



Optimization of alcoholic soybean oil extraction as a step towards developing *in-situ* transesterification for fatty acid isopropyl esters



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ABSTRACT

As a step towards developing *in-situ* transesterification (*in-situ* TE) for seed-to-biodiesel production, four solvents (methanol, ethanol, isopropanol and acetone; neat and in blends) were investigated for their potential in soybean oil extraction. Neat isopropanol compared favorably with the other solvents tested in terms of oil yield and properties of biodiesel product; thus, isopropanol was selected for process optimization of liquid-solid ratio (L-S ratio), shaking speed, extraction time and temperature. L-S ratio had the most significant effect on oil yield, and an increase in extraction temperature was able to reduce the solvent loading and improve the oil yield. Finally, *in-situ* TE was accomplished by applying the optimal conditions of isopropanol soybean oil extraction together with use of sodium catalyst. Applying optimal catalyst concentration and other process conditions, the yield of fatty acid isopropyl ester was 86.7% of the maximum theoretical yield. Moreover, the biodiesel had a low cloud point with -10°C . This promising biodiesel yield, simple process and superior cold flow property suggests *in-situ* TE may be feasible as a small decentralized process for rural areas.

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1. Introduction

Rural communities could potentially produce and use their own biodiesel from locally-grown oil crops. However, there remains a need for innovative technology to accomplish this. Biodiesel production commonly begins with a complex process involving multiple seed preparation steps, vegetable oil extraction *via* screw press and/or solvent, multiple oil refining steps, biodiesel synthesis and multiple biodiesel purification steps. The oilseeds are typically transported from the agriculture site to a large centralized processing plant. For remote agriculture areas, however, smaller decentralized plants may be a more viable approach. The decentralization allows for inexpensive transportation of feedstock to the plant and biodiesel to the community. However, it is not practical to decentralize conventional seed-to-biodiesel facilities due to high capital cost. This is especially true in the case of the hexane-based vegetable oil extraction process, which also raises fire safety and employee health concerns.

A reactive extraction process known as *in-situ* transesterification (*in-situ* TE) might be a suitable alternative process for use in small on-site plants. Alcohol with catalyst is utilized as an oil extraction solvent and also acts as the reactant in biodiesel synthesis (TE reaction). In this approach, the oil in oilseeds is converted to biodiesel and simultaneously extracted by catalyzed alcohol, which significantly reduces the size and complexity of the production system (Haagenson et al., 2010; Hass and Scott, 2007; Hass et al., 2004; Qian et al., 2013; Zakaria and Harvey, 2014). Nevertheless, *in-situ* TE requires a larger amount of alcohol than the conventional TE reaction. Generally, the TE process requires 6–15 mol of alcohol for 1 mol of triglyceride, while *in-situ* TE must use more than 200 mol of alcohol. This is because the oil extraction process needs at least 2–6 cm³ of solvent (*i.e.*, alcohol) for 1 g of oilseed to ensure adequate oil extraction performance (Gandhi et al., 2003; Kwiatkowski and Cheryan, 2002; Zhang et al., 2002).

Methanol, which is the predominant alcohol used in conventional TE, is of limited use as an oil extraction solvent due to its high polarity. This reduces its effectiveness with *in-situ* TE. Several studies have attempted to counter the poor oil extraction performance of methanol such as applying ultrasonication (Suganya et al., 2014; Zhang et al., 2014), using super critical or subcritical alco-

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hol (Gunawan et al., 2014; Levine et al., 2013) and introducing co-solvent (Choi et al., 2014).

In conclusion, the performance of the oil extraction step is an important factor of the *in-situ* TE process. Hence, the use of a co-solvent with methanol (acetone and isopropanol) and the use of neat ethanol and isopropanol which are less polar than methanol were evaluated in this study to enhance the oil yield. Isopropanol provided a promising oil yield, thus it was selected to optimize the following oil extraction conditions: liquid–solid ratio (L–S ratio), time, shaking speed and temperature. The optimal conditions were then applied in the *in-situ* TE process using sodium metal as catalyst. To our knowledge, this is the first report of isopropanol as the sole alcohol in the *in-situ* TE process.

2. Materials and methods

2.1. Materials

Methanol (99.9% purity), ethanol (99.8% purity), acetone (99.8% purity), sulfuric acid (96% purity) and *n*-hexane (98% purity) were purchased from CARLO ERBA Reagents (Italmar Co., Ltd, Thailand). Isopropanol (99.8% purity) and sodium hydroxide (analytical grade) were obtained from RCI Lab scan Limited (Thailand). Soybean oil (analytical grade) was purchased from Sigma-Aldrich Co., LLD (St. Louis, MO). Sodium metal was purchased from Panreac Quimica Sau (Barcelona, Spain). The source of soybean (*Glycine max*) in this study was Phetchabun province, Thailand. After the harvest and hulling of the soybeans, the soybeans were sun dried for three days, and then stored in a high-density polyethylene (HDPE) plastic bag. The initial moisture content of soybeans was 5.1% mass (wet basis). The oil content of soybeans was 23.1% mass (dry basis) determined by Soxhlet *n*-hexane extraction (American Society for Testing and Materials, 2009). The acid value of the extracted oil was 0.33 mg KOH g⁻¹.

