them to the proposed competitive adsorption model.

2. Materials and methods

2.1. Materials

2.1.1 Japanese squids (*Todarodes pacificus*)

Japanese squids (*Todarodes pacificus*) were captured at Tsugaru Strait near Hakodate bay (Hokkaido prefecture, Japan). The squid liver was separated from the body as soon as possible and was stocked in a refrigerator (–20 °C).

2.1.2 adsorbent

As an adsorbent, silica particles (silica gel 60, Kanto Chemical Co. Inc., Japan) were used in this study without further modification.

2.1.3 reagents

Methyl alcohol (99.7 %), toluene (99.5 %), and chloroform (99.0 %) were purchased from Fujifilm Wako Pure Chemical Co. (Japan). Hydrogen chloride-methanol (10 wt.%) solution and hexane (96.0 %) were purchased from Kanto Chemical Co. Inc. (Japan). Methyl tricosanoate (99.9 %) was purchased from AccuStandard (U.S.). They were used without further purification.

2.2. Preparation of fatty acid methyl ester

The liver was taken out and chopped by a homogenizer. The lipid was extracted by Bligh and Layer method [14]. 40 g of squid liver was weighed and homogenized in a homogenizer for 5 seconds. 80 mL of methanol (99.7 %) and 40 mL of chloroform (99.0 %) were added

and homogenized for another 1 minute. Then 40 mL of chloroform was added and homogenized with a mixer for 30 seconds. 40 mL of distilled water was added and homogenized for another 15 seconds. The mixture was filtered under reduced pressure (quantitative filter paper 5C) using a Buchner funnel and a suction bottle. After allowing the filtrate to stand overnight in a 500 mL separating funnel, the lower chloroform layer was separated into a 500 mL beaker, then, nitrogen gas was blown in to evaporate the chloroform, and the mass of the lipid was weighed on an electronic balance. A portion of the lipid was placed in a test tube with a lid, and the air in the tube was replaced with nitrogen before storage in a refrigerator (–20 °C).

A certain amount of lipid was set in a 100 mL bottle with a lid. Desired amounts of toluene and lipid were added to the bottle, and it was shaken to dissolve the lipid in toluene. Then, a certain amount of hydrogen chloride-methanol (10 wt.%) solution was added as a liquid catalyst of esterification with methanol. The bottle was placed in a water bath and was heated at 90 °C for 120 minutes. After natural-air cooling, fatty acid methyl esters were collected by liquid extraction using hexane and were stocked in a refrigerator (–20 °C).

2.3. Procedure of adsorption experiment

All adsorption experiments in this study were conducted with a batch operation, and the manner was almost the same as the procedure in the previous study [9]. Silica gel powder was washed with distilled water and was dried at 180 °C for two hours in an incubator. After cooling, it was stocked in a desiccator. A certain amount of silica gel powder was set in 100 mL Erlenmeyer flask. By pouring a small amount of hexane into the flask, the adsorbent was soaked in hexane and was deaerated by decompression using an aspirator. A mixture of SFAME, methanol, and toluene was prepared in another glass vessel. The adsorption

experiment was started by adding the desired amount of the mixed solution to the flask. In most experiments, the final volume of the adsorption system was 49.5 mL. It was stirred with a magnetic stirrer for the time necessary to attain the adsorption equilibrium. Then silica gel powder was separated from the liquid phase by filtration with a membrane filter having 3 μm of an average pore size. The determinations of toluene, and methanol were conducted with ultraviolet spectrometry [15] (Jasco V-630, Japan), and colorimetric spectrometry [16,17], respectively. The determination of FAMEs was conducted with gas chromatography (Shimadzu GC-2014, Japan) with an internal standard method using methyl tricosanoate (C23:0). The measurement conditions of gas chromatography were as follows: column: fused silica capillary column, Omegawax320 (Supelco, U.S., 30 m × 0.32 mm i.d., film thickness 0.25 μm); carrier gas: helium, 25 cm/sec; detector: FID, 260 ºC; injection: spilit 100:1, 1.0 mL, 250 ºC; column temperature (oven): 140 ºC (5 min) → 4ºC/min → 200 ºC (50 min). The adsorbed amount of each substance onto the silica surface was determined from the difference amount between the concentrations in the initial and the equilibrium state. All data for evaluation were obtained in duplicate (n = 2), and the average values were shown in figures.

3. **Results and Discussion**

3.1. Composition of fatty acid methyl ester derived from squid liver

After esterification, the composition of SFAME was measured by gas chromatography. The result is shown in Table 1. Palmitic acid, oleic acid, eicosapentaenoic acid, and docosahexaenoic acid were found to be the main components, which was the most similar composition reported in the literature [3]. The average molecular weight (*Mwa*) of the SFAME used in this study was determined based on the result (Table 1) for a comprehensive discussion in the following part.

$$Mwa = \sum\left[\left(\frac{\text{each compositio n [\%]}}{100}\right)\times \text{each molecular weight}\right] \quad (1)$$

The value of *Mwa* was calculated as 293.52. In the following parts, this value will be used, and the concentration of SFAME will be expressed as molar concentration.

