



Pyrogenic transformation of oil-bearing biomass into biodiesel without lipid extraction



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ABSTRACT

This study mechanistically investigated the pseudo-catalytic transesterification of oil-bearing biomass through a thermo-chemical pathway. As a case study, all experimental work was conducted with sesame seed and sesame oil. The pseudo-catalytic transesterification occurred in the presence of porous material (silica) since porous material provided reaction space as a micro reactor and drove the heterogeneous reactions between the mobile phase of methanol and the stationary phase of triglycerides (TGs) in sesame. The experimental work verified that the main driving force of pseudo-catalytic transesterification was temperature in the presence of porous material, which led to the direct derivatization of oil-bearing biomass into fatty acid methyl esters (FAMES). Thermal cracking was observed at temperatures higher than 350 °C and the main experimental parameter initiating this thermal cracking was temperature and time. However, the optimal conditions identified in this study were temperatures lower than 350 °C, where the total yield of FAMES reached up to $96.4 \pm 0.3\%$ of lipid in sesame seed. The introduced technology would be applicable to the production of biodiesel and comprehensive lipid analysis in oil-bearing biomass.

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1. Introduction

Industrial development from the industrial revolution onwards has been evaluated as a catalyst to improve our life quality, but our excessive dependence of fossil fuels has posed numerous side effects such as global climate change [1,2]. In addition to these adverse environmental impacts, energy security issues have been considered as one of top priorities in most developed countries [3,4], due to uneven distribution of natural resources (fossil fuels). In order to alleviate these adverse environmental impacts resulting from our dependence on fossil fuels and to ensure energy security, harnessing energy from renewable and/or sustainable sources has been actively proposed and developed as an alternative [5–9]. Among them, exploiting biomass as an initial feedstock for biofuels has gained public acceptance due to its intrinsic carbon neutrality [10], thus, biofuels (*i.e.*, biodiesel and bioethanol) have replaced fossil fuels to some extent, especially in the transportation sector [5,11,12]. Approximately 85% of all petro-derived oil produced is consumed in the transportation sector, thus, biodiesel and bioethanol are now regarded as feasible alternatives for transportation

fuel due to their compatibilities with current internal combustion engine and distribution networks [5,13,14].

However, displacing a large portion of petro-derived liquid fuels with biofuels is challenging due to economic barriers and ethical dilemmas [4,5,15–21]. Nevertheless, our effort for replacing petro-derived fuels with biofuels (*i.e.*, biodiesel and bioethanol) in developed countries has been expanded gradually via political support and legitimate enactments like the renewable fuel standard (RFS), due to their well-known environmental benefits [18,22]. Furthermore, the intensive biofuel studies based on the concept of second and third generations of biofuels have been conducted to enhance the economic feasibility and to resolve ethical dilemmas [8,23–25]. In addition, considering the only conversion process for biofuels (*i.e.*, biodiesel and bioethanol), the expansion of second and third generations of biodiesel would be more advantageous over those of bioethanol, since all generations of biodiesel could be transformed via the same conversion platform, known as the transesterification process [9,23,26–35]. According to cost analysis of the first generation of biodiesel, the cost of lipid feedstock has been identified as the major portion of total production, which is estimated as $\sim 70\%$ of the biodiesel production cost [5,9,10,15–17,19,29–36]. Thus, in order to enhance the economic feasibility of biodiesel, bioengineering oriented studies such as plant breeding with and/or without gene modification have been conducted, with an aim to achieve a high content of

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lipids in oil-bearing biomass and to upgrade/modify the physico-chemical properties of lipids in oil-bearing biomass as an initial feedstock of biodiesel [37–39].

Thus, in order to quantify the lipid content and qualify the lipid profiles in bred plants (i.e., oil-bearing biomass), an accurate lipid analysis for oil-bearing biomass should be established conducted by derivatizing triglycerides (TGs) into fatty acid methyl esters (FAMES). The most common way to derivatize TGs is carried out by the transesterification reaction [40–42]. However, the problem of transesterification is time-consuming and very sensitive to impurities such as extractives and water attributed to the extraction process [41,43]. Thus, the technical improvement of lipid analysis for oil-bearing biomass should be implemented. In addition, the lipid analysis of oil-bearing biomass without the mechanical and chemical extraction of lipids would be very desirable due to the prevention of unwanted loss [41]. Furthermore, the direct derivatization of oil-bearing biomass into FAMES would significantly enhance the economic feasibility of biodiesel, since the lipid extraction in the third generation of biodiesel has been pointed out as one of main technical and economic obstacles. Therefore, the main objectives of this study are to introduce an innovative derivatizing technique for the lipid analysis and for the production of biodiesel from oil-bearing biomass without lipid extraction: this work mechanistically verifies a new derivatizing method with sesame seed as a case study. In order to complete the technical advantages, this work also investigates the thermal cracking behavior of FAMES. The experimental findings of this work could be applied in various research fields sharing the platform for transesterification.

2. Material and methods

2.1. Chemical reagents

The sesame used in this study was purchased from a local market. Methanol (Lot: 34860, $\geq 99.9\%$), n-Hexane (Lot: 32293, $\geq 99\%$) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich (St. Louis, USA). Silica with pore diameters of 60 Å (Lot: 236799-100G, 60–100 mesh) was also purchased from Sigma Aldrich (St. Lois, USA).

