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Estimating total lipid content of *Camelina sativa* via pyrolysis assisted *in-situ* transesterification with dimethyl carbonate

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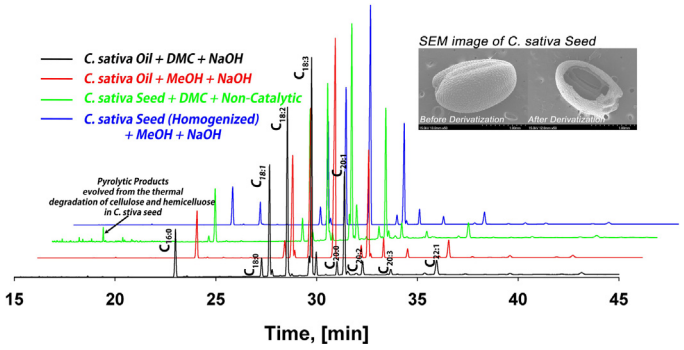
HIGHLIGHTS

- Rapid derivatization of *C. sativa* seed to FAMEs via *in-situ* methylation.
- *In-situ* methylation of *C. sativa* seed with dimethyl carbonate on silica.
- High tolerance against impurities when derivatizing triglycerides.

GRAPHICAL ABSTRACT



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ABSTRACT

Direct derivatization of *C. sativa* seed into FAMEs without lipid extraction was conducted for the quantification of lipid analysis via *in-situ* thermal methylation with dimethyl carbonate as an acyl acceptor on silica (SiO_2). The introduced method had an extraordinarily high tolerance against impurities such as pyrolytic products and moisture. To ensure the technical completeness of *in-situ* methylation, thermal cracking of FAMEs transformed from *C. sativa* seed was also explored. Thermal cracking of unsaturated FAMEs such as $C_{18:1}$, $C_{18:2}$, $C_{18:3}$ and $C_{20:1}$ occurred at temperatures higher than 365 °C due to their thermal instability. Thus, experimental findings in this study suggests not only that qualitative analysis of fatty acid profile in *C. sativa* seed via *in-situ* methylation using SiO_2 could be achieve, but also that the total lipid content (42.65 wt.%) in *C. sativa* seed could be accurately estimated.

1. Introduction

Our society has been facing with an unprecedented antithetical viewpoint associated with the fundamental element of carbon (Kaufman et al., 2008; Kwon et al., 2013a,b). The enormous demand and supply for carbon sources to sustain the current chemical and energy industries has become top priority in developed countries (Chen et al., 2015; Kwon et al., 2013b; Vicente et al., 2010). Notwithstanding our inevitable dependence on carbon for chemical and fuel production, our recent recognition for global climate change triggered by anthropogenic carbon input as a form of carbon dioxide (CO_2) has limited the expansion of petro-derived chemicals and fuels (Kwon et al., 2015). Therefore, a great deal of attention to lower carbon footprint has been compelled for scientists to explore new sustainable energy alternatives via the concept of biorefinery (Kwon et al., 2015, 2013b). As an initial stage of biorefinery, bioethanol and biodiesel from the edible

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crops (*i.e.,* 1st generation of biofuels) have been fully implemented and commercialized (Kwon et al., 2012a; Mahesh et al., 2015; Yaakob et al., 2014). Moreover, their expansion was politically supported by means of renewable fuel standard (RFS) and renewable fuel portfolio (RFP) (Kwon et al., 2015). In particular, biodiesel has been publicly accepted due to its compatibility with modern diesel engines and distribution networks, as well as its environmentally friendly characteristics (Lardon et al., 2009). Biodiesel contained 10–11 wt.% oxygen and has higher cetane number compared to diesel fuel, no aromatics, and almost no sulfur (Cuellar-Franca and Azapagic, 2015; Ozcelik et al., 2015; Strahan et al., 2016). Furthermore, it provides a similar energy density to petro-diesel and can be used in most diesel engines in pure form or may be blended with petro-diesel at any concentration (Cuellar-Franca and Azapagic, 2015; Ozcelik et al., 2015; Perrier et al., 2015; Strahan et al., 2016).

A common procedure for producing biodiesel from biomass involves three steps: drying, lipid extraction and transesterification (Sun et al., 2014). A large amount of solvent is needed for traditional oil extraction methods (Sun et al., 2014; Yoo et al., 2012), which causes environmental pollution increases costs and consumes much energy in the extraction process. Microwave reveals characteristics of even and rapid heating, little consumption of solvents and short extraction times. Comparably, ultrasound can enhance the molecular energy of solvents in the liquid as well as strong penetration to destroy the cell wall so that the solvent can efficiently extract oil. Biodiesel is produced by esterification and/or transesterification reaction of various lipid sources with alcohol in the presence of a homogeneous base, acid or heterogeneous (*i.e.,* solid) catalyst. A base catalyst is commonly used for producing biodiesel because of higher reaction rate than other catalysts (Stojković et al., 2016). However, the base catalyst and form soap by reaction with free fatty acids, which consumes the catalyst. Homogeneous acid-catalytic process is slow compared to a base-catalytic process (Adewale et al., 2016). Heterogeneous catalysts are used for producing biodiesel, such as sulfate zirconia, zeolite, CaO, ZnO-La_2CO_3 (Carrero et al., 2015; Man et al., 2012). Heterogeneous catalysts can be easily re-used and the undesired soap formation can be avoided.

