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Scale-up and Energy Consumption of Bubble Stripper for Residual Methanol Removal from Crude Biodiesel Fuel

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Based on the principle of nitrogen gas stripping for the residual methanol removal from crude biodiesel fuel (BDF) that we reported previously (Yamane *et al.*, *Eur. J. Lipid Sci. Technol.*, **115**, 1183-1192 (2013)), two scaled gas stripping setups whose working volume were 5 L and 25 L were constructed to study its scale-up. As a scale-up index, (flow rate of nitrogen gas)/(volume of crude BDF), Q/V , gave the best correlation among the three indices, i.e. Q/V , P_g/V (= energy consumption of gas pump for gas stripping)/(volume of crude BDF), and u (= linear gas velocity = $Q/(\text{cross-sectional area})$). The three items, i.e. P_a , P_g , and P_b , composed of the total energy consumption, P_{total} , of the two gas stripping setups were measured. P_{total}/V was approximately 0.1 [kWh/L] when Q/V was 1.5 [1/min] in 25 L-scaled gas stripping setup. As the simplest as well as inexpensive purification process, the purification process composed of the intensive residual methanol removal by a nitrogen gas stripping system followed by filtration with aid of appropriate filter aid was proposed.

以前報告した粗バイオディーゼル燃料 (BDF) から残留メタノールを取り除く窒素ガス放散の原理 (Yamane *et al.*, *Eur. J. Lipid Sci. Technol.*, **115**, 1183-1192 (2013)) に基づいて、スケールアップの研究のために仕込み容量が 5 L と 25 L である 2 つの規模のガス放散装置を製作した。スケールアップの指標として、(窒素ガス通気量) / (粗 BDF の容積) である Q/V は、3 つの指標 (Q/V (エアポンプの動力) / (粗 BDF の容積) である P_g/V , および線速度 $u = Q/(\text{装置断面積})$) の中で最も相関が良かった。2 つのガス放散装置の総消費電力量 P_{total} に影響を及ぼす 3 つの項目について測定した。25 L ガス放散装置で $Q/V = 1.5$ [1/min] であるとき、 P_{total}/V はおよそ 0.1 [kWh/L] であった。安価で簡潔な精製工程として、窒素によって残留メタノールを徹底的に除去するガス放散装置の次にろ過助剤の助けによるろ過とで構成される精製工程を提案した。

Key Words

Biodiesel fuel, Residual methanol removal, Bubble stripping, Scale-up, Energy consumption, Crude biodiesel fuel, Biodiesel purification

1. Introduction

Biodiesel fuel (often abbreviated as BDF), which is chemically identical to fatty acid methyl ester (FAME), is an alternative for fossil diesel fuel. It is produced by transesterification reaction of triacylglycerols (TAG) with methanol. As TAG vegetable oil such as Jatropha oils and fats is usually utilized, but used cooking oil is mostly used in Japan. Therefore, BDF is a one of renewable energy sources. The most popular reaction of BDF manufacture is alkaline-catalyzed reaction using potassium hydroxide as a catalyst.

Excess methanol is usually used to ensure very high conversion of TAG to FAME. Once the transesterification reaction is completed, crude BDF is separately obtained as the upper layer from byproduct glycerol by just gravity settling. The crude BDF contains several kinds of impurities including residual methanol, potassium from the catalyst, soaps/free fatty acids, mono-, di-, tri-acyl glycerols, free glycerol, and so on. These contaminants can lead to severe operational problems when BDF is used such as engine deposits, filter clogging, and fuel deterioration. To avoid these engine troubles the Japanese standard (JIS K2390) limits the amounts of these contaminants in BDF¹⁾. The purification of the crude BDF is therefore an issue of great importance to successful usage of BDF as the fuel of diesel engines. Crude BDF is purified by either "wet" or "dry"

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process. “Wet” process is conventional, i.e. consists of first mild methanol removal, followed by washing with hot water, and finally removal of included water²⁾³⁾. “Dry” process does not use water washing, i.e. purification without water.

