Valorization of sewage sludge via non-catalytic transesterification

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ABSTRACT

To seek a way to valorize sewage sludge (SS), it was chosen as a raw material for biodiesel production. As such, non-catalytic transesterification of dried SS was carried out, to enhance its value. Note that picking a waste material such as SS as an inexpensive lipid feedstock for biodiesel production, without lipid extraction, greatly increases the economic viability of biodiesel. Also, to enhance biodiesel sustainability, ethanol (EtOH) was employed as the acyl acceptor, in this study, and this was experimentally justified by results showing that employing EtOH as an acyl acceptor provided an effective means for compensating for the lower heating value arising from the large amount of palmitic (C_{16}) acid in SS. This study experimentally proved that the fatty acid ethyl ester (FAEE) yield at 380 °C reached up to 13.33 wt% of dried SS. Given that the lipid content of dried SS is 14.01 ± 0.64 wt%, the FAEE yield of 13.33 wt% implied that 95.14 wt% of lipid in dried SS had been converted into FAEEs. The introduced SS valorization in this study offered an excellent opportunity to address diverse environmental hazards arising from SS and associated emerging contaminants. Given that the optimal temperature for the non-catalytic conversion for biodiesel production from SS was found to be 380 °C, emerging contaminants, such as microplastics and antimicrobials, were simultaneously degraded, due to their inferior thermal stabilities. Lastly, considering that the introduced biodiesel conversion process is thermally induced, the SS reside after the biodiesel conversion process can be further used in thermo-chemical processes as raw materials for gasification and pyrolysis (future work).

1. Introduction

Fossil fuels contribute three quarters of the world's primary energy (Shafiee and Topal, 2009); however, despite the numerous socio-economic benefits from their use, their mass consumption results in global environmental issues, such as global warming (Liu et al., 2015). Moreover, it has been reported that anthropogenic CO_2 emissions are exceeding the Earth's capacity to assimilate carbons through natural carbon cycles (Brown and Zeiler, 1993). Note that global CO_2 emissions are equivalent to 35.9 Gt in 2014, which was 60% above global emissions for 1990, the reference year for the Kyoto Protocol (Li et al., 2018; Rogelj et al., 2012; Tavoni et al., 2014). To address the global environmental issues triggered by CO_2 emissions, considerable research on renewable energy-including tidal energy (O Rourke et al., 2010), wind power (Díaz-González et al., 2012), solar thermal energy (Tian and Zhao, 2013), photovoltaics (Parida et al., 2011), geothermal energy

(Lund and Boyd, 2016), and bioenergy (Raheem et al., 2018) - has been conducted over the last three decades. The utilization of renewable energies offers an effective means for reducing CO_2 emissions from combustion of fossil fuels. Note that (aforementioned) renewable energies are indeed carbon-free/-neutral. In particular, the use of biodiesel has gained public acceptance, as it is highly compatible with petro-diesel (Aklin et al., 2018), and in a blend with petro-diesel, can share distribution networks (Lardon et al., 2009). Moreover, biodiesel can be used in current internal combustion (IC) engines without requiring their modification (Damanik et al., 2018).

Given that 20% of global energy production was consumed by the transportation sector, in 2018 (Achour and Olabi, 2016), the use of biodiesel (as a renewable energy) as a substitute for petro-diesel (a non-renewable energy) provides a strategic way to reduce the environmental burdens arising from CO_2 emission (Mofijur et al., 2015). Thus, the commercialization of biodiesel has been rapidly achieved, and its

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use has been mandated by legislative instruments, such as renewable fuel standards (RFSs) (Huh et al., 2015). According to the World Energy Outlook 2018, published by International Energy Agency (IEA), its new policies scenario has assumed that global biodiesel consumption will increase to 3.86 million barrels per day, by 2040. Biodiesel, particularly mono-alkyl esters of vegetable oil or animal fat using methanol (MeOH) as an acyl acceptor (1st generation of biodiesel), has been considered as a substitute for petro-diesel (Lardon et al., 2009). Exhaust from bio-diesel contains fewer pollutants than petro-diesel (Can et al., 2017), as its compositional matrix (i.e. low sulphur, benzene derivatives, and oxygen content) result in less emission of pollutants such as carbon monoxide, particulate matter, unburned hydrocarbons, and sulphur oxides (Can et al., 2017; Hosseinzadeh-Bandbafha et al., 2018).

