



Fractionation of plant-cuticle-based bio-oils by microwave-assisted methanolysis combined with hydrothermal pretreatment and enzymatic hydrolysis

Shuntaro Tsubaki^{a,*}, Kiriyo Oono^b, Ayumu Onda^b

^a School of Materials and Chemical Technology, Tokyo Institute of Technology, Ookayama 2-12-1 E4-3, Meguro, Tokyo, 152-8550, Japan

^b Research Laboratory of Hydrothermal Chemistry, Faculty of Science and Technology, Kochi University, Akebono-cho 2-5-1, Kochi, 780-8520, Japan

ARTICLE INFO

Keywords:

Agriculture
Biotechnology
Plant cuticles
Fractionation of cutin
Microwaves
Methanolysis
Pretreatment

ABSTRACT

Microwave-assisted methanolysis was performed to fractionate a mixture of fatty acid methyl-esters from the cuticles of various wild plants and agricultural wastes. A combination of hydrothermal pretreatment and enzymatic hydrolysis effectively removed hemicellulose and cellulose to afford plant cuticles concentrated in residual materials. The subsequent methanolysis treatment afforded bio-oil from plant cuticles in ~10% yield with a maximum higher heating value (HHV) of 32 MJ kg⁻¹ from bagasse. The proposed cascading treatments allow the total use of herbaceous soft biomass by utilizing hemicellulose and cellulose fractions as well as plant cuticles to produce bio-oils with high HHVs.

1. Introduction

The production of sugars and oils comprises important biorefinery processes to produce biomaterials, biochemicals, and biofuels from renewable natural resources. Lignocellulosic biomass is an important source of the sugar platform in which cellulose and hemicellulose are hydrolyzed to produce reducing sugars (Naik et al., 2010). On the other hand, oil plants and microalgae are used as fatty acid feedstock in biodiesel production (Yusuf et al., 2011). The utilization of non-food biomass is very important for sustainable biorefinery applications to avoid competition of biomass production with food production, land usage, and water exploitation.

Plant cuticles cover the aerial parts of higher plants, protecting them from biotic and abiotic stress, and are ubiquitously present in the plant kingdom (Walton and Kolattukudy, 1972; Kolattukudy and Purdy, 1973; Heredia, 2003). The plant cuticle predominantly consists of wax and cutin. Wax is a mixture of long-chain aliphatic hydrocarbons, carboxylic acids, esters, and triterpenoids (Belding et al., 1998; Pereira et al., 2005; Buschhaus et al., 2007), while cutin is an aliphatic polyester consisting of hydroxyl fatty acids with C16–C18 chain lengths (Pollard et al., 2008). The estimated annual plant cuticle production is 180–1500 kg ha⁻¹ and thus, plant cuticles show great potential as an alternative biomass feedstock for the production of fatty acids and related aliphatic compounds

(Benítez et al., 2004; Heredia-Guerrero et al., 2009, 2017). The plant cuticle can be obtained from non-food biomass such as agricultural residue and food processing wastes (Kolattukudy and Purdy, 1973). Plant cuticles have previously been used to obtain sugarcane wax from sugar production residues (Nuissier et al., 2002) and bio-mimetic polyester from cutin (Heredia-Guerrero et al., 2009, 2017; San-Miguel et al., 2014; Zhang and Uyama, 2016).

Despite the wide availability of plant cuticles for biorefinery, effective plant cuticle fractionation has not been extensively studied to date. Previous studies have revealed that food processing residues from plant leaves and fruit peel, such as tea residues and persimmon fruit peels, contain abundant aliphatic compounds originating from the plant cuticle (Tsubaki et al., 2008, 2010, 2012, 2013a). However, removal of the cell wall components is necessary to obtain high purity plant cuticles. This suggests that conventional pretreatment methods can effectively remove polysaccharides to afford plant cuticles of the required purity. Previous literature has revealed that hydrothermal and alkaline pre-treatments with enzymatic hydrolysis of tea residues were effective in removing pectin, hemicellulose, cellulose, and proteins to afford the plant cuticle fraction as a residual material (Tsubaki et al., 2008; Tsubaki and Azuma, 2013b).