In our previous article⁴⁾, we reported a bubble stripping (gas desorption) in closed system as a novel, simple, but very effective dry process to remove intensively the residual methanol from the crude BDF. Its principle is shown in Fig. 1. Inert gas (nitrogen gas) is supplied by a gas pump into the crude BDF as fine bubbles. At the gas-liquid (BDF) interphase of the gas bubbles methanol molecules transfer from the bulk BDF (liquid) phase into gas phase. The gas bubbles containing methanol vapor leave the crude BDF container, and the gas is then introduced to a condenser where methanol becomes liquid and is collected in a methanol reservoir. Then, the gas almost free of methanol from the condenser returns totally into the inlet port of the gas pump, thus gas is circulated in a tightly closed system completely insulated from outside atmosphere.

In the previous article⁴⁾, the experiments were carried out with a very small stripper, just 500 mL three-neck round-bottom flask made of glass. The working volume of the crude BDF was only about 190 mL. Therefore, we constructed equipment of two larger sizes whose working volumes were 5 L and 25 L as more realistic process in order to get information of scale-up and energy consumption in their running times. The obtained experimental data will be useful to design and operation of industrially scaled bubble stripping system for the residual methanol removal from crude BDF and also to compare our “dry” process with other “dry” processes and also with conventional “wet”

process in terms of energy consumption.

2. Materials and methods

2.1 Materials

Crude BDF was gifted from Ohta Oilmill Co., Ltd. It had been manufactured from used cooking oil, and contained about 2-3% methanol. Diatomaceous earth powder was reagent-grade Celite No.545 (Wako Pure Chemical Industries, Ltd.). Active clay powder (Galleon Earth NV) was a gift from Mizusawa Industrial Chemicals, Ltd.

2.2 Experimental setup

Schematic diagram of the experimental setups is shown in Fig. 2. Fig. 2(a) is the one for the working volume of 5L, and Fig. 2(b) is the one for the working volume of 25 L.

In the setup for 5 L of the working volume, the stripper was a cylindrical flat-bottomed separable flask made of Pyrex glass having 10 L volume (Inner Diameter = 210 mm and height = 200 mm). The nitrogen gas was dispersed from 4 sintered cylindrical ceramics mounted radially (Inner Diameter = 5 mm, Outer Diameter = 10 mm, and length = 30 mm, Ibuki Air Stone, King Whetstone Co., Ltd.). The cover also made of Pyrex glass had 4 ports, for the inlet and outlet of gas, heater and thermocouple. The temperature of the crude BDF was kept at 65 °C by a coiled heater connected with a temperature controller (Model SPC-10, AS ONE Co., Ltd.) as well as a mantle heater. Nitrogen gas was circulated by an air pump (diaphragm type air pump, Type APN-110KVX-1, power consumption of motor 45 W, Output 10 W/100 V, IWAKI CO., LTD.). The purity of the nitrogen gas was more than 99.99% (grade of industrially general use). Its flow rate was changed by a needle valve installed in the rotameter. The flow rate were set at four levels (3.75, 5.0, 6.25, and 7.5 L/min for the 5 L-scale experiments and 18.8, 25, 31.3 and 37.5 L/min for 25 L-scale experiments).

Chilled saline water (20% sodium chloride solution) was circulated by a magnet pump (type MD-6K-N, IWAKI CO.,LTD.) to a Dimroth condenser from a chilled saline water bath whose temperature was controlled at -4 °C by a refrigerator with temperature controller (Compact Handy Cooler Type 202TN, 430 W/100 V, AS ONE Co., Ltd.).