Despite the fact that lipid, such as triglyceride (TG) is one of the most ubiquitous chemical compounds, TGs from edible resources (animal fat, rapeseed oil, sunflower oil, soybean oil, etc.) have been commercially converted into biodiesel (Farobie and Matsumura, 2015; Leung et al., 2010; Wan Mahari et al., 2018a), in a trend criticized for leading to deforestation, disputes over food prices and land use, and human right violations (Tait, 2011). Therefore, identifying lipid feedstocks that can be produced without causing harm to the environment is important (Tait, 2011), and as such, employing sewage sludge (SS) as a lipid feedstock for biodiesel production could be ideal, since SS contains 10–30 wt% lipid (dry basis) (Kargbo, 2010; Kwon et al., 2012; Manara and Zabaniotou, 2012). Note that refining TGs contributes 70–75% of the total production cost of biodiesel (Kwon et al., 2012), and so using low-quality lipid from SS offers a strategic means of achieving total biodiesel production cost savings (Kwon et al., 2013a; Kwon et al., 2012). According to EU statistics, 10 million tons (dry basis) of SS were generated from 27 EU countries, in 2010 (Kelessidis and Stasinakis, 2012), and it is expected that, in line with ongoing industrialisation and urbanization, 13 million tons of SS will be generated from the 27 EU countries, in 2020 (Kacprzak et al., 2017; Kelessidis and Stasinakis, 2012).

Using SS as a lipid feedstock for biodiesel production does have issues; however, including the presence of impurities such as water, and large amounts of free fatty acids (FFAs), which are common in most water-based wastes (Kwon et al., 2012). Also, oil extraction from SS is challenging, as the process increases the concentrations of impurities (Mercer and Armenta, 2011). These are issues that it would be desirable to address when pursuing the goal of developing an economically viable, biodiesel conversion technology. Biodiesel is produced through transesterification of refined TGs (i.e. with a low content of FFAs) and methanol (MeOH), in the presence of homogeneous acid/base catalysts, H_2SO_4, KOH, or NaOH (Kwon et al., 2013a; Kwon et al., 2012; Kwon et al., 2013b). Using homogeneous catalysts to transform such inexpensive lipid feedstocks into biodiesel without additional pre-treatment steps is not easy; however, since they are very sensitive to water and FFAs (Kwon et al., 2013a; Kwon et al., 2012; Kwon et al., 2013b), unwanted saponification and hydrolysis side reactions cannot be avoided (Kwon et al., 2013a; Kwon et al., 2012; Kwon et al., 2013b). To circumvent these difficulties around the use of homogeneous catalysts, much research has been conducted on biodiesel production using heterogeneous catalysts, under subcritical conditions (Dhawane et al., 2018), though the resultant technical advances have not yet been fully commercialized (Kwon et al., 2012). Application of supercritical methanol technology is one method that has received considerable attention lately (Kwon et al., 2013a; Kwon et al., 2012); although, to date, its economic viability remains low, as its high temperature and pressure requirements have impeded practical implementation (Kwon et al., 2013a; Kwon et al., 2012; Kwon et al., 2013b).

This study has therefore focussed closely on synthesizing biodiesel through non-catalytic transesterification of SS. Moreover, to enhance economic viability, direct conversion of SS into biodiesel, without oil extraction, was performed. Considering the fact that SS TGs contain large amounts of $C_{14–16}$ fatty acids, compared to vegetable oil (Kwon

et al., 2013a; Kwon et al., 2012), this study routinely used ethanol (EtOH) as the acyl acceptor, as a strategic means of increasing energy density (Kwon et al., 2013c; Wan Mahari et al., 2018b). Note that the main fatty acid constituents in most vegetable oils are C_{18} fatty acids (Kwon et al., 2013c), and to gain a fundamental understanding of fatty acid ethyl esters (FAEEs), a series of the thermo-gravimetric analysis (TGA) tests were also carried out, as part of this study. Additionally, the FAEE yield from non-catalytic transesterification of dried SS, as a function of reaction temperature, was tested, in support of the main objective of the study reported here, which was to experimentally support use of SS as a promising raw feedstock for biodiesel production.