Damasceno et al. (2018) prepared FAMEs from commercially available macauba kernel oil for adsorption experiments and reported their composition in detail as follows, laurate (C12:0), methyl myristate (C14:0), methyl palmitate (C16:0), methyl staerate (C18:0), methyl oleate (C18:1), and methyl linoleate (C18:2) [8]. The composition is based on (1). Based on this composition, the average molecular weight (*Mwa*) was calculated to be 245.1 using equation (1). The FAMEs they used have relatively low carbon numbers, and there are few monounsaturated and polyunsaturated FAMEs, resulting in a slightly smaller average molecular weight than ours value.

3.2. Influence of coexisting substances on adsorption of SFAME

The adsorption experiment was conducted at the same initial concentration (mol/L) ratio of methanol (ME), toluene (TL), and SFAME. In the previous study [9], glycerin was not affected by the amount adsorbed of ME, TL, and methyl palmitate (MP), therefore, glycerin was not added to the present adsorption system. Fig. 1 shows the adsorption isotherm of ME, TL, and SFAME. The solid symbols correspond to the amount adsorbed of ME, TL, and MP reported in the previous study [9]. The amount adsorbed of ME and TL in this study was mostly the same as those reported in the previous study. Note that the relationships between the equilibrium concentration and the equilibrium amount adsorbed are quite different for SFAME, TL, and ME. For example, the equilibrium amount adsorbed of SFAME and TL are about 1.3 mmol/g and 0.1 mmol/g at an equilibrium concentration of about 0.1 mol/L, respectively. However, ME has an equilibrium amount adsorbed of about 4.5 mmol/g at the equilibrium concentration of 0.05 mol/L. This fact indicates that the binding strength of ME to silica gel is much higher than that of SFAME and TL. However, the amount adsorbed of SFAME was larger than that of MP. In the equilibrium concentration range of 0.1-0.3, the amount adsorbed of SFAME was mostly about 1.4-fold larger than that of MP. MP is saturated fatty acid methyl ester, however, SFAME is consist of not only methyl ester of saturated fatty acids but also methyl ester of monounsaturated and polyunsaturated fatty acids. This will be discussed later, however, the fact that SFAME contains not only SF but also MF and PF is related to the larger amount adsorbed compared to MP. The polarity of the molecule itself should have a significant effect on this phenomenon.

The amount adsorbed of overall FAME increased up to an equilibrium concentration of about 0.1 mol/L and decreased at higher equilibrium concentration range, in other words, the maximum amount of FAME adsorption was observed about the equilibrium concentration of 0.1 mol/L. This trend was also observed in the single methyl palmitate system described in the

previous paper, and it was found that a similar trend was observed. Adsorption equilibrium relationships with maxima in the adsorption isotherm may seem strange at first glance, but they are often reported in systems with more than two adsorbents and adsorbates. The following examples are reported. For example, activated carbon and binary system of reactive yellow and reactive black dyes [18], acid soil and binary system of Cu^{2+}/Zn^{2+} [10], mesoporous silica compound [19] (MCM-41 and AlMCM-41) and binary system of methylene blue and rhodamine B dyes [20], goethite and gibbsite and two binary systems of phosphate/arsenate and phosphate/selenite [11], multiwalled carbon nanotube and $Pb^{2+}/Cu^{2+}/Cd^{2+}$ systems [21], iminodiacetic acid (IDA) chelating resin and $Pb^{2+}/Cu^{2+}/Cd^{2+}$ systems [22], rice husk ash and aqueous binary system of Cd^{2+}/Ni^{2+} [23] and so on. Moreover, the followings are results reported in literature about the adsorption kinetics process that was observed to show not only the adsorption equilibrium relationship but also the maximum adsorption amount in the adsorption kinetics process leading to equilibrium, for example, a cation exchange resin (IRN-77) and binary system of Co^{2+}/Cr^{3+} and ternary system of $Co^{2+}/Ni^{2+}/Cr^{3+}$ system [24], iminodiacetic acid (IDA) chelating resin and binary system of Pb^{2+}/Cu^{2+} (at the initial concentration 2 mmol/L) [22] and so on. As described above, a lot of adsorption isotherms with maxima have been reported for divalent metal ions adsorption systems. We considered that methanol has a stronger binding force with silica gel. The extremely high abundance of methanol in the system and its strong binding strength are thought to be responsible for the change in the adsorption isotherm of SFAME, which has a maximum value.