This study investigates the fractionation of plant cuticles from soft biomass derived from herbaceous plants (e.g. wild plants: *Eichhornia*

* Corresponding author.

E-mail addresses: shuntaro.tsubaki@gmail.com, tsubaki.s.aa@m.titech.ac.jp (S. Tsubaki).

<https://doi.org/10.1016/j.heliyon.2019.e01887>

Received 26 February 2019; Received in revised form 5 May 2019; Accepted 30 May 2019

2405-8440/© 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

crassipes, *Solidago canadensis*, and *Miscanthus sinensis*) and agricultural wastes (rice straw, rice hulls, and bagasse). Wild herbaceous plants are regarded as unutilized biomass comprising numerous plant cuticles; moreover, plant cuticles can also be found in agricultural wastes in concentrated form (Kolattukudy and Purdy, 1973). The wax and cutin present in plant cuticles are directly converted to fatty acid methyl ester (FAME) mixtures through methanolysis using acid (HCl) and alkali (NaOMe) catalysts. These depolymerized fatty acids can be further used as bio-oils and precursors for cutin-biomimetic polymers (Heredia-Guerrero et al., 2009, 2017; San-Miguel et al., 2014; Zhang and Uyama, 2016). Hydrothermal pretreatment and enzymatic hydrolysis were further used to remove polysaccharides and concentrate the plant cuticles. In addition, microwave (MW) reactors can rapidly heat the reaction media and enhance the susceptibility of lignocellulosic biomass to enzymatic hydrolysis. Thus, MWs have been used to shorten the methanolysis and hydrothermal pretreatments by inducing rapid heating (Azuma et al., 1984; Tsubaki et al., 2016; Gaudino et al., 2019). Finally, the bio-oil yield and higher heating values (HHVs) were measured to evaluate the availability of the products as bio-based fuels originating from plant cuticles.

2. Materials and methods

2.1. Materials

Wild *E. crassipes*, *S. canadensis*, and *M. sinensis* were collected from the Ishido-ike Pond (33.529272, 133.608102), Kochi University Asakura Campus in Kochi, 33.546538, 133.485194), Japan on 1st–4th December, 2012. This study utilized the whole aerial parts of these wild plants. Rice straw, rice hulls, and bagasse were kindly supplied by a local farmer in Kochi, Japan. All the samples were air dried and powdered by a blender prior to the experiments.

2.2. Compositional analysis of the soft biomass

The compositions of the soft biomass samples were determined according to previously reported methods (Tsubaki et al., 2010, 2013a,b). Briefly, the native soft biomass samples were first delipidated using a 1:1 chloroform:methanol mixture at room temperature. The holocellulose content was determined by the Wise method using sodium chlorite solution as the oxidant. The α -cellulose content was determined as the insoluble material after the extraction of holocellulose with 17.5% aqueous sodium hydroxide solution. The acid-insoluble content was determined by two-step hydrolysis using 72 wt% and 4% sulfuric acid (Tsubaki et al., 2008). Finally, the ash content was determined by dry ashing at 550 °C for 5 h in an electric furnace. All the analyses were conducted in triplicate.

2.3. MW-assisted methanolysis and hydrothermal treatments

MW-assisted methanolysis was performed in an HPR-100 TFM reactor (Teflon 100 mL closed reactor) using a multimode MW oven (START-D; frequency, 2.45 GHz; maximum output, 1 kW; Milestone, Sorisole, Italy) (Tsubaki et al., 2008). One gram of the sample was suspended in 20 mL methanol solution containing 1% hydrochloric acid (HCl) or sodium methoxide (NaOMe) and microwaved at 100 °C for 10 min, with 4 min of come-up time required to reach the desired temperature. The reaction temperature was controlled by a proportional integral derivative (PID) controller with direct temperature measurement of the reactant using a thermocouple thermometer to trace the temperature program. A homogeneous MW distribution was maintained using a diffuser and a stirrer bar was used to mix the reactant during MW irradiation. After the reaction, the reactor was immediately cooled in an ice bath. The solid residues after MW irradiation were separated by centrifugation and subsequently dried by freeze drying.