In the setup for 25 L of the working volume, the stripper was a drum can made of stainless steel (Inner Diameter = 390 mm, height = 482 mm, thickness = 1.2 mm) with a separable flat top cover-plate. The side wall, the top cover and the bottom of the drum can were covered with heat insulating material (glass wool). The nitrogen gas was dispersed from 4 sintered cylindrical ceramics mounted radially (Inner Diameter = 8 mm, Outer Diameter = 23 mm,

Fig. 1 Principle of gas stripping for removal of residual methanol from crude BDF (1, Crude biodiesel; 2, Bubble(s); 3, Disperser; 4, Recovered (condensed) methanol; 5, Chiller; 6, Inlet of the chilled water; 7, Outlet of the chilled water; 8, Circulating gas pump; 9, Methanol molecule)

Fig. 2 Schematic diagram of experimental setups. (a) 5 L-setup, and (b) 25 L-setup (1, crude BDF; 2, bubble; 3, the condensed methanol; 4, separable flask in (a), and stainless steel drum can in (b); 5, conical flask(s); 6, gas disperser; 7, temperature controller; 8, heater(s); 9, thermocouple; 10, condenser; 11, air pump; 12, digital manometer; 13, flow meter; 14, chilled saline water; 15, magnet pump; 16, refrigerator; 17, cooling coil; 18, mantle heater in (a), and valve in (b))

and length = 60 mm). The top cover plate had 8 ports, for 1 inlet of gas, 2 outlets of gas, 4 ports of two coiled heaters, and thermocouple). The heater was a coiled heater whose heat capacity was 1 kW. The bottom of the drum can had a port having a valve for discharge of BDF after methanol removal. For nitrogen gas circulation an air pump (Type DAU-100, Power of motor 300 W/100 V, ULVAC KIKO Inc.) was used. The refrigerator with temperature controller to get the chilled saline water was the same as the one used in the 5 L setup. The chilled saline water was circulated by a magnet pump (type MD-15R-N, IWAKI CO., LTD.).

Methanol removal experiments using the gas stripper setup were carried out as follows. First, the required amount of the crude BDF were weighed and put into the stripper. Gas phase of the closed system was replaced from air to nitrogen gas supplied from a nitrogen gas cylinder. The saline water started cooling down to -4°C by the temperature-controlled refrigerator connected with a wattmeter (Watt Checker Plus, Model TAP-TST7, SANWA SUPPLY Inc., Okayama City, Japan). The heater, air pump and chilled saline water pump were switched on. In case of 5 L stripper, the temperature of BDF was raised by both the mantle heater and the coiled heater until 55°C , and a little later kept at 65°C using only one heater connected with the automatic temperature regulator during the methanol removal experiments that lasted for 60-150 min. The kept temperature of 65°C was decided because the boiling temperature of methanol at 1 atmospheric pressure is 64.7°C . In case of 25 L stripper, the temperature of BDF was elevated up to 55°C using the two heaters, then a little later it was kept at 65°C during the methanol removal

experiments in the same way as in the case of 5 L stripper. The condensed methanol in the conical flask was weighed at 5-20 min intervals by detaching it quickly from the condenser and putting it on a load cell precision balance (Accuracy 0.1 g, maximum range 6000 g, Model PFB6000-1, Kern & Sohn GmbH, Balingen-Frommern, Germany). As soon as a flask was detached, another conical flask was immediately connected to the condenser. Since the detection limit of the balance was 0.1 g, when the amount of the condensed methanol during the measurement interval became about 0.3-0.5 g, the methanol removal experiment was stopped.

2.3 Filtration of BDF after residual methanol removal

After intensive methanol removal from crude BDF by the bubble stripper at 65°C , followed by cooling it down to the room temperature, BDF is usually slightly turbid and has always some insoluble precipitate (insoluble sediment). In the previous experiments⁴⁾, the precipitate was removed by centrifugation and finally BDF was purified by adsorption. To improve the subsequent purification process, filtration with filter aid (diatomaceous earth or active clay) was attempted. To filtrate BDF a funnel (ID = 135 mm) having filter aid of ca. 10 to 20 mm depth upon the filter paper (No. 4A, ADVANTEC MFS, Inc., Tokyo) was applied.