Üstün (1996) has conducted adsorption experiments of FAME derived from tall oil using molecular sieve X13 as an adsorbent [6]. Nine solvents (methanol, ethanol, isopropanol, petroleum ether, petroleum naphtha, hexane, isooctane, acetone, and benzene) were used to dissolve FAME. The results has been reported that the equilibrium amounts adsorbed of

FAME at the equilibrium concentrations in the neighborhood range for each solvent were mainly, 345 g/g-X13 for methanol (76.9 g/L,), 331 g/g-X13 for ethanol (84.4 g/L), 240 g/g-X13 for isopropanol (77.7 g/L), 170 g/g-X13 for acetone (81.1 g/L), 108 g/g-X13 for isooctane (79.5 g/L), and 101 g/g-X13 for hexane (85.7 g/L), respectively. Özgül-Yücel and and Türkay (2003) have conducted FAME (crude methyl ester derived from rice bran) adsorption experiments using rise hull ash and silica gel as adsorbents to purify the crude FAME (removal of FFA (free fatty acid)) [7]. The adsorption experiments were performed at 25°C in 50 mL of hexane in a batch system. The FFA equilibrium concentration and the equilibrium amount adsorbed of FFA were in the range of about 0.2-1.6 g/L and 5-45 mg/g-silica, respectively. The amount adsorbed of FFA onto silica gel was higher than that onto rice hull ash. They reported that the addition of too many adsorbents (rise hull ash and silica gel) may increase the amount adsorbed of FAME itself, and that the adsorption equilibrium relationship between adsorbents (rise hull ash and silica gel) FFA was expressed by the Freundlich adsorption isotherm.

Our results show that the maximum adsorption volume adsorbed in the SFAME experiment is about 1.3×10^{-3} mol/g (0.382 g/g-silica) at an equilibrium concentration of about 0.1 mol/L (29.4 g/L), which is a very small adsorption volume compared to Ustun's results. In comparison with the FFA adsorption of Özgül-Yücel and Türkay (2003), which is not FAME, the maximum adsorption value obtained in their experiments is 0.045 g/g-silica [7], which is smaller than our amount adsorbed. However, the equilibrium concentration shown in this study was quite larger than that reported by Özgül-Yücel and Türkay (2003), suggesting greatly influence of the presence of methanol.

The competitive adsorption model was applied to the present results. The adsorption model is based on the following two reactions: (1) competitive adsorption between MP and FAME onto the hydrogen atom of the silanol functional group on the silica surface; (2)

competitive adsorption between FAME and TL onto the methyl functional group of methanol adsorbed on silanol group on the silica surface. Finally, each amount adsorbed, X, was represented as follows.

$$X_{\mathrm{SFAME}} = \frac{X_{\mathrm{S}} K_{\mathrm{SFAME1}} C_{\mathrm{SFAME}}}{1 + K_{\mathrm{SFAME1}} C_{\mathrm{SFAME}} + K_{\mathrm{M1}} C_{\mathrm{M}}} + \frac{X_{\mathrm{M}} K_{\mathrm{SFAME2}} C_{\mathrm{SFAME}}}{1 + K_{\mathrm{SFAME2}} C_{\mathrm{SFAME}} + K_{\mathrm{TL}} C_{\mathrm{TL}}} \tag{2}$$

$$X_{\mathrm{M}} = \frac{X_{\mathrm{S}} K_{\mathrm{M1}} C_{\mathrm{M}}}{1 + K_{\mathrm{SFAME1}} C_{\mathrm{SFAME}} + K_{\mathrm{M1}} C_{\mathrm{M}}} + \frac{X_{\mathrm{S}} K_{\mathrm{M2}} C_{\mathrm{M}}}{1 + K_{\mathrm{M2}} C_{\mathrm{M}}} \tag{3}$$

$$X_{\mathrm{TL}} = \frac{X_{\mathrm{M}} K_{\mathrm{TL}} C_{\mathrm{TL}}}{1 + K_{\mathrm{SFAME2}} C_{\mathrm{SFAME}} + K_{\mathrm{TL}} C_{\mathrm{TL}}} \tag{4}$$

Where, X_{SFAME} is the overall amount adsorbed of SFAME. X_{M} and X_{TL} are the amounts adsorbed of methanol and toluene, respectively. X_{S} represents the total number of adsorption sites existing on the silica surface, which correspond to all silanol groups on the silica surface. K_{SFAME1} and K_{SFAME2} are the overall equilibrium adsorption constants of SFAME with sites 1 and 2. K_{M1} and K_{M2} are the equilibrium adsorption constants of ME with sites 1 and 2, respectively. K_{TL} is the equilibrium adsorption constant of TL. C represents the equilibrium concentration of each adsorbate. As for SFAME and TL, The maximum adsorbed amounts of SFAME and TL are regarded as the same as the amount adsorbed of ME. By fitting of the data to Eqs. (2)-(4) using a least squares regression, the equilibrium adsorption constant and the saturated adsorption density were determined. The estimated adsorption parameters are listed in Table 2. The calculated lines using these estimated adsorption parameters are shown as the solids lines in Fig. 1. As seen in Fig. 1, good agreements between the experimental data and the calculated value are confirmed. In comparison with the previously determined adsorption parameters of the MP-ME-TL system, K_1 for SFAME was 2.4-fold larger than K_1 for PM.

