Short Communication

Wet *in situ* transesterification of spent coffee grounds with supercritical methanol for the production of biodiesel

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ABSTRACT

This work introduces biodiesel production from wet spent coffee grounds (SCGs) with supercritical methanol without any pre-drying process. Supercritical methanol and subcritical water effectively produced biodiesel via *in situ* transesterification by inducing more porous SCG and enhancing the efficiency of lipid extraction and conversion. It was also found that space loading was one of the critical factors for biodiesel production. An optimal biodiesel yield of 10.17 wt% of dry SCG mass (86.33 w/w% of esterifiable lipids in SCG) was obtained at reaction conditions of 270 °C, 90 bars, methanol to wet SCG ratio 5:1, space loading 58.4 ml/g and reaction time 20 min. Direct use of wet SCG waste as feedstock for supercritical biodiesel production eliminates the conventional dying process and the need of catalyst and also reduces environmental problems caused by landfill accumulation.

1. Introduction

Due to global warming and climate change crisis in our current society, the need of efficient, renewable and sustainable green energy is increasing over time. In recent years the waste after coffee brewing, wet spent coffee ground (SCG) gained attention as a new source of green energy. Wet SCG is usually considered as waste and dumped into landfill, and this causes environmental problems such as disordering the ecosystem of soil and greenhouse gas increase in the atmosphere. However, SCG can be a valuable feedstock for biodiesel production because oil takes 10–15% of its dry weight (Campos-Vega et al., 2015). Therefore, utilization of SCG as a sustainable feedstock for diverse processes and products such as biofuels has been under research for the past few years (Calixto et al., 2011).

Combining extraction and conversion of wet SCG into a single step to reduce time and energy, named wet *in situ* transesterification, was explored in a previous study (Park et al., 2016). Wet *in situ* transesterification usually employs acidic catalysts, since it is less sensitive to presence of water and free fatty acids (FFA) (Kim et al., 2015; Park et al., 2015). To eliminate the need of catalyst, supercritical methanol process can be utilized for wet *in situ* transesterification. The process requires extreme conditions since temperature and pressure need to be above the critical point of methanol (Jazzar et al., 2015). At supercritical methanol conditions, water is in a subcritical state as the critical point of methanol is 239.4 °C and 79.5 bars. Subcritical water (SCW) inside SCG for the supercritical methanol process possesses many advantages because the water of wet SCG itself can be utilized as a co-solvent. In a study with microalgae, SCW accelerated the supercritical process to be completed in a shorter time, at lower temperatures and achieve higher biodiesel yield (Levine et al., 2010). It is also a non-toxic, eco-friendly medium for use in chemical reactions.

Thus, this study introduces a simplified efficient process utilizing wet SCG and supercritical methanol by eliminating both biomass drying and catalyst usage and by integrating the extraction and conversion processes to produce fatty acid methyl ester (FAME). The effects of reaction parameters such as methanol to wet SCG ratio, temperature and reaction time for the production of biodiesel were investigated. Additional factors such as space loading and SCW effect were also studied. The chemical and physical changes of SCG before and after the reaction were understood with microscopic, spectroscopic, and Brunauer–Emmett–Teller (BET) investigations.

2. Material and method

2.1. Chemicals and reagents

Wet spent coffee grounds (SCGs) were collected from an espresso machine at a local café and preserved in a frozen state. The water content of wet SCGs was measured in quadruple samples and the average was 59.68 wt%. Extra pure methanol was purchased from Daejung, South Korea. Sulfuric acid (98 w/w%, extra pure grade) and trichloromethane (guaranteed reagent grade) that were used for the

maximum biodiesel yield experiment were provided from Junsei chemical, Japan. Methyl heptadecanoate (C17:0), which was an internal standard reagent for the gas chromatography (GC) analysis was acquired from Sigma-Aldrich, USA.

2.2. Maximum FAME yield for biodiesel

The maximum FAME yield experiment was conducted by modifying the two-step lipid extraction-conversion method by varying the reaction temperature and reaction time (Folch et al., 1957; Im et al., 2015). 0.1–0.2 g of dried SCG and 4 ml of methanol/chloroform solution (1:2 v/v) were put in a 14 ml glass tube and was sonicated in a sonication bath (50 Hz) for 30 min for the extraction of lipid. Then 1 ml of methanol and 0.3 ml of sulfuric acid were added for the conversion reaction to proceed. The tube was tightly sealed and placed in a thermostat bath at 95 °C for 2 h, and then was cooled to room temperature. 1 ml of chloroform containing 0.5 mg of methyl heptadecanoate and 1 ml of diluted NaOH solution were then added and thoroughly mixed. The tube was again tightly sealed and centrifuged at 4000 rpm for 10 min. The lower organic solvent (chloroform) phase extracted and analyzed by GC. Since the target material was biodiesel, FAMEs with the carbon number of 14–22 were only considered for counting the FAME yield. The resulting maximum FAME yield for biodiesel was 11.78 ± 0.17 wt% dry SCG based.