MW-assisted hydrothermal treatment was performed using the same

equipment described above. One gram of sample was suspended in 20 mL ultrapure water and microwaved at 200 °C for 5 min, with 4 min of come-up time. The solid residues after MW irradiation were separated by centrifugation. The other procedures were conducted as described above. All the MW reactions were conducted in triplicate.

2.4. Enzymatic hydrolysis by cellulase

The native soft biomass and residue remaining after the MW reactions were hydrolyzed using commercial cellulase (Meicelase CEP 17320; 1.0% w/w; Meiji Co., Ltd.) in 50 mM sodium acetate buffer (pH 5.0) at 37 °C for 48 h. The liquefaction rates were calculated from Eq. (1):

$$\text{Liquefaction rate (\%)} = 100 \times \frac{W_i - W_r}{W_i} \quad (1)$$

where W_i and W_r represent the initial weight and the weight after MW treatment (methanolysis and hydrothermal pretreatment) or enzymatic hydrolysis, respectively. The amounts of reducing sugars and glucose after enzymatic hydrolysis were determined by the dinitrosalicylic acid (DNS) method and the mutarotase-glucose oxidase (GOD) assay using a glucose CII test kit and a glucose standard (Wako Pure Chemical Industries, Ltd., Osaka, Japan), respectively. The yields of the reducing sugars and glucose were calculated by multiplying the glucose equivalent yield by a factor of 0.9 (glucose unit in glucan/glucose = 162/180). All treatments and analyses were conducted in triplicate.

2.5. Bio-oil characterization

The bio-oil yield was determined from the weight difference of each sample before and after methanolysis. The C, H, and N contents were determined using a FlashEA 1112 CHNS analyzer (Thermo Fisher Scientific Inc., MA, USA). The HHV of the alkali-soluble fraction was further determined from the carbon and hydrogen contents using Eq. (2) according to Yin (2011):

$$\text{HHV (MJ kg}^{-1}\text{)} = 0.2949 \times \text{C (\%)} + 0.8250 \times \text{H (\%)} \quad (2)$$

where C and H are the carbon and hydrogen contents, respectively. Bio-oil characterization was conducted in triplicate.

2.6. Characterization of the residues after MW-assisted methanolysis combined with hydrothermal pretreatment and enzymatic hydrolysis

The residues collected after MW-assisted methanolysis, hydrothermal pretreatment, and enzymatic hydrolysis were characterized by Fourier transform infrared (FT-IR) spectroscopy (FT/IR-4100, JASCO Co.) using the KBr method at a resolution of 2.0 cm^{-1} in the wavelength range 400–4000 cm^{-1} for 100–200 scans. The IR peaks attributed to the cuticle were estimated based on data from previous reports (Johnson et al., 2007; Villena et al., 2000; Järvinen et al., 2011; Takahashi et al., 2012). The ash contents were determined via calcination of the residue by dry ashing at 550 °C for 5 h in an electric furnace.

3. Results and discussion

3.1. Chemical composition of the soft biomass

The holocellulose, α -cellulose, CHCl_3 :MeOH extract, acid-insoluble residue, and ash contents in the six types of soft biomass are listed in Table 1. The CHCl_3 :MeOH extract was employed to estimate the amount of wax, pigments, and phenolic compounds. Among the six soft biomass samples, wild *E. crassipes* and *S. canadensis* presented the highest amounts of CHCl_3 :MeOH extract. The amount of acid-insoluble residues was used to estimate the cutin content since no official quantification method is available to date. Cutin is strongly durable to acids and thus, the removal of polysaccharides by sulfuric acid hydrolysis produces acid-insoluble

Table 1

Holocellulose, α -cellulose, CHCl_3 :MeOH extract, acid-insoluble residue, and ash contents (wt%) of the six types of soft biomass.