3.3. Influence of degree of unsaturation of SFAME on adsorption

In a previous study, we pointed out that the difference in the amount adsorbed of ME, TL, and MP is strongly related to their dielectric constant [25]. The silanol group on the silica surface rather strongly binds the substances having a larger dielectric constant. In table 3, the dielectric constants of octadecanoic fatty acids [25] were listed. It is found that the value of the dielectric constant becomes larger as an increase in the number of the double bond of the adsorbates. The reason why the amount adsorbed of SFAME became larger than that of MP was considered that the existences of unsaturated fatty acid methyl esters contribute to the increase in the amount adsorbed of SFAME. We divide SFAME into three groups, saturated (SF), monounsaturated (MF), and polyunsaturated (PF) FAME. The three categorized groups are summarized in Table 4. In the same as the case of MP or overall SFAME, each categorized SF, MF, and PF could adsorb competitively onto ME and TL. Each amount adsorbed of SF, MF, and PF, Eq. (2) could be extended for 3 categorized SFAME as follows.

$$X_{\mathrm{SF}} = \frac{X_{\mathrm{S}} K_{\mathrm{SF1}} C_{\mathrm{SF}}}{1 + K_{\mathrm{SF1}} C_{\mathrm{SF}} + K_{\mathrm{MF1}} C_{\mathrm{MF}} + K_{\mathrm{PF1}} C_{\mathrm{PF}} + K_{\mathrm{M1}} C_{\mathrm{M}}} + \frac{X_{\mathrm{M}} K_{\mathrm{SF2}} C_{\mathrm{SF}}}{1 + K_{\mathrm{SF2}} C_{\mathrm{SF}} + K_{\mathrm{MF2}} C_{\mathrm{MF}} + K_{\mathrm{PF2}} C_{\mathrm{PF}} + K_{\mathrm{TL}} C_{\mathrm{TL}}} \tag{5}$$

$$X_{\mathrm{MF}} = \frac{X_{\mathrm{S}} K_{\mathrm{MF1}} C_{\mathrm{MF}}}{1 + K_{\mathrm{SF1}} C_{\mathrm{SF}} + K_{\mathrm{MF1}} C_{\mathrm{MF}} + K_{\mathrm{PF1}} C_{\mathrm{PF}} + K_{\mathrm{M1}} C_{\mathrm{M}}} + \frac{X_{\mathrm{M}} K_{\mathrm{MF2}} C_{\mathrm{MF}}}{1 + K_{\mathrm{SF2}} C_{\mathrm{SF}} + K_{\mathrm{MF2}} C_{\mathrm{MF}} + K_{\mathrm{PF2}} C_{\mathrm{PF}} + K_{\mathrm{TL}} C_{\mathrm{TL}}} \tag{6}$$

$$X_{\mathrm{PF}} = \frac{X_{\mathrm{S}} K_{\mathrm{PF1}} C_{\mathrm{PF}}}{1 + K_{\mathrm{SF1}} C_{\mathrm{SF}} + K_{\mathrm{MF1}} C_{\mathrm{MF}} + K_{\mathrm{PF1}} C_{\mathrm{PF}} + K_{\mathrm{M1}} C_{\mathrm{M}}} + \frac{X_{\mathrm{M}} K_{\mathrm{PF2}} C_{\mathrm{PF}}}{1 + K_{\mathrm{SF2}} C_{\mathrm{SF}} + K_{\mathrm{MF2}} C_{\mathrm{MF}} + K_{\mathrm{PF2}} C_{\mathrm{PF}} + K_{\mathrm{TL}} C_{\mathrm{TL}}} \tag{7}$$

$$X_{\mathrm{M}} = \frac{X_{\mathrm{S}} K_{\mathrm{M1}} C_{\mathrm{M}}}{1 + K_{\mathrm{SF1}} C_{\mathrm{SF}} + K_{\mathrm{MF1}} C_{\mathrm{MF}} + K_{\mathrm{PF1}} C_{\mathrm{PF}} + K_{\mathrm{M1}} C_{\mathrm{M}}} + \frac{X_{\mathrm{S}} K_{\mathrm{M2}} C_{\mathrm{M}}}{1 + K_{\mathrm{M2}} C_{\mathrm{M}}} \tag{8}$$

$$X_{\mathrm{TL}} = \frac{X_{\mathrm{M}} K_{\mathrm{TL}} C_{\mathrm{TL}}}{1 + K_{\mathrm{SF2}} C_{\mathrm{SF}} + K_{\mathrm{MF2}} C_{\mathrm{MF}} + K_{\mathrm{PF2}} C_{\mathrm{PF}} + K_{\mathrm{TL}} C_{\mathrm{TL}}} \tag{9}$$

