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Sequential extraction and reactive extraction processing of spent coffee grounds: An alternative approach for pretreatment of biodiesel feedstocks and biodiesel production

Nattapong Tuntiwiwattanapun[a], Chantra Tongcumpou[a,b,*]

[a] Environmental Research Institute, Chulalongkorn University, Pathumwon, Bangkok 10330, Thailand
[b] Center of Excellence on Hazardous Substance Management, Chulalongkorn University, Pathumwon, Bangkok 10330, Thailand

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ABSTRACTS

An alternative approach to producing biodiesel from spent coffee grounds (SCGs) has been developed with methanol washing applied as a pretreatment step, followed by *in-situ* transesterification. Under optimal conditions, methanol washing was able to reduce the high acid value of SCGs to 0.78 mg KOH g^{-1} with a negligible loss of their oil content, which ended up being 11.43% by mass. Pretreated SCGs were then directly treated with a potassium methoxide solution and isopropanol as co-solvents in the *in-situ* transesterification process. A central composited rotatable design was applied to determine the optimal conditions for KOH concentration and proportion of isopropanol. The results showed that both KOH concentration and proportion of isopropanol had significant effects on the biodiesel yields, residual triglyceride in the biodiesel, and extraction performance (p-value < 0.05). The optimal conditions were provided by KOH concentration of 2.5 g in a 100 mL mixture of methanol and 25% volume of isopropanol, using 2.7 mL of the reagent to 1 g of SCGs at 30 °C for 2 h. Under these conditions, 88.8% biodiesel yield (i.e., 102 mg of biodiesel per 1 g of SCGs), with a less than 0.1% mass of residual triglycerides in the biodiesel, was achieved.

1. Introduction

As a type of waste from the coffee industry, spent coffee grounds (SCGs) show promise as a biodiesel feedstock since their use can reduce the conflict between the food and energy nexus. SCGs have an oil content between 12.0–21.5% by mass depending on the coffee species and coffee roasting and brewing processes used (Caetano et al., 2012; Kwon et al., 2013; Rocha et al., 2014; Tuntiwiwattanapun et al., 2017; Vardon et al., 2013). In 2016, more than 9 million tons of coffee was consumed globally, and this number has been increasing annually (International Coffee Organization, 2017). This continuous growth in coffee consumption could guarantee a sufficient feedstock with which to supply the biodiesel industry. Accordingly, up to 2 million tons of SCGs biodiesel could be produced annually. However, several issues regarding the use of SCGs as biodiesel feedstock are of concern, including (1) its high moisture content and (2) high acid value.

After the coffee brewing process, the moisture content in SCGs exceeds 50% based on its mass (Caetano et al., 2014; Haile et al., 2013; Kondamudi et al., 2008; Tuntiwiwattanapun et al., 2017; Vardon et al., 2013). This high moisture content can reduce oil extraction as well as lower its quality due to increased microbial activities and hydrolysis reactions. As a result, enormous energy can be required to reduce the high moisture content in wetted SCGs. Given the moisture content in wetted SCGs at 50%, up to 2.5 MJ was required to evaporate the moisture in 1 kg of dried SCGs, calculated based on amount of water (1.0 kg) and its specific heat (4.2 kJ kg^{-1} $°C^{-1}$) and latent heat (2230 kJ kg^{-1}) at room temperature of 30 °C.

Furthermore, the high acid value of SCGs oil can neutralize an alkaline catalyst, which is commonly used in biodiesel synthesis (transesterification). Soap formation is generated, leading to reduced biodiesel yields and quality. The range of the acid value in SCGs oil is a broad one, from 5 to 40 mg KOH g^{-1}, depended on the coffee specie, the coffee roasting and brewing processes as well as the drying and storage conditions of the SCGs (Haile et al., 2013; Kwon et al., 2013; Tuntiwiwattanapun et al., 2017; Vardon et al., 2013). The high acid value comes from the free fatty acid in the SCGs oil due to the hydrolysis of triglycerides. The recommend acid value in oil for alkaline transesterification is lower than 1 mg KOH g^{-1} (Van Gerpen and Knothe, 2005). Similar to waste cooking oil, which contains a high acid value, acid reduction steps such as distillation and esterification must be implement prior to transesterification (Wan Omar et al., 2009).