2. Materials and methods

2.1. Sample preparation and chemical agents used in this study

SS was collected from Jungnang Water Reclamation Centre (37.557650, 127.065363) in Korea, where 159 million tons of waste-water are treated daily. The collected SS was dried at 105 °C for 1 d. Methanol (Batch 517127), ethanol (Batch 459844), dichloromethane (Batch 34856), chloroform (Batch 372,978), and sulfuric acid (Batch 339741), were purchased from Sigma-Aldrich (St. Louis, MO, USA). Silica gel (Batch 236799) was also purchased from Sigma-Aldrich (St. Louis, MO, USA), and had a particle size range from 60 to 100 mesh, and average pore size of 60 Å. Soybean oil and avocado oil were purchased from a local supermarket. Ultra-high purity, gas chromatography operating gases (He, Air, and H_2) were purchased from Green Gas (Gwangju, South Korea).

2.2. Characterization of the SS thermolysis and lipid extracted

A series of TGA tests (STA 449 F5 Jupiter, Netzsch, Germany) was conducted, to characterize SS thermolysis, in N_2. 10 ± 0.05 mg of sample were loaded in an alumina crucible for each TGA test, which was carried out at a heating rate of 10 °C min^{-1}, from 35 to 900 °C. 20 mL min^{-1} of protective gas, and 50 mL min^{-1} of purge gas (i.e. the total N_2 flow rate was 70 mL min^{-1}), were set during the TGA test, and their flow rates were automatically controlled by imbedded mass flow controllers in the TGA unit. Prior to each TGA test, a reference test (i.e. no sample loading) was carried out, to cancel out buoyancy effects arising from N_2 thermal expansion. To characterize the thermolysis of lipid in the sewage sludge sample, the same TGA tests of soybean and avocado oil was conducted to use the experimental results as the reference.

2.3. Lipid extraction of dried SS

Prior to lipid extraction, dried SS was uniformly ground, using a vibratory micro-mill (Pulverisette, Fritsch, Germany), and the dried SS average size was adjusted to 200 μm. An equivalent volumetric mixture of dichloromethane, MeOH, and chloroform was prepared, and the mixture was used as solvent for lipid extraction (Zhu et al., 2014). To extract lipid (TGs) from the dried SS sample, a Soxhlet apparatus (ST243 Soxtec 230 V, Foss, Denmark) was used. 50 ± 0.2 g of dried SS was correctly loaded into the Soxhlet device, and 1.2 L of the solvent mixture was added. Lipid extraction was carried out at 80 °C for 24 h, after which the solvent mixture was recovered using a rotary evaporator (R-300 Rotavapor Manual Lift, Büchi, Switzerland). The defatted SS sample was collected from the lipid extraction. 35.17 wt% of the SS extractives (oil and impurities) was recovered, and the acid value (AV) (Kwon et al., 2012; Kwon et al., 2013b) of the SS extract was determined to be 15.37.

2.4. Acid catalyzed transesterification using EtOH

The SS extracts were transesterified, using EtOH in the presence of

H_2SO_4, to obtain FAEEs. To be precise, 10 g of the SS extracts, 0.5 g of H_2SO_4, and 5 mL of EtOH, were used for the acid-catalyzed transesterification reaction, which was conducted at 60 °C for 24 h, under a constant stirring speed of 300 rpm.

2.5. Non-catalytic conversion of SS extracts and dried SS into FAEEs

To synthesize FAEEs from the SS extracts and dried SS, non-catalytic transesterification was conducted, in the presence of silica gel (Jung et al., 2016). A bulkhead union (SS-400-41, Swagelok, USA) was employed as the batch reactor main body. One end of this union was sealed, with a stainless stopper (SS-400-C, Swagelok, USA), and 320 mg of silica gel, 200 μL of EtOH, and either the SS extract (9 mg), or dried SS (15 mg), were placed into the bulkhead union. After all reactants had been added into the bulkhead union, its other end was also sealed with a stainless stopper. The conversion of SS extract or dried SS into FAEEs was carried out under various temperatures (from 200 to 390 °C) to monitor FAEE yield. Once the target temperature for non-catalytic transesterification reaction is reached, the FAEE conversion was ended due to the fast reaction kinetics (Ref). A muffle furnace (Nabertherm, Germany) was used as an external heating source, to maintain experimental temperatures. The inner temperature of the bulkhead union was measured with K-type thermocouples (CASS-18-19, Omega, UK), and the temperature readouts (readout display and recording by OMB-DAQ-56, Omega, UK) were used in this study.