2.3. Experimental methods

In situ transesterification of undried wet SCG was conducted by mixing SCG with methanol in a STS-316 micro-reactor having an internal volume of 58.4 ml. For the water content variation experiments to study the effect of SCW, wet SCG was completely dried in a vacuum oven at 60 °C for 4 days and then homogenized with deionized water for 30 min prior to usage. An external PID controlled heating mantle was used to heat the reactor. The reaction conditions were manipulated within the following ranges: the reaction temperature varied from 240 to 300 °C, the reaction time from 10 to 60 min, the ratio of methanol to wet coffee (vol./wt.) from 4:1 to 6:1. After the reaction, the reactor was submerged in ice water and cooled down to room temperature. 1 ml methanol including 0.5 mg methyl heptadecanoate was added and centrifuged at 4000 rpm for 10 min. The methanol phase containing FAME and solid residual SCG were analyzed.

2.4. Analyses

The analysis of biodiesel was performed with GC using 1 μl sample of the organic phase that was filtered by a syringe filter (ChromTech HLB 0.45 μm, Futecs, South Korea). Agilent 7890B GC with HP-5 column (30.0 m × 0.32 mm × 0.25 μm) and FID detector operating at 280 °C using helium as a carrier gas with a flow rate of 2.1 ml/min were used. For qualification, Clarus 600 MS with Elite-5 column (30.0 m × 0.32 mm × 0.25 μm) was applied. FT-IR (Nicolet IS50, Thermo Fisher Scientific, USA) was used to observe the chemical bonding change of SCG. Surface characterization of the residual reacted SCG was obtained with SEM (Magellan400, FEI company, USA) and N_2 adsorption-desorption isotherms at 77K (3Flex Surface Characterization Analyzer, Micromeritics, USA).

3. Results and discussion

3.1. Optimization of reaction conditions

The methanol to wet SCG (ml/g) ratio, reaction temperature and time were important factors in affecting the biodiesel yield. The reaction parameters were varied to figure out the effect of each parameter on the biodiesel yield. As shown in Table 1, the ratio of 4:1 was not enough for methanol to effectively extract and convert lipids and

resulted in a low biodiesel yield of 47.20 w/w%. On the other hand, the ratio of 5:1 was adequate to promote the reaction forward and showed a sharp increase in the biodiesel yield. However, since methanol was already sufficient at the ratio of 5:1, the biodiesel yield was insensitive to the increase of the ratio to 6:1.

The biodiesel yield was relatively low at 240 °C but increased with the rising temperature and maximized at 270 °C. Since transesterification is an endothermic reaction, higher temperature enables faster reaction kinetics, which results in more production of biodiesel (Park et al., 2017). However, the reaction temperature above 270 °C decreased the biodiesel yield and increased the amount of shorter chain products (C6–C13), mainly due to hydrothermal breakdown and cracking of reactants and products to shorter carbon chains as observed in the microalgal cell conversion (Patil et al., 2011).

As sufficient reaction time is necessary to break the cell walls, extract lipids and reach reaction equilibrium (Im et al., 2014), reaction time of 10 min was too short of a time to complete the transesterification reaction. However, compared to the conventional transesterification reaction that takes hours to achieve the desired conversion (Go and Yeom, 2017), the proposed supercritical process excels the conventional process in the view of reaction time since the equilibrium biodiesel yield was achieved in just 20 min. As a result, the optimal reaction parameter values were methanol to wet SCG (ml/g) ratio of 5:1, reaction temperature of 270 °C and reaction time of 20 min.

3.2. Effects of space loading and pressure on the biodiesel yield

Space loading is an additional crucial factor for this process. It is important to process as much SCG as possible for economic efficiency. On the other hand, a sufficient volume in the reactor is also required for the liquid and gas to expand (Go et al., 2014). SCG has high density and is normally sticky in nature due to its considerable oil content, so it is important to ensure that SCGs do not result in aggregation and reduction of effective contact area with solvent (Lim and Lee, 2011). Considering the mentioned properties, overloading or under-loading of solid SCG could both lower reaction efficiency (Lim and Lee, 2013). Consequently, finding an optimal space loading for this process was necessary.

The volume of the reactor was fixed (58.4 ml) and the amount of wet SCGs loaded into the reactor was varied from 1.0 to 5.0 g. Space loading is measured by reactor volume to dry solid mass (ml/g), so high space loading means that less SCGs were put into the reactor. As shown in Table 2, the FAME yield was maximized at a space loading of 58.4 ml/g and the pressure of 90 bars. Even though higher space loading means more volume for the reaction, it decreased the FAME yield. This was due to the lower pressure of the system, resulting in decrease of lipids supercritically extracted from SCGs and efficiency of transesterification reaction. On the other hand, lower space loading also decreased the FAME yield. This may be due to the decreased volume available for the reaction. In addition, the overloaded solids tend to stay at the bottom and even stick to the wall of the reactor resulting in inefficient contact with the solvent.

3.3. Effect of water content on the biodiesel yield (subcritical water effect)

SCW offers many positive effects for the process (Coniglio et al., 2014; Kim et al., 2017). SCW enables hydrolysis of triglycerides to form free fatty acids that accelerates the reaction forward. This also permits the process to operate at lower temperatures, minimizing the degradation of the products. The ionic product (K_w) of SCW increases with temperature and maximizes up to about 10^{-11} (three orders of magnitude higher than water at room temperature) at around 270 °C (Kruse and Dinjus, 2007). The increase of the H_3O^+ ion concentration, which acts as an acidic catalyst precursor drives the transesterification reaction forward. On the other hand, the dielectric constant of SCW decreases with the increasing temperature. The lower dielectric constant