The data shown in Fig. 1 was applied to Eqs. (5)-(9), and by a least squares regression, the adsorption parameters could be determined. The values of parameters are summarized in Table 5. Fig. 2 shows the fitting of the data of Fig. 1 to Eqs. (5)-(9). The solid dashed, and dotted lines are the calculated values using the adsorption parameters in Table 5. As for ME and TL, it seems to be almost the same as Figs. 1b and 1c, in addition, show a good agreement between the experimental and the calculated values. As for SFAME, the amount adsorbed of PM was larger than that of SF and MF. In comparison to these values, K_{PF1} and K_{PF2} were 2.3 and 3.1 fold larger than K_{SF1} and K_{SF2}. The value of X_{S} was almost the same in the case of the overall SFAME adsorption. In this case K_{M1} and K_{M2}, they were 1.4 fold larger than the values in the case of the overall SFAME adsorption. The degree of unsaturation, that is, the number of double bonds between carbons, of FAMEs was found to affect significantly their adsorption behavior on the silica surface.

4. Conclusions

The influence of coexisting substances on the adsorption behavior of FAME derived from squid liver, as a model substance of biodiesel fuel, onto silica surface in the presence of methanol and toluene was investigated, assuming the adsorption of diesel fuel from the solution after the reaction in the biodiesel production process.

The overall and the categorized FAME adsorption behaviors could be explained well by the competitive adsorption model based on Langmuir type adsorption. The equilibrium adsorption constant and the saturated adsorption density were determined by fitting of the data to the model equations using a least squares regression. The equilibrium constant of K_1 and K_2 of PF were larger than these of SF and MF, which corresponds to 2.3 and 3.2 fold larger than that of PF. The occupied surface area of a single silanol group estimated from X_S was mostly the same as the reported values in the literature. It was found that the presence of the double bond of carbon molecules in the molecular structure significantly affected the adsorption behavior onto the silica surface.

In a further study, for confirmation of the applicability of this model, we will conduct adsorption experiments using samples with different FAME compositions, and investigate the influence of the application of the proposed model on the estimation of adsorption parameters, especially the adsorption equilibrium constants. In particular, when considering three categories, as in the present study, it is desirable to use lipids extracted from other organisms, such as scallop midgut or fish viscera, and when confirming whether the adsorption behavior of individual FAMEs is compatible with the present proposed model in detail, a model system in which reagents are artificially prepared is desirable.

Author contributions

Conceptualization, Hideo Maruyama; Data curation, Hideo Maruyama and Akito Furukawa; Methodology, Akito Furukawa; Supervision, Hideo Maruyama; Writing – original draft, Hideo Maruyama; Writing – review & editing, Hideshi Seki.

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Conflict of Interest and other Ethics Statements

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Notation

C_M = Equilibrium concentration of methanol [mol/m^3]

C_{SFAME} = Equilibrium concentration of fatty acid methyl ester derived from squid liver [mol/m^3]

C_{TL} = Equilibrium concentration of methyl toluene [mol/m^3]

K_{M1} = Equilibrium adsorption constant of methanol binding with hydrogen atom of silanol group [m^3/mol]

K_{M2} = Equilibrium adsorption constant of methanol binding with oxygen atom of silanol group [m^3/mol]

K_{MF1} = Equilibrium adsorption constant of monounsaturated SFAME binding with hydrogen atom of silanol group [m^3/mol]

K_{MF2} = Equilibrium adsorption constant of monounsaturated SFAME binding with methyl group of methanol adsorbed onto silica group [m^3/mol]

K_{PF1} = Equilibrium adsorption constant of polyunsaturated SFAME binding with hydrogen atom of silanol group [m^3/mol]

K_{PF2} = Equilibrium adsorption constant of polyunsaturated SFAME binding with methyl group of methanol adsorbed onto silica group [m^3/mol]

K_{SF1} = Equilibrium adsorption constant of saturated SFAME binding with hydrogen atom of silanol group [m^3/mol]

K_{SF2} = Equilibrium adsorption constant of saturated SFAME binding with methyl group of methanol adsorbed onto silica group [m^3/mol]

K_{SFAME1} = Overall equilibrium adsorption constant of SFAME binding with hydrogen atom of silanol group [m^3/mol]

K_{SFAME2} = Overall equilibrium adsorption constant of SFAME

binding with methyl group of methanol adsorbed onto silica group [m^3/mol]

K_{TL} = Equilibrium adsorption constant of toluene

binding with methyl group of methanol adsorbed onto silica group [m^3/mol]