In this study, a methanol washing step was applied as the

* Corresponding author at: Environmental Research Institute, Chulalongkorn University, Pathumwon, Bangkok 10330, Thailand.
E-mail address: tchantra@chula.ac.th (C. Tongcumpou).

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pretreatment for reducing the high acid value in SCGs before biodiesel production. Methanol can completely dissolve free fatty acid, but has poor oil (i.e., triglyceride) solubility. In our previous study, the high acid value in SCGs could be reduced to a recommended level of < 1 mg KOH g^{-1} using this simple methanol washing step (Tuntiwiwattanapun et al., 2017).

After washing the SCGs with methanol, the pretreated SCGs were promptly used as biodiesel feedstock. In a conventional process, a hazardous *n*-hexane is commonly used as the oil extraction solvent, and then the extracted oil is converted to biodiesel via transesterification. To reduce the complexity and avoid the use of a hazardous solvent, an alternative biodiesel production approach, namely *in-situ* transesterification (*in-situ* TE), was introduced in this study. It is a reactive extraction process using catalyzed alcohol as the biodiesel reagent and extraction solvent. An alkaline catalyst (such as NaOH or KOH) and methanol are generally used in this process. This methoxide solution (i.e., the mixture of the alkaline catalyst and methanol) converts the triglycerides inside the SCGs into biodiesel and glycerol, which are completely dissolved in the methanol solution and able to be simultaneously extracted from the SCGs. In summary, *in-situ* TE combines vegetable oil extraction with biodiesel synthesis, and thus reduces the steps in a biodiesel production process.

In-situ TE has shown promise in biodiesel production for its ability to process different kinds of biodiesel feedstock, such as soybeans (Tuntiwiwattanapun et al., 2016), canola seeds (Haagenson et al., 2010), palm fruit (Jairurob et al., 2013), jatropha (Hailegiorgis et al., 2013), cotton seeds (Georgogianni et al., 2008) and algae (Suganya et al., 2014). Our previous study successfully produced biodiesel from SCGs using methanol washing and *in-situ* TE (Tuntiwiwattanapun et al., 2017). A batch type reactor with an agitator was used, and a more than 80% biodiesel yield was achieved at 50 °C. However, at the pilot scale (with a 4 kg SCGs load), we found difficulty in separating the pretreated SCGs from the methanol solvent during the transfer step from the methanol washing pretreatment to the *in-situ* TE process.

Hence, the main objective of this work is to develop a sequential process consisting of methanol washing as a pretreatment step and *in-situ* TE for biodiesel production. A percolator was used as a reactor within which the SCGs could be pretreated by methanol and then continue on to being treated by a mixture of catalyzed alcohol in the *in-situ* TE step. A central composited rotatable design (CCRD) was applied to optimize the process conditions in terms of the KOH concentration and proportion of isopropanol as the co-solvent. A high performance liquid chromatography with evaporative light scattering detector (HPLC-ELSD) was used to directly quantify the biodiesel and triglyceride contents in the *in-situ* liquid fraction. Finally, the quality of the SCGs biodiesel was evaluated based on its water content, kinematic viscosity, density, acid value and cloud point.

2. Materials and methods

2.1. Materials

Analytical grade methanol, isopropanol, *n*-hexnae, KOH, 1,1-diphenyl-2-picrylldydrazyl (DPPH) and butylated hydroxyanisole (BHA) were purchased from the Sigma-Aldrich Corporation (St. Louis, MO, USA). HPLC grade methanol and isopropanol were obtained from Fisher Chemical (Leicestershire, UK).

The SCGs were kindly provided by the coffee shop Inthanin Coffee located within the Central Library of Chulalongkorn University, Thailand. The coffee beans (*Coffea* arabica) were processed by an espresso machine. The SCGs were collected and kept in 4 °C within the same day. The initial water content of the SCGs was approximately 50% by mass. It was dried in a hot air oven at 105 °C overnight to reduce the water content. More than 90% of the dried SCGs size were between 0.25 and 0.42 mm, and thus at suitable particle sizes for *in-situ* TE (Tuntiwiwattanapun et al., 2017).