2.4 Measurement of energy consumption and chemical analyses

Electric power and electric energy of the residual methanol removal by the gas stripper were measured by the wattmeter. Total energy consumption (P_{total}) was

calculated by summing up three items, i.e.

$$P_{\text{total}} = P_a + P_g + P_b \quad (1)$$

where P_a is energy consumption for elevating the temperature of crude BDF from room temperature to 65 °C and keeping it at 65 °C during the residual methanol removal time, P_g is energy consumption of nitrogen gas supply, and P_b is energy consumption for the refrigerator both to cool down the chilled saline water from room temperature to -4 °C, and to keep it at -4 °C including the pump for its circulation to the condenser during the residual methanol removal time.

Methanol concentration in purified BDF after the filtration was measured according to METI method (water-extraction followed by gas chromatography analysis)¹⁾.

Analyses of mono-, di-, tri-acyl glycerols, and free glycerol contents of the purified BDF were carried out by Prof. Koji Yamane, School of Engineering, Department of Mechanical Systems Engineering, The University of Shiga Prefecture.

FAME and alkaline metal (sodium + potassium) contents of the purified BDF were analyzed by Shimadzu Techno-research Inc.

3. Results and Discussion

Time course of residual methanol removal by the bubble stripping in the closed system is approximately simulated by the following equation⁴⁾:

$$W_t = VC_0 \{1 - \exp(-Ma \cdot t)\} \quad (2)$$

Ma is a good parameter to evaluate quantitatively performance of the gas stripper. When Ma is large, methanol is removed quickly resulting in short methanol removal time, while when it is small, it takes longer time to complete the methanol removal.

From Eq. (2), when the data of $\ln\{1 - W_t/(VC_0)\}$ are plotted against time t , a straight line is obtained, and its slope gives the value of $-Ma$. Thus, in this study values of Ma were calculated by obtaining time courses of

methanol removal at various gas flow rates, Q . As scale-up indices for gas absorption in an agitated aerated tank, several parameters are known⁵⁾. Since gas stripping (gas desorption) is just the reverse of the gas absorption, three scale-up indices, Q/V , P_g/V and u , were studied. In general u is (gas flow rate)/(cross-sectional area of vessel). The results of Ma vs. three indices are plotted in Figs. 3(a), 3(b) and 3(c).

It is clear that the data of Ma vs. Q/V are within narrow range between the two scaled bubble strippers (5 L and 25 L), but in the plots of Ma vs. P_g/V and of Ma vs. u the data scatter much, indicating that only Q/V can be used as a scale-up index of the bubble stripper for residual methanol removal from crude BDF while the other two indices are not suitable.

Among 1st-order, 2nd-order and power equations to fit the experimental data, a power equation was found to be most rational by considering plausible trend below 0.75 of Q/V [1/min].

Before obtaining an approximated curve with a power expression, analysis of covariance was carried out by transforming the experimental data into their logarithms. The data were composed of two groups. The results of analysis of covariance were: 1) null hypothesis 1 "The two slopes of linear regression equations are the same" resulting in p -value = 0.296, 2) null hypothesis 2 "The two average values adjusted by the covariates are the same" resulting in p -value = 0.232. Both p values were much greater than the significance level $\alpha = 0.05$ so that both null hypotheses could not be rejected (or could be accepted with 95% confidence level). Therefore, it was concluded that log (the experimental data of both groups) could be expressed by a single linear regression equation.

The approximated curve with a power expression for the data in Fig. 3(a) by the least-squares method is

$$Ma = 0.0254 \times (Q/V)^{2.0566} \quad (0.75 \leq Q/V \leq 1.5) \quad (3)$$

The coefficient of determination of Eq. (3) is: $R^2 = 0.916$.

The three items of the energy consumption (Eq. (1))

Fig. 3 The three scale-up indices of the gas bubble strippers. The scale-up index is, (a) Q/V ; (b) P_g/V ; and (c) u . The blue diamond markers are for 5 L gas stripper; the red square markers are for 25 L gas stripper. The curve in Fig. 3 (a) represents Eq. (3)

for 5 L and 25 L scale experiments are shown in Fig. 4(a). One can get rough estimates of P_a , P_g , P_b and P_{total} from the figure. The energy consumption is roughly proportional to the operating time required for the methanol removal. In general the times decreased with increases in Q/V , resulting in lesser energy consumptions. However, it is difficult to mention clear tendency of P_a , P_g , P_b and P_{total} from the figure because many factors affect their values, such as nature of porous ceramic gas disperser, temperature of external open air, efficiency of heat insulation, quality of raw BDF, etc as well as gas flow rate. This study is the first trial to measure actual energy consumptions of the bubble stripper, and further studies by taking these factors into consideration are necessary for saving its energy.