X_M = Total equilibrium adsorbed amount of methanol [mol/kg]

X_{MF} = Equilibrium adsorbed amount of monounsaturated SFAME [mol/kg]

X_{M1} = Equilibrium adsorbed amount of methanol

binding with hydrogen atom of silanol group [mol/kg]

X_{M2} = Equilibrium adsorbed amount of methanol

binding with oxygen atom of silanol group [mol/kg]

X_{PF} = Equilibrium adsorbed amount of polyunsaturated SFAME [mol/kg]

X_S = Total number of silanol groups onto silica gel [mol/kg]

X_{SF} = Equilibrium adsorbed amount of saturated SFAME [mol/kg]

X_{SFAME} = Overall equilibrium adsorbed amount of SFAME [mol/kg]

X_{TL} = Equilibrium adsorbed amount of toluene

binding with methyl group of methanol adsorbed onto silica group [mol/kg]

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Figures and tables captions

Fig. 1. The adsorption isotherms of (a) SFAME, (b) TL, and (c) ME. Solid symbols correspond to the previous data of methyl palmitate/methanol/toluene system [6]. The solid lines were calculated values using Eqs. (2)-(4) and parameters in Table 2.

Fig. 2. The adsorption isotherms of (a) SF, MF, and PF (b) TL, and (c) ME. The solid lines were calculated values using Eqs. (5)-(9) and parameters in Table 5.

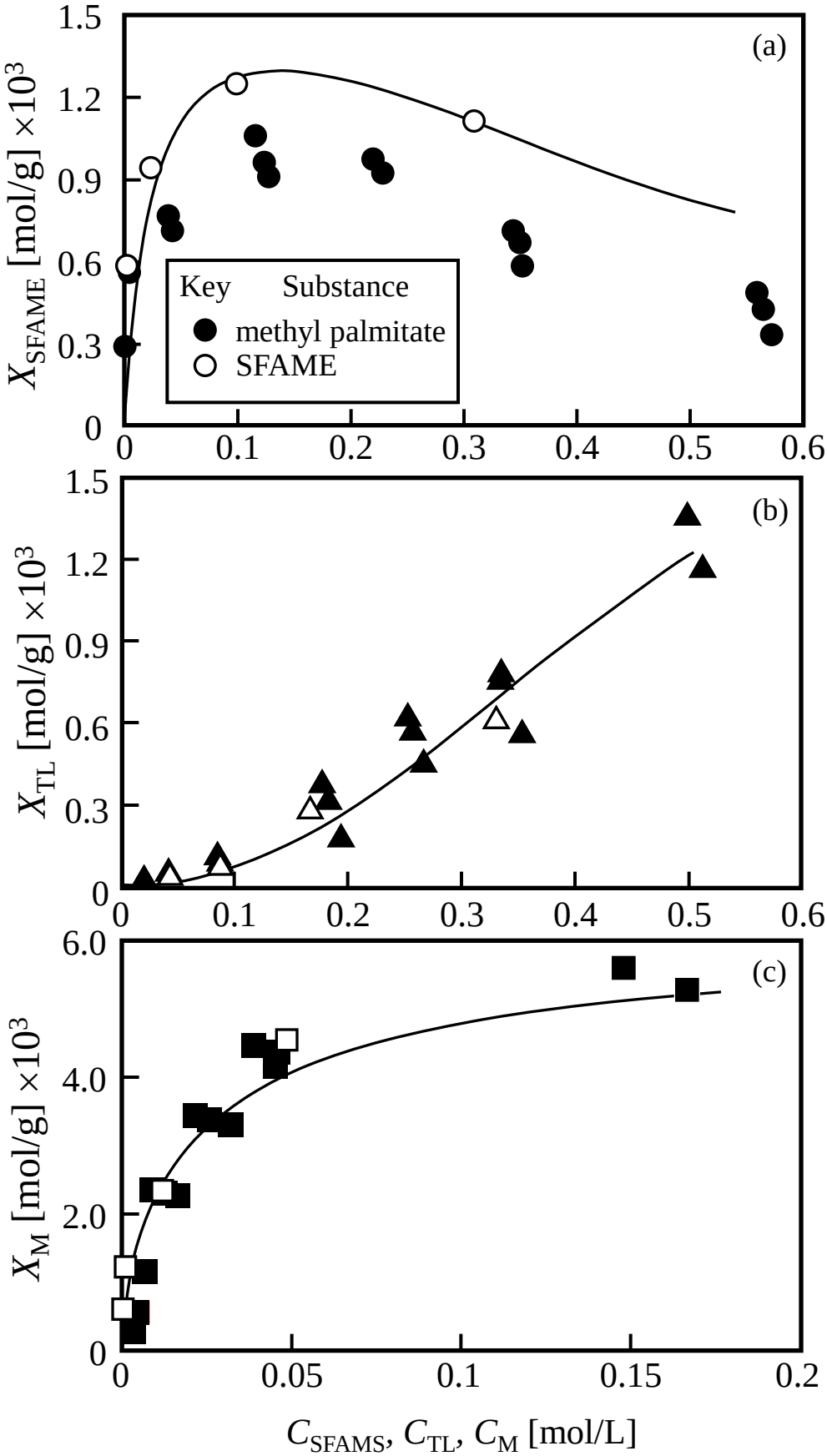
Table 1 The contents of Fatty acid derived from squid liver in this study.