Biomass	Components (wt%)				
	Holo-cellulose ¹	α -Cellulose	CHCl_3 :MeOH extract ^{2,3}	Acid insoluble residue ⁴	Ash
<i>E. crassipes</i>	34.9	25.2	22.6	12.9	8.6
<i>S. canadensis</i>	42.7	29.0	30.9	6.1	12.6
<i>M. sinensis</i>	61.6	37.4	15.6	16.3	8.8
Rice straw	59.6	39.8	13.5	13.0	13.4
Rice hull	63.0	40.9	9.4	23.4	14.8
Bagasse	54.8	33.6	17.2	16.2	1.5

¹ Holocellulose: sum of cellulose and hemicellulose.

² CHCl_3 :MeOH = 1:1 (v:v).

³ CHCl_3 :MeOH extract: sum of wax, pigments, and phenolic compounds.

⁴ Acid-insoluble residue: sum of cutin and lignin-like aromatic polymer.

cutin in residue form (Tsubaki et al., 2008, 2013a,b). *M. sinensis* and bagasse afforded relatively high amounts of acid-insoluble residues. Rice hull, however, presented the highest amount of acid-insoluble residue since lignin-like aromatic polyphenol should also be contaminated in this fraction. The cellulose and holocellulose (sum of hemicellulose and cellulose) contents indicate the amount of polysaccharide feedstock producing reducing sugars. Of the studied samples, *M. sinensis* and rice straw presented the highest sugar contents.

Although the six waste biomass samples presented different plant-cuticle-to-polysaccharide ratios, their effective fractionation was necessary to exploit both the plant cuticles and polysaccharides in the soft biomass.

3.2. Effects of MW-assisted methanolysis combined with hydrothermal pretreatment and enzymatic hydrolysis

Sequential treatments of MW-assisted methanolysis combined with hydrothermal pretreatment and enzymatic hydrolysis were tested to fractionate bio-oil from the plant cuticles and reduce sugars from the polysaccharides. The combinations of these treatments (II–V) are indicated in Scheme 1 together with the control treatment (I). Methanolysis is a general method for the synthesis of FAMES from free fatty acids and triglycerides. Thus, this process was used to decompose the plant cuticles,

using acid (HCl) and base (NaOMe) catalysts (Vicente et al., 2004; Meher et al., 2006), and for the compositional analysis of cutin and wax (Holloway and Deas, 1971). In treatments II and III, methanolysis was first conducted to fractionate the plant cuticles; this was followed by enzymatic hydrolysis of the polysaccharides. In treatment IV, the polysaccharides were first hydrolyzed to increase the concentration of the plant cuticles, which were then fractionated by methanolysis. Hydrothermal pretreatment was additionally conducted prior to enzymatic hydrolysis to loosen the recalcitrant structure of the biomass and thus facilitate enzymatic degradation (Mosier et al., 2005; Hendriks and Zeeman, 2009). The enzymatic hydrolytic processes in treatments II–IV also produced reducing sugars.

Fig. 1 illustrates the effects of each treatment on the liquefaction rate of the six types of soft biomass. Only 12–48% in liquefaction rate were achieved by sole enzymatic hydrolysis (Fig. 1A, treatment I). After combined methanolysis and enzymatic hydrolysis (treatments II and III), the liquefaction rates improved by 30–80%. The *S. canadensis*, *E. crassipes*, and bagasse samples were highly susceptible to methanolysis, while the *M. sinensis*, rice straw, and rice hull samples were more recalcitrant. Methanolysis using NaOMe was more effective in improving the enzymatic susceptibility of *S. canadensis*, *M. sinensis*, rice straw, and bagasse than that using HCl. On the other hand, HCl was preferred for the methanolysis of *E. crassipes* and rice hull. A combination of methanolysis with hydrothermal pretreatment and enzymatic hydrolysis was the most