The economic viability of biodiesel is dependent on raw material and conversion cost (Cheirsilp and Louhasakul, 2013). Scientific and engineering researches to increase the economic viability of biodiesel have been widely investigated (Macias-Sanchez et al., 2015; Seo et al., 2015). Methanol can be replaced by dimethyl carbonate (DMC) to enhance sustainability of biodiesel production. DMC is inexpensive, neutral, and non-toxic solvent and it has been used as the acyl acceptor in transesterification of lipid (Gharat and Rathod, 2013; Min and Lee, 2011). In addition, production of glycerol as by-product is loss to the washing step and some of glycerol are discarded as waste. The limitations could be solved using DMC as reactant in the presence of alkali. Since alkali acted as solid catalyst in DMC solution, separation could be simply done by filtration or centrifugation thereby yielding high biodiesel purity and higher valued byproduct, glycerol carbonate.

Therefore, transformation of a cheap and well-grown biomass into biodiesel without lipid extraction is highly desirable. As a case study, transformation of *Camelina sativa* (*C. sativa*) into FAMEs (biodiesel) via pyrolysis assisted *in-situ* transesterification with DMC in the presence of porous material (*e.g.,* silica) was mainly investigated in this study. *C. sativa* is a promising alterative feedstock for biodiesel production that is normally cultivated in the northwestern parts of the United States such as Montana, Minnesota, North Dakota and South Dakota. It is commonly known false fax or gold-of-pleasure, a spring planted annual oil crop species of the genus *Cruciferae* that grows well in temperate climates (Das et al., 2014; Iskandarov et al., 2014; Pavlista et al., 2016; Peng et al., 2014). *C. sativa* has been demonstrated to grow in marginal lands, has low fertilizer and pesticide requirements, is highly resistant to a cold environment, and can be used as rotation crop with wheat. Thus, the systematic experimental approaches to validate the introduced pyrolysis assisted *in-situ* transesterification were performed at the fundamental level. In this respect, this study provided 1) the characterization of thermal decomposition of *C. sativa*, 2) the validation of introduced pyrolysis assisted in-situ transesterification with DMC and *C. sativa*, 3) the thermal cracking of FAMEs transformed from *C. sativa*. and 4) the optimal conditions for pyrolysis assisted *in-situ* transesterification.

2. Materials and methods

2.1. Materials and oil extraction

C. sativa seed was obtained from *C. sativa* plants grown in Canada. SiO_2, MeOH (⩾99.9%), dichloromethane (⩾99.9%) and dimethyl carbonate (⩾99%) were purchased from Sigma-Aldrich (St. Louis, USA). Sodium hydroxide (NaOH) was purchased from Daejung Science (Korea). A Soxhlet device equipped with a reflux condenser was used for *C. sativa* oil extraction from 20 g of *C. sativa* seed by dichloromethane at 60 °C for 72 h, followed by recovering dichloromethane using a rotary evaporator.

2.2. Characterization of C. sativa seed

Thermo-gravimetric analysis (TGA) of *C. sativa* seed was conducted using a SDT Q600 simultaneous thermal analyzer (TA Instruments, USA). The TGA experiment was carried out from 25 to 850 °C at a heating rate of 10 °C min^{-1}. Total sample loading in each TGA test was 5 ± 0.01 mg.

2.3. Conventional transesterification

A 10 mL of a mixture of NaOH, MeOH and *C. sativa* oil (NaOH/oil = 0.011 (w/w); MeOH/oil = 6 (mol/mol)) were placed in 20 mL vial and vial containing the mixture were placed on heating and stirring plate. The 10 mL of mixture solution was heated at 60 °C with stirring at 500 rpm for 2 h.

2.4. In-situ transesterification in the presence of a porous material

A bulkhead unit (Swagelok, 2507–400-61) was used as a batch reactor in this study. First, 0.3 of SiO_2 was packed in the reactor. Second, for reaction with extracted *C. sativa* oil, 10 μL of extracted *C. sativa* oil and 200 μL of MeOH or DMC were put in the reactor. For reaction with *C. sativa* seed that is equivalent to 13 mg of *C. sativa* seed and 200 μL of MeOH or DMC were put in the reactor. Then, 0.3 g of SiO_2 was packed subsequently. The other side of the bulkhead was capped and placed in the furnace and heated up to a target temperature (heating rate: 30 °C min^{-1}). After reaction, the sealed bulkhead was cooled down to ambient temperature by quenching in 4 °C water. In order to ensure the reproducibility, the experimental work based on each text matrix was repeated three times.

2.5. Chemical analysis

A Varian 450 GC-FID with Agilent DB-Wax column was used for analysis of *C. sativa* lipids. N_2 (total flow rate: 30 mL min^{-1}) was used as a carrier gas. Oven setting followed: 1) 50 °C for 3 min; 2) 180 °C (10 °C min^{-1}) for 5 min; and 3) 230 °C (5 °C min^{-1}) for 28 min. FAME calibrations were conducted with FAME standard