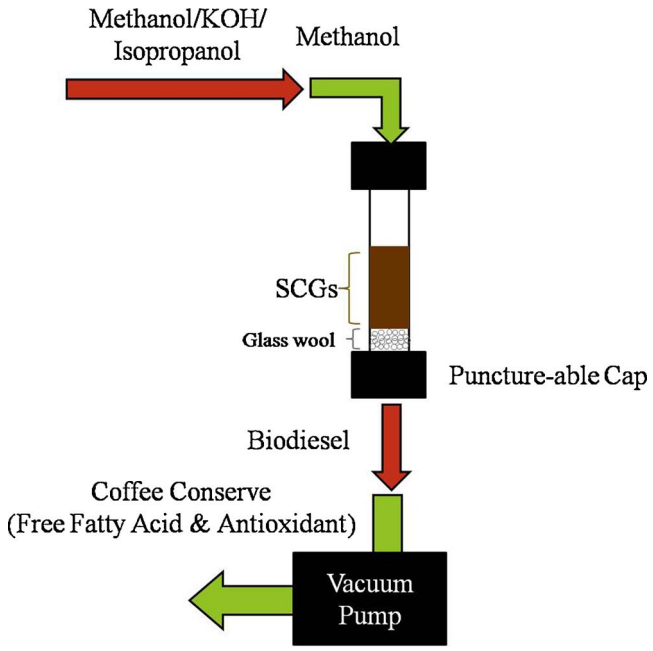

Fig. 1. Percolator reactor for the sequential process used in this study.

There was 14.8 g of oil in 100 g of SCGs based on Soxhlet *n*-hexane extraction method. The fatty acid profile of extracted SCGs oil was analyzed based on gas-liquid chromatography technique at the Halal Science Center (Chulalongkorn University, Thailand). The results showed that SCGs oil was comprised of high percentage of polyunsaturated fatty acid with 45% of linoleic acid (C18:2) and 9% of oleic acid. In the case of saturated fatty acid, the majority fatty acid was palmitic acid (C16:0) responded to 35%, followed by 6% of stearic acid (C18:0) and 3% of arachidonic acid (C20:0). The fatty acid profile of SCGs oil in this study was similar to SCGs oil and its biodiesel described in the other literatures of which the majority of fatty acid are palmitic acid and linoleic acid (Campos-Vega et al., 2015; Haile et al., 2013; Kondamudi et al., 2008; Vardon et al., 2013).

2.2. Methanol washing

Fifteen grams of dried SCGs was loaded into a 100 mL glass percolator, which had glass wool at the bottom for separating the solid fraction from the liquid fraction (Fig. 1). The extraction was then performed at 30 °C with 4 sets of extraction cycles (i.e., I, II, III and IV) using methanol as the solvent. In each extraction cycle, the SCGs were submerged in the methanol for 15 min before applying 6.0–6.2 kPa of vacuum pressure to draw the liquid fraction out from the percolator. The methanol evaporated from the liquid fraction using a rotary evaporator (Heidoph model Heizbad HB digit, Germany) under a vacuum pressure of 6.0 kPa at 70 °C. After methanol evaporation, the coffee conserve was analyzed for its antioxidant activity based on a DPPH assay. The solid fraction (i.e., the pretreated SCGs) was removed from the percolator and incubated in a hot air oven at 105 °C overnight to remove the residual methanol. Then the residual oil content and acid value of the dried pretreated SCGs were determined.

2.3. In-situ transesterification

After the methanol washing step, the pretreated SCGs in the percolator were directly treated with a potassium methoxide solution (i.e., dissolved KOH in a methanol solution) with and without isopropanol as the co-solvent. This reactive extraction was performed at 30 °C with 4 sets of extraction cycles. In each extraction cycle, 10 mL of the potassium methoxide solution was loaded into the percolator, and the