2.2. Oilseed pretreatment

Soybeans were ground by a food blender (Kassel model KBL-550, China). Then the ground soybean was fractionated based on the particle size, and only particles between 0.251 and 0.425 mm were retained. The fractionated ground soybean was incubated in a hot air oven at 75 °C overnight to reduce moisture content to 1.7% mass (wet basis), yet retain the quality of the soybean oil (Hass and Scott, 2007) for the below experiments as presented in Fig. 1.

2.3. Soybean oil extraction process and selection of solvent system

Five grams of dried, ground soybean were suspended in 20 cm³ of solvent system. The suspension was mixed for 60 min with a 15.7 rad s⁻¹ shaking speed using a shaking water bath (GFL model 1086, Germany) at temperature levels 30 and 60 °C. The slurry was then filtered through a Whatman® No. 40 paper filter (England) using a vacuum pump (KNF Neuberger model N026.1.2.AN.18, Germany) at 6.0–6.2 kPa. The glassware and solid fraction on the paper filter were rinsed by 10 cm³ of solvent. The liquid and rinsed fraction was desolventized in a hot air oven at 105 °C overnight and weighed. Finally, oil yield was calculated using Eq. (1).

$$\text{Oil yield (\%)} = \frac{\text{Weight of recovered oil (g)}}{\text{Oil content (\%mass)} \times \text{Weight of soybean (g)}} \times 100 \quad (1)$$

2.4. In-situ transesterification process

The soybean oil extraction process was adapted for *in-situ* TE, using the selected solvent system, the optimum extraction conditions and sodium metal as catalyst. To prepare catalyzed alcohol,

sodium metal was dissolved in selected alcohol, and adjusted the concentration to desired level.

After *in-situ* TE the solid fraction on paper filter was recovered, and rinsed with 10 cm³ of the selected solvent. The post *in-situ* TE soybean meal was incubated in a hot air oven at 105 °C overnight. Residual oil was then determined using Soxhlet *n*-hexane extraction described in AOCS official method AM2-93 (American Society for Testing and Materials, 2009). Finally, *n*-hexane was evaporated from the miscella, and the residual oil was dissolved in 25 cm³ isopropanol and saved for triglyceride and biodiesel content analysis by HPLC-ELSD.

The filtrate from the *in-situ* TE process and rinse fraction were pooled together, adjusted to 25 cm³ by isopropanol, and evaluated for triglyceride and biodiesel contents by HPLC-ELSD. The biodiesel standard (fatty acid isopropyl ester) was synthesized following the procedure of Wang et al. (2005). The recovered biodiesel and unreacted triglyceride were calculated from biodiesel and triglyceride contents by HPLC-ELSD multiplied by volume of filtrate and rinse fraction.

2.5. Determination of triglyceride and biodiesel content using HPLC-ELSD

A Shimadzu-HPLC with auto injector (model Shimadzu-10Avp, Japan) and a Sedere-ELSD (model Sedex 75, France) were operated under the following conditions: a C18 column, 5 μm, 4.6 × 250 mm (Inertsil® ODS-3, Japan) was warmed to 70 °C; the mobile phase was a mixture of methanol and isopropanol (gradient elution: starting at 100% methanol and ending at 15% methanol after 30 min) with a flow rate of 0.75 cm³ min⁻¹; the detection temperature and pressure of the ELSD were 40 °C and 210–220 kPa, respectively; and the injection volume was 0.2 mm³.

2.6. Biodiesel quality analysis

After *in-situ* TE, 0.05 cm³ of sulfuric acid (96% purity) was added in the filtrate and rinse fraction to neutralize the alkaline catalyst, and then the alcohol in this fraction was evaporated using a rotary evaporator (Heidolph model Heizbad HB digit, Germany) at 90 °C for 20 min under the vacuum pressure of 6.0–6.2 kPa. The crude biodiesel was washed with 25 cm³ of a mixture of *n*-hexane and water (1:1 volume ratio) in a separatory funnel. It should be noted that in this study *n*-hexane was used to clearly separate biodiesel from glycerol phase and recover biodiesel that adhered to the glassware. For industrial-scale biodiesel production, *n*-hexane is not needed.

The *n*-hexane phase was collected and desolventized in a hot air oven at 75 °C overnight. The biodiesel sample was analyzed for moisture content, kinematic viscosity, acid value and cloud point following ASTM method D6751-09.

2.7. Experimental design

2.7.1. Selecting a suitable solvent system

Methanol, ethanol, isopropanol and acetone (neat and in blends) were evaluated for oil yields at 30 and 60 °C. Oil yield was set as the most important criterion to select a suitable solvent for the subsequent experiments. The other selection criteria included specific properties of the solvent (boiling point and toxicity) and anticipated properties of the resulting biodiesel product.

2.7.2. Optimizing the soybean oil extraction

After selecting a suitable solvent system, the optimization was divided into two phases which were (1) the effects of L–S ratio, extraction time and shaking speeds and (2) the effects of L–S ratio and temperature. A central composite rotatable design (CCRD) was

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