2.6. Quantification of converted FAEEs

To quantify the converted FAEEs from the SS extract and dried SS, Gas Chromatography (GC) Time-of-Flight Mass Spectrometry (Agilent 7890B and ALMSCO Bench TOF-MS), equipped with a DB-WAX column (30 m × 0.25 mm × 0.25 μm) was used. In parallel, GC with Flame-Ionization Detection (Varian 450-GC coupled CP-8410 Autosampler, Varian, USA), equipped with the same sized, DB-WAX column (30 m × 0.25 mm × 0.25 μm), was used. FAEE standard mixture (49454-U, Sigma-Aldrich, USA) was used for multiple calibrations, and the GC operational conditions were 50 °C (3 min holding, initial oven temperature), 180 °C (heating rate of 10 °C min^{-1}, and 5 min holding), and 230 °C (heating rate of 5 °C min^{-1}, and 19 min holding time). Note that the total GC operational time was 50 min. FAEE yield was calculated using the following equation:

$$Biodiesel\ yield\ (\%) = \frac{Converted\ FAEE\ mass}{Dried\ sludge\ mass} \times 100$$

3. Results and discussion

3.1. Thermolysis characterization of dried SS and defatted SS

A series of the TGA tests was conducted to characterize the thermolytic behavior of dried SS and defatted SS in an inert condition. Note that the thermolytic behavior of SS is of great importance in that non-catalytic transesterification is initiated by adding thermal energy from an external heating source (Jung et al., 2017; Jung et al., 2016; Kwon et al., 2013a; Kwon et al., 2012; Kwon et al., 2013b, 2013c). Prior to the TGA test of dried SS, a TGA test was conducted on soybean, for use as a reference. As noted, TGA testing of soybean oil and dried SS was conducted at a heating rate of 10 °C min^{-1}, from 35 to 900 °C. Mass decay of soybean oil and dried SS are depicted in Fig. 1, and their thermal degradation rates (differential thermogram: DTG) have also been incorporated.

Fig. 1(a) shows that mass decay of soybean occurred from 338 to 485 °C, which signified that the mass decay of soybean oil could be attributed to volatilization of fatty acids, in that TGs do not have a boiling point (T_b) (Jung et al., 2017; Jung et al., 2016; Lam et al., 2016; Liew et al., 2018). As such, the mass decay seen in Fig. 1(a) indirectly

demonstrated the consecutive thermolytic mechanisms of soybean oil. In short, fatty acids in soybean oil are randomly dissociated from the glyceride backbone, by thermal energy, and then the dissociated fatty acids evaporate, when they reach their own boiling points. In addition, the negligible residual mass in Fig. 1(a) strongly suggested that dehydrogenation of soybean oil was not a major thermolytic pathway. Considering that the final residual mass of soybean oil was < 0.3 wt%, its thermal cracking through dehydrogenation was likely to be negligible. Note that dehydrogenation expedites cyclization, thereby resulting in char formation and high aromaticity (Kwon and Castaldi, 2008).

The identified random bond dissociations of fatty acids from the glyceride backbone signified that the transesterification reaction could be non-catalytically initiated, in that an initial step for the transesterification reaction is bond dissociations of fatty acids from the glyceride backbones of TGs (Kwon et al., 2012). The conversion mechanisms for non-catalytic transesterification were reported in previous studies (Kwon et al., 2012); however, the reaction kinetics for non-catalytic transesterification were very slow, thereby resulting in a low biodiesel yield (Kwon et al., 2012). To enhance the reaction kinetics for non-catalytic transesterification, a porous material was used (Kwon et al., 2012). As such, the heterogeneous reactions were developed by adding thermal energy, due to the low boiling point of an acyl acceptor, such as MeOH (65 °C) (Kwon et al., 2012). As noted before, TGs do not have a boiling point (T_b) (Jung et al., 2016); therefore, different mobility was indeed imparted, from the two different phases (i.e. the gas phase of MeOH and the liquid phase of TGs): the gas phase of MeOH acted like a mobile phase, and the liquid phase of TGs acted like a stationary phase (Kwon et al., 2012). In a confined space (i.e. a pore), the different mobilities would greatly increase the collision frequencies between the two reactants, MeOH and TGs, thereby resulting in fast reaction kinetics for non-catalytic transesterification (Kwon et al., 2012). Such reaction phenomena were similar to catalytic mechanisms, and we therefore named the process as 'non-catalytic (pseudo-catalytic) transesterification', in our previous studies (Jung et al., 2017; Jung et al., 2016; Kwon et al., 2013a; Kwon et al., 2012).