2.2. Thermo-gravimetric analysis (TGA) of sesame seed and oil

The thermal degradation of sesame oil and sesame seed in N_2 was characterized with a Mettler Toledo TGA/DSC Star System (Mettler, Switzerland). A series of TGA tests were carried out at a heating rate of $35\text{ }^\circ\text{C min}^{-1}$ from 25 to $900\text{ }^\circ\text{C}$. The flow rate of the purge and protective gas was total of 60 mL min^{-1} and $9 \pm 0.05\text{ mg}$ of the seed and oil was separately loaded. Prior to the TGA experimental work, lipid of sesame was homogenized (crushed) and then chemically extracted using a soxhlet device with n-Hexane for 12 h. The extraction temperatures were varied on the boiling point (T_b) of the organic solvent (i.e., n-Hexane: $T_b = 68.5\text{ }^\circ\text{C}$), but the extraction temperature was adjusted at $T_b + 5\text{ }^\circ\text{C}$. A vacuum rotary evaporator (Cole-Parmer, USA) was used for the recovery of n-Hexane.

2.3. Transforming sesame oil into FAME under the presence of basic catalyst (NaOH)

Prior to the transesterification reaction, NaOH and methanol (MeOH) were mixed at $40\text{ }^\circ\text{C}$ for 10 min and the weight ratio of NaOH to MeOH was adjusted to 1.1%. The mixture solution of NaOH and MeOH was added into the sesame oil and the molar ratio of MeOH to sesame oil (triglycerides: TGs) was adjusted to

7.5. Total 100 mL of the mixture solution was heated at $60\text{ }^\circ\text{C}$ for 2 h and mixed with a magnetic stirrer at the speed of 500 rpm.

2.4. Pseudo-catalytic transformation of sesame seed and oil into FAME

A Swagelok bulkhead union (SS-400-61, inner volume: 1 mL) was used as a batch reactor in this study. Reaction temperature of the batch reactor was measured using a K-type thermocouple combined with a bored-through straight fitting (Swagelok SS-100-R-6M, USA). One side of the bulkhead was sealed with the Swagelok fitting (SS-400-C) and then 0.3 g of silica was inserted. For transesterification of sesame oil, 200 μL of oil and MeOH mixture (the volumetric ratio of MeOH to oil is 10:1) was carefully inserted into the bulkhead. For transesterification of sesame seeds, 200 μL of MeOH and sesame seeds (the mass ratio of MeOH to sesame seeds is 5:1) were carefully inserted into the bulkhead. After that, 0.3 g of silica was inserted again. Next, the other side of the bulkhead was sealed with Swagelok. And then, the reactor was placed horizontally in a furnace and heated to a desired temperature (heating rate: $30\text{ }^\circ\text{C min}^{-1}$). Right after a reaction finished, the sealed bulkhead cooled down to ambient temperature by putting in cold water ($4\text{ }^\circ\text{C}$). After reaching ambient temperature, reaction product and silica were transported to a vial, and then the reaction product was filtered. In order to ensure reproducibility, the experimental work based on each text matrix was conducted in triplicate.

2.5. Chemical analysis

Prior to being injected into the GC unit, the filtered reaction product was 15-fold diluted with dichloromethane. GC/FID (Varian 450 High Resolution Gas Chromatograph) equipped with DB-Wax column (Agilent J&W GC column, $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) was used for the analytic measurement. The GC/FID analysis methods are summarized in Table SI-1 (Supplementary Information). Multiple calibrations of FAME were conducted with FAME STD (37 FAME MIX, CRM47885, Sigma Aldrich, St. Louis, USA). The MDL values of 19 target compounds averaged as $0.57 \pm 0.29\text{ ng}$ (per $1\text{ }\mu\text{L}$ injection). Refer to Table SI-3 for detailed information regarding the basic quality assurance (QA) parameters derived from the calibration analysis (method detection limit (MDL) and relative standard error (RSE)). GC/MS-TOF (Bench-TOP TOF, UK) analysis was carried out for identification of FAME components derived from sesame oil and sesame seed.

3. Result and discussions

3.1. Lipid content in sesame oil and lipid profiles of sesame oil

The lipid content of sesame seed was measured as $41.5 \pm 0.5\text{ wt}\%$ using the solvent extraction. In order to ensure the lipid content in sesame seed and to characterize the thermal degradation of sesame oil, a series of TGA tests at the heating rate of $35\text{ }^\circ\text{C min}^{-1}$ were conducted in N_2 and their representative thermograms were depicted in Fig. 1(a) and the differential thermograms (DTG) of sesame oil and seed were illustrated in Fig. 1(b).

As denoted in Fig. 1(b), the temperature indicating the maximum thermal degradation rate shown as the DTG curves of sesame oil and sesame seed was nearly identical, with a temperature at approximately $400\text{ }^\circ\text{C}$. This indicates that lipid (TGs) is thermally degraded via the bond dissociation from the triglyceride backbone rather than devolatilization of TGs. This observation strongly suggests that the thermal degradation and/or stability of lipid in sesame seed are not different from that of oil, which implies that the derivatizing lipid in sesame seed without lipid extraction via

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