Table 2 Estimated adsorption equilibrium constants.

Table 3 Dielectric constant of octadecanoic fatty acids.

Table 4 The categories of fatty acid methyl ester derived from squid liver in this study.

Table 5 Estimated adsorption equilibrium constants for the categorized FAME and the saturated adsorption density.



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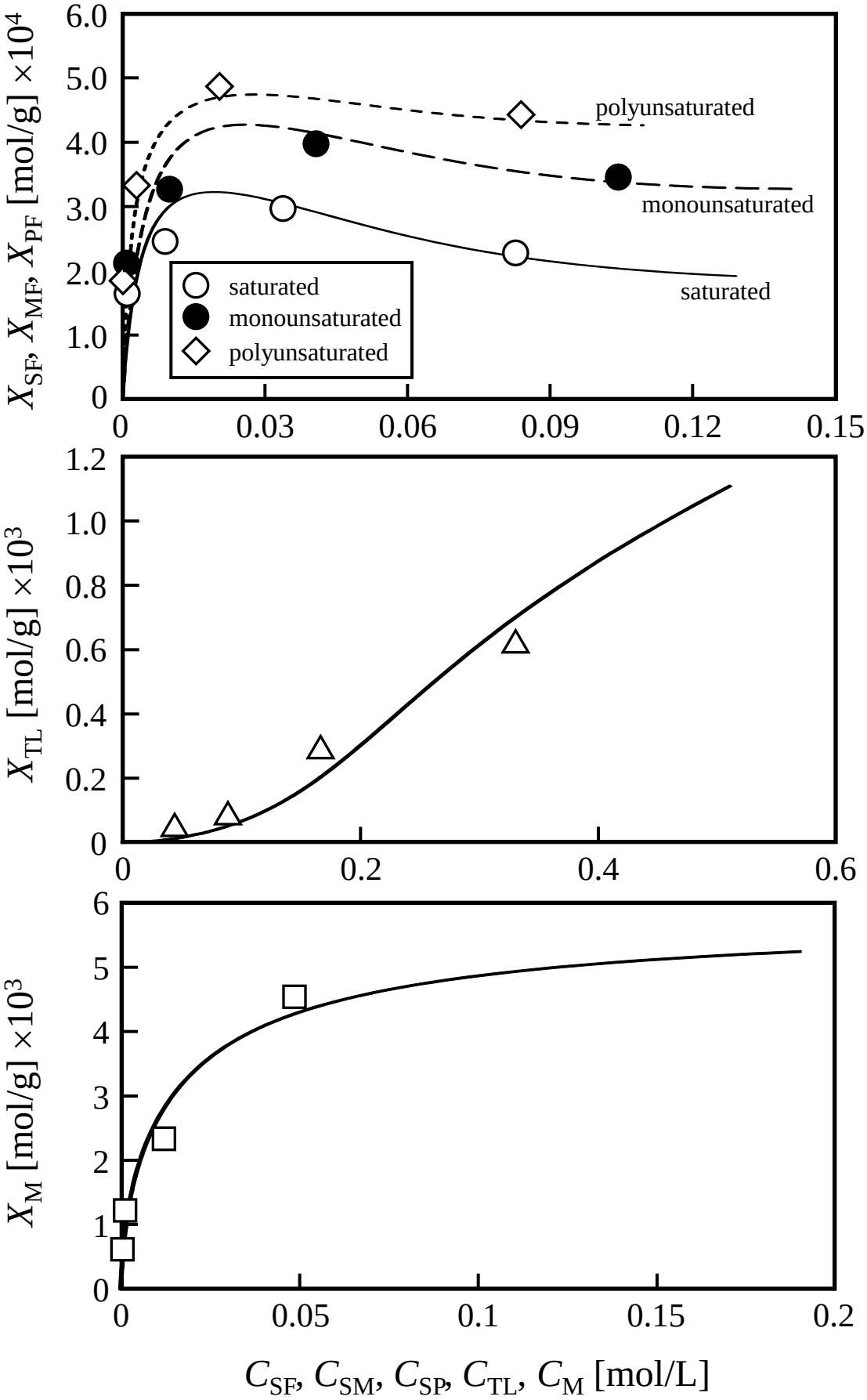

Fig. 2. The adsorption isotherms of (a) SF, MF, and PF (b) TL, and (c) ME. The solid lines were calculated values using Eqs. (5)-(9) and parameters in Table 5.