To check the lipid content, TGA testing of dried SS was carried out. As shown in Fig. 1(b), the mass decay from 338 to 485 °C was equivalent to 25.59 wt% of the dried SS. This observation suggests that dried SS had a large amount of lipid (TGs) although it was hard to quantify the exact lipid content. The highest thermal degradation rates of soybean oil and dried SS were seen to occur at 416 and 365 °C, respectively. Such a temperature difference signified that the mass decay of dried SS from 338 to 485 °C was not solely attributable to the volatilization of fatty acids in dried SS. In short, as depicted in the TGA tests (Fig. S1, supplementary information), the temperature regime indicating mass decay by volatilization of fatty acids randomly dissociated from the glyceride backbone of soybean oil, in reference to avocado oil, was identical. Therefore, such observations also implied that the compositional matrix of TGs did not affect the mass decay, by volatilization, of fatty acids dissociated from the glyceride backbone of TGs.

For the further investigation, defatted SS TGA testing was carried out. Mass decay of defatted SS and its thermal degradation rate are shown in Fig. 2(b). Note that the operational parameters for the TGA test in Fig. 2 were identical to those applied in the testing illustrated in Fig. 1. Interestingly, the final residual mass of defatted SS, in reference to dried SS, was 34.23 wt% less. The difference in the final residual mass in Fig. 2 was nearly the same as the mass of the SS extracts. Particularly, 35.17 wt% of the original dried SS sample mass was experimentally identified as the SS extracts, by solvent extraction using a Soxhlet device. Note that the difference in mass can be the experimental error, but such the difference is not much different. Also, the mass decay at ≤ 485 °C in Fig. 2(b) can be key evidence for this claim in line with the lipid content in dried SS. In short, the mass decay from 338 to 485 °C was not solely attributable to the thermolysis of TGs in SS, and
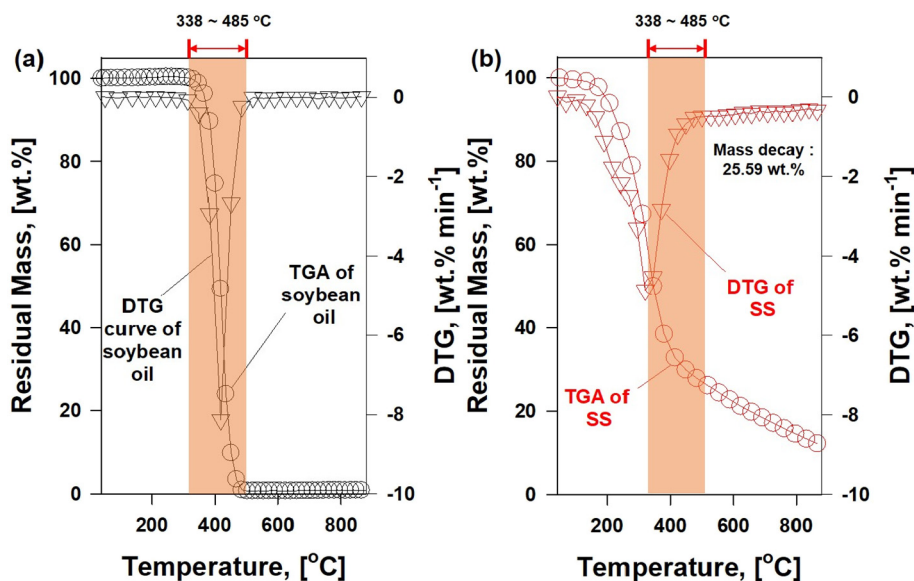
Fig. 1. (a) mass decay of soybean oil and its thermal degradation rate, in N_2, (b) mass decay of dried SS and its thermal degradation rate, in N_2.

therefore, the SS extracts must have contained large amount of impurities. In addition, such data interpretation suggested that conventional transesterification of SS extracts, using homogeneous acid/base catalysts (H_2SO_4/KOH), was not a suitable approach to synthesize biodiesel, as the conventional method for synthesizing FAEEs has been reported to be very sensitive to impurities (Kwon et al., 2013a; Kwon et al., 2012; Kwon et al., 2013b).