The energy consumption between 5 L and 25 L gas strippers was compared on the basis of P_{total}/V , the results of which are shown in Fig. 4(b), indicating that P_{total}/V between the two scaled stripper setups were almost the same and that they decreased slightly with increases in Q/V because the operating time of methanol removal became shorter when Q/V was elevated. A somewhat difference in declining tendency of P_{total}/V against Q/V between 5 L and 25 L stripper experiments was observed. More intensive studies are necessary to describe general declining tendency of P_{total}/V and that of each component of P_{total} against Q/V .

Energy consumption is directly related to running cost, and the data obtained in this study will be useful to compare the running cost of our gas stripping process with those of other “dry” methanol removal processes (distillation

under normal pressure, distillation under reduced pressure (vacuum distillation), vacuum flash evaporation, falling film evaporation etc.), and also with those of conventional “wet” purification processes, although so far no data are available for those reported processes.

The contents of FAME, methanol, alkaline metals, mono-, di-, tri-acyl glycerols, and free glycerol contents of the purified BDF after the filtration were 98.6 wt%, 0.07 wt%, < 2.0 mg/kg, 0.07 wt%, 0.19 wt%, 0 wt%, 0 wt%, respectively. All these values clear the JIS standard (JIS K2390) requirements. Filtrations with diatomaceous earth and activated clay as filter aids gave almost the same results. Although more detailed study about filtration with filter aid after the intensive gas stripping is necessary to reach final decision it is suggested that it will be the simplest and the cheapest post-treatment.

In this study the effect of the gas flow rate on the residual methanol removal rate at two scaled bubble strippers was examined. Higher gas flow rate is better because the operating time becomes shorter and thus the energy consumption is less. However, it was observed that greater flow rates than 1.5 [l/min] of Q/V caused excessive foaming resulting in flowing of some BDF out to the condenser. There is an upper limit of Q/V (likely around 1.5 [l/min]) in this respect.

4. Conclusion

Two scaled gas stripper setups whose working volumes were 5 L and 25 L were constructed to study its

Fig. 4 Energy consumption of the gas stripper setups. (a) The three items of the energy consumption. The shaded bars, the energy for elevating and keeping the temperature of the crude BDF; the meshed bars, the energy for the gas supply (P_g); the white bars, the energy for the refrigerator plus the magnet pump for chilled saline water circulation. The figures over the bars are the total values of the three energies. (b) P_{total}/V vs. Q/V for the 5 L and 25 L gas stripping setups

scale-up for removing residual methanol from crude BDF. As a scale-up index, Q/V gave the best correlation among the three indices, i.e. Q/V , P_g/V and u . The three items, i.e. P_a , P_g , and P_b composed of the total energy consumption, P_{total} , of the two gas stripping setups were measured. P_{total}/V was about 0.1 [kWh/L] when Q/V was 1.5 [1/min] in 25 L-scaled gas stripper. Intensive residual methanol removal by a nitrogen gas stripper setup followed by filtration with aid of appropriate filter aid was proposed.

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Nomenclature

Symbols

C : methanol concentration of crude BDF [g/L]

D : diameter of the gas stripper [mm]

Ma : volumetric coefficient of methanol transfer [min⁻¹]

P : electric energy consumption [kWh]

Q : gas flow rate [Lmin⁻¹]

t : time [min]

u : linear gas velocity [m·min⁻¹] ($= 10^3 \times Q/(\pi D^2/4)$)

V : volume of crude BDF [L]

W : weight of methanol removed [g]

Subscripts

0: at time 0

g: gas (nitrogen gas) supply (for a & b, refer to Eq. (1))

t: at time t

total: total value

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