Table 1

The contents of Fatty acid derived from squid liver in this study.

Fatty Acid Methyl Ester	M.W. [g/mol]	Content [%]
Myristic Acid (C14:0)	228.38	5.07
Myristoleic Acid (C14:1n5)	242.40	0.17
Pentadecanoic Acid (C15:0)	240.40	0.22
cis-10-Pentadecanoic Acid (C15:1n5)	256.43	0.48
Palmitic Acid (C16:0)	254.41	18.53
Palmitoleic Acid (C16:1n7)	270.46	5.74
Heptadecanoic Acid (C17:0)	268.43	0.67
cis-10-Heptadecanoic Acid (C17:1n-7)	284.48	0.92
Stearic Acid (C18:0)	282.46	3.55
Oleic Acid (C18:1n9c)	298.51	10.87
cis-11-Octadecenoic Acid (C18:1n7c)	296.50	4.77
Linoleic Acid (C18:2n6c)	296.50	1.02
Linolenic Acid (C18:3n3)	294.48	0.59
cis-6,9,12,15-Octadecatetraenoic Acid (C18:4n3)	292.46	0.95
cis-9-Eicosenoic Acid (C20:1n11)	276.41	5.66
cis-11-Eicosenoic Acid (C20:1n9)	324.54	3.45
cis-11,14-Eicosenoic Acid (C20:2n6)	324.54	0.37
Arachidonic Acid (C20:4n6)	322.53	2.10
cis-11,14,17-Eicosadienoic Acid (C20:3n3)	318.50	0.52
cis-5,8,11,14,17-Eicosapentaenoic Acid (C20:5n3)	322.53	11.60
cis-11-Docasenoic Acid (C22:1n11,13)	316.48	4.58
Behenic Acid (C22:0)	352.60	0.86
cis-13,16-Docosadienoic Acid (C22:2n6)	354.62	0.00
cis-4,7,10,13,16,19-Docosahexaenoic Acid (C22:6n3)	342.51	12.65

Table 2 Estimated adsorption equilibrium constants.

K_{SFAME1} [L/mol]	K_{SFAME2} [L/mol]	K_{M1} [L/mol]	K_{M2} [L/mol]	K_{TL} [L/mol]	X_S [mmol/g]
21.9	0.01	212	38.7	0.61	3.24

Table 3 Dielectric constant* of octadecanoic fatty acids.

C18:0	C18:1	C18:2	C18:3	
2.3	2.5	2.7	2.9	F/m

*Ref. [25]

Table 4

The categories of fatty acid methyl ester derived from squid liver in this study.

	Fatty Acid Methyl Ester
Saturated FAME	Myristic Acid (C14:0)
	Pentadecanoic Acid (C15:0)
	Palmitic Acid (C16:0)
	Heptadecanoic Acid (C17:0)
	Stearic Acid (C18:0)
	Behenic Acid (C22:0)
Monounsaturated FAME	Myristoleic Acid (C14:1n5)
	cis-10-Pentadecanoic Acid (C15:1n5)
	Palmitoleic Acid (C16:1n7)
	cis-10-Heptadecanoic Acid (C17:1n-7)
	Oleic Acid (C18:1n9c)
	cis-11-Octadecenoic Acid (C18:1n7c)
	cis-9-Eicosenoic Acid (C20:1n11)
	cis-11-Eicosenoic Acid (C20:1n9)
	cis-11-Docasenoic Acid (C22:1n11,13)
Polyunsaturated FAME	Linoleic Acid (C18:2n6c)
	Linolenic Acid (C18:3n3)
	cis-6,9,12,15-Octadecatetraenoic Acid (C18:4n3)
	cis-11,14-Eicosenoic Acid (C20:2n6)
	Arachidonic Acid (C20:4n6)
	cis-11,14,17-Eicosadienoic Acid (C20:3n3)
	cis-5,8,11,14,17-Eicosapentaenoic Acid (C20:5n3)
	cis-13,16-Docosadienoic Acid (C22:2n6)
	cis-4,7,10,13,16,19-Docosahexaenoic Acid (C22:6n3)

Table 5 Estimated adsorption equilibrium constants for the categorized FAME and the saturated adsorption density

K_{SF1} [L/mol]	K_{SF2} [L/mol]	K_{MF1} [L/mol]	K_{MF2} [L/mol]	K_{PF1} [L/mol]	K_{PF2} [L/mol]	K_{M1} [L/mol]	K_{M2} [L/mol]	K_{TL} [L/mol]	X_S [mmol/g]
35.4	0.072	38.6	0.198	82.0	0.230	293.0	56.0	0.548	3.14