3.2. Conversion of SS extracts into fatty acid ethyl esters (FAEEs)

As reported, acid value (AV) of the SS extracts was higher than 15, which strongly suggested that base-catalyzed transesterification of the SS extracts was not technically possible, due to interference by the unwanted saponification side-reaction (Kwon et al., 2012). As an alternative, acid-catalyzed transesterification of the SS extracts was conducted, using H_2SO_4, for 24 h; however, the FAEE yield was negligible (< 1%), due to the high impurity content. To convert the SS extracts into FAEEs, non-catalytic conversion was carried out, and the representative chromatogram has been prepared as Fig. 3, while the FAEEs constituents from non-catalytic transesterification of the SS extracts, at 380 °C, have been summarized in Table 1. Note that the 380 °C
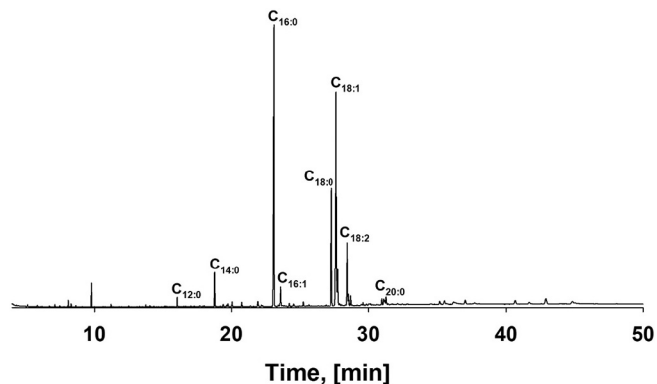

Fig. 3. Chromatogram of FAEEs from non-catalytic transesterification of SS extracts, at 380 °C.

reaction temperature was chosen as we had identified the optimal temperature for non-catalytic transesterification used in the synthesis of FAMEs as 380 °C in our previous study (Jung et al., 2016).
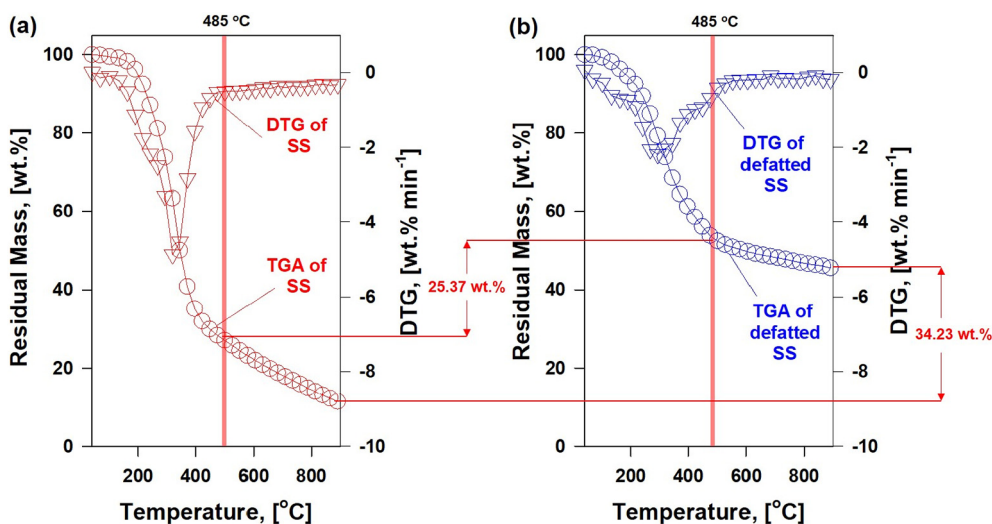

Fig. 2. (a) mass decay of dried SS, and its thermal degradation rate, in N_2, (b) mass decay of defatted SS, and its thermal degradation rate, in N_2.

Table 1
Compositional matrix of FAEEs converted from non-catalytic transesterification of SS extracts.

| Name of fatty acid	Degree of unsaturation	Fatty acid content [wt%]
Lauric acid	$C_{12:0}$	01.48 ± 0.006
Myristic acid	$C_{14:0}$	03.65 ± 0.091
Palmitic acid	$C_{16:0}$	36.98 ± 0.741
Palmitoleic acid	$C_{16:1}$	02.79 ± 0.004
Stearic acid	$C_{18:0}$	12.97 ± 0.075
Oleic acid	$C_{18:1}$	35.73 ± 0.658
Linoleic acid	$C_{18:2}$	05.51 ± 0.181
Arachidic acid	$C_{20:0}$	00.89 ± 0.021

As shown in Fig. 3, the major FAEE constituents from the non-catalytic transesterification of SS extracts were identified as $C_{16:0}$, $C_{18:0}$, and $C_{18:1}$ FAEEs. In reference to vegetable oil, the results shown in Fig. 3 and Table 1 supported the suggestion that SS contained particularly large amount of palmitic acid ($C_{16:0}$)—an observation that was in good agreement with previous work (Kwon et al., 2012). Given that the combustion heat of FAEEs is proportional to the number of carbons in fatty acid, using EtOH as an acyl acceptor provided a strategic means for compensating for the lower heating value arising from the large amount of palmitic acid in the SS (Kwon et al., 2012; Kwon et al., 2013c). In addition, the unlabelled peaks in Fig. 3 are most likely caused by the impurities proven to be in the SS extracts. Thus, detection of the impurities in the chromatogram (Fig. 3) also signified that this non-catalytic conversion platform for biodiesel production had an extremely high tolerance for impurities.

To quantify the total lipid content in the SS extracts, a series of the non-catalytic, SS extract transesterification reactions was performed, and the FAEE yield was monitored, as a function of reaction temperature.

As shown in Fig. 4, the FAEE yield at 380 °C was 39.84 ± 1.82%. This result signified that the lipid content in the SS extract was roughly equivalent to 40 wt%, in that the maximum FAMEs yield achieved through non-catalytic transesterification of SS extract, at 380 °C, was 98.5 ± 0.5%, in our previous work (Kwon et al., 2012). Furthermore, our previous work showed that non-catalytic transesterification had an extremely high tolerance to impurities (water and hydrocarbons) (Jung et al., 2016; Kwon et al., 2013a; Kwon et al., 2012; Kwon et al., 2013b, 2013c). Considering 40 wt% of the lipid content in the SS extractives, we were able to assume that the dried SS used in this study contained 14.01 ± 0.64 wt% lipid.

3.3. Direct FAEE conversion of dried SS via non-catalytic transesterification

As discussed, lipid extraction from SS adds cost to the process of biodiesel synthesis, which significantly reduces its economic viability
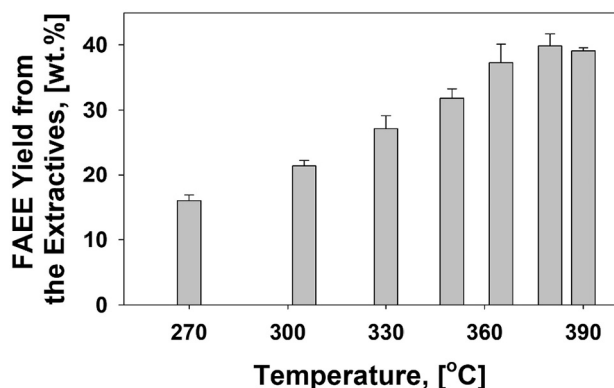
Fig. 4. FAEE yield from non-catalytic SS extract transesterification, as a function of reaction temperature.

(Jung et al., 2016; Kwon et al., 2012). Moreover, rigorous lipid extraction from SS appeared to be a key factor in increasing the amount of impurities in the lipid feedstock (Jung et al., 2016; Mercer and Armenta, 2011; Santori et al., 2012). To enhance economic viability, non-catalytic transesterification of dried SS was performed, and the FAEE yield, as a function of the reaction temperature, was monitored.

The results shown in Fig. 5(a) demonstrated that the FAEE yield was proportional to the reaction temperature, which was in good agreement with previous work (Jung et al., 2016; Kwon et al., 2012). Moreover, the compositional matrix of FAEEs were demonstrated in Fig. 5(b). As depicted in Fig. 5(a), the maximum FAEE yield via the non-catalytic conversion of dried SS was achieved at 380 °C - a reaction temperature also in good agreement with previous work (Jung et al., 2016). As shown in Fig. 5(a), the FAEE yield at 380 °C reached up to 13.33 wt% of the dried SS. Note that, as we assumed that the dried SS used in this study contained 14.01 ± 0.64 wt% lipid content (Fig. 4), the FAEE yield of 13.33 wt% in Fig. 5 implied that 95.14 wt% of lipid in the dried SS had been converted into FAEEs.

The chromatogram developed from the non-catalytic transesterification of dried SS at 380 °C has been presented in Fig. 6. The overall elution patterns for the individual FAEEs in Fig. 6 were nearly the same as seen in Fig. 3, but the chromatogram in Fig. 6 demonstrated the presence of more impurities. Nevertheless, at 380 °C, 95.14 wt% of the lipid in the dried SS was being converted successfully, indicating that the outcomes illustrated in Figs. 5 and 6 proved experimentally that non-catalytic transesterification of dried SS had an extremely high tolerance to impurities. Note that the impurities in Fig. 6 could be attributed mainly to SS thermolysis. Interestingly, Fig. 5(a) reflects the result that the FAEE yield began to decrease at temperatures ≥ 390 °C, which was most likely due to the thermal cracking of FAEEs, as evidenced in Fig. 5(b).

4. Conclusions

In sum, all this studies' results significantly suggest that SS can be a promising lipid feedstock. The non-catalytic conversion for biodiesel production offers a strategic means for valorizing SS, in that the introduced biodiesel conversion technique has an extremely high tolerance against any impurities. Note that the biodiesel yield from SS with/without lipid extraction is not much different in this study. Valorization of SS in line with the thermally-induced, non-catalytic transesterification reaction of SS provides a great opportunity to resolve diverse environmental hazards arising from SS, and emerging contaminants. Given that the optimal temperature for non-catalytic conversion in biodiesel production from SS is 380 °C, emerging contaminants, such as microplastics and antimicrobials, are simultaneously treated, due to their inferior thermal stabilities, during the thermally-induced, biodiesel conversion process of SS. In addition, employing EtOH as an acyl acceptor offers a strategic way to enhance biodiesel sustainability. Note that, as opposed to EtOH, MeOH is being produced by the chemical industry, so that, unilateral use of MeOH as an acyl acceptor in biodiesel production significantly reduces biodiesel's sustainability credentials. Finally, considering that the proposed biodiesel conversion process is thermally induced, the SS residues (left over after SS conversion to biodiesel) can be further harnessed as a raw material in thermo-chemical processes, such as gasification and pyrolysis.
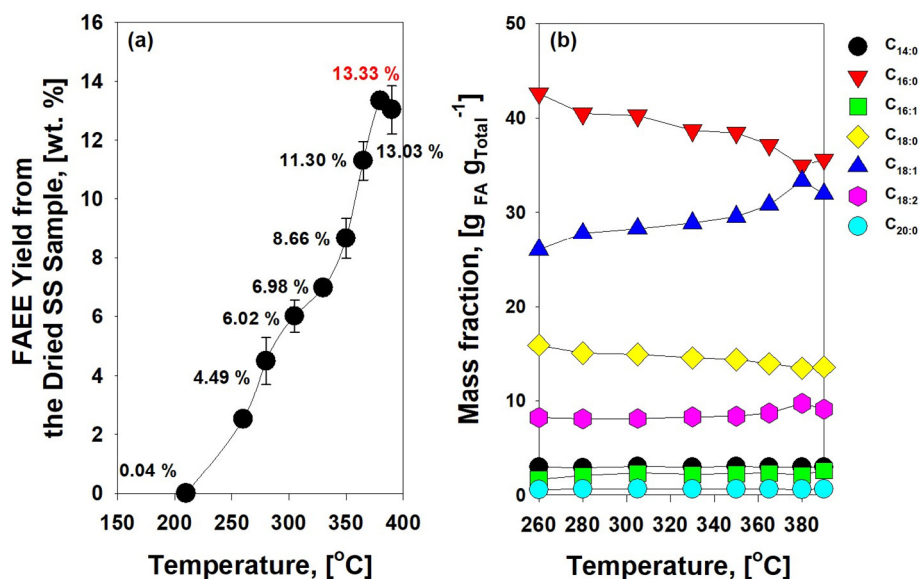
Acknowledgement

Fig. 5. (a) FAEE yield from the non-catalytic transesterification of dried SS, as a function of reaction temperature, (b) the composition of FAEEs under various reaction temperatures, derived from the non-catalytic transesterification of dried SS.
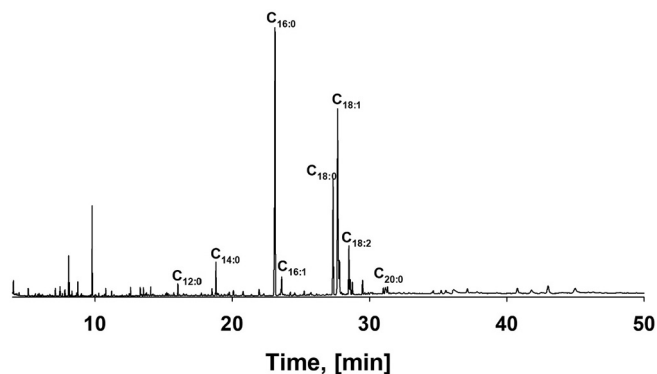

Fig. 6. Chromatogram for the FAEEs from dried SS achieved via non-catalytic transesterification, at 380 °C.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2019.105035.

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