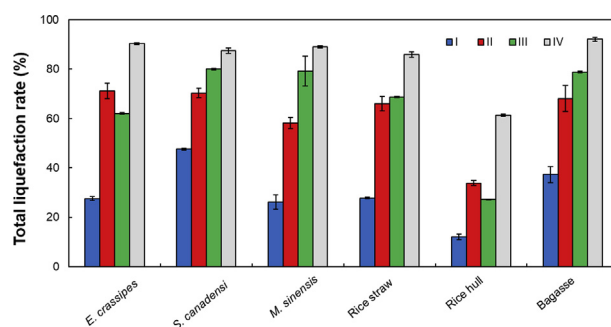
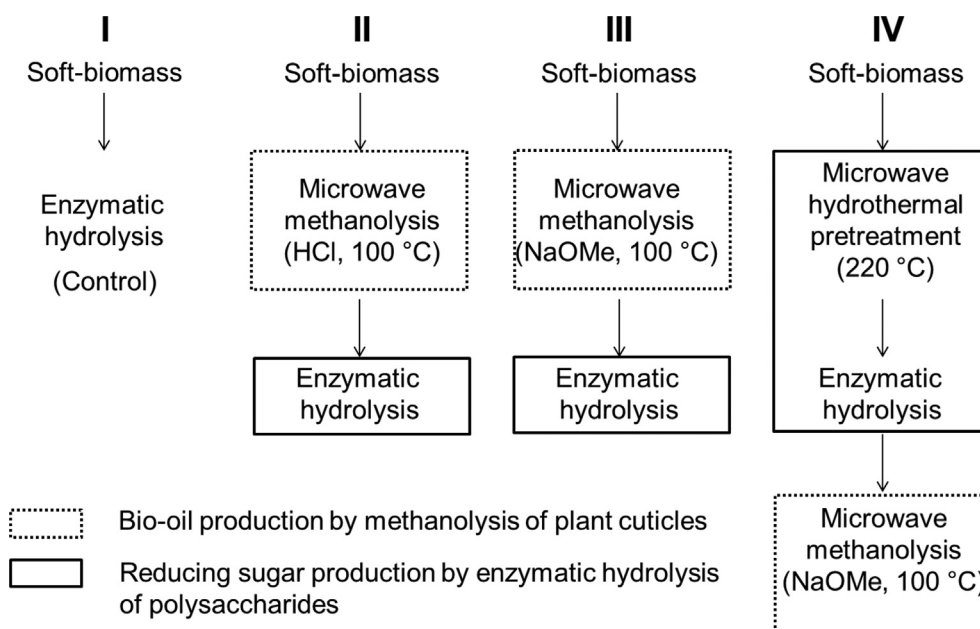


Fig. 1. Effects of combined microwave (MW)-assisted methanolysis on the liquefaction rates of the six types of soft biomass. The error bars indicate the standard deviations ($n = 3$).



Scheme 1. Combinations of microwave (MW)-assisted methanolysis with hydrothermal pretreatment and enzymatic hydrolysis.

effective in increasing liquefaction, achieving rates in the range 61–92% (treatment IV).

Notably, methanolysis should contribute towards the degradation of the cuticle fractions and hemicellulose and lignin-like polyphenolic compounds. However, the hydrothermal pretreatment afforded the highest liquefaction rates because the reaction temperature was much higher than that used in methanolysis and the components were sufficiently softened to improve susceptibility to enzymatic treatment. Therefore, the solid residues produced after each treatment (I–IV) were next analyzed by FT-IR to evaluate the structural changes in the six biomass substrates after each treatment (Section 3.3).

3.3. Structural changes in the biomass substrate during MW-assisted methanolysis combined with hydrothermal pretreatment and enzymatic hydrolysis

The effects of each treatment on the biomass structure were evaluated by probing the FT-IR peaks of the plant cuticles (Fig. 2). The IR peaks were assigned to the cuticle components based on previously reported data of isolated plant cuticles (Johnson et al., 2007; Villena et al., 2000; Järvinen et al., 2011; Takahashi et al., 2012), waste biomass (tea residue; Tsubaki et al., 2013a,b), and plant tissue (Stewart, 1996). The FT-IR spectrum of the enzymatically prepared cuticle of *S. canadensis* is displayed in Fig. S1 for the identification of peaks corresponding to cutin. The peaks at 2850–2950 cm^{-1} were assigned to the alkyl groups of wax and cutin, as well as to the small contributions by the aromatic compounds and sugars; the shoulder peak at 1730 cm^{-1} to esters, including wax, cutin, and triglycerides; and the peaks at 1600–1650 cm^{-1} to the amide I vibrations of the proteins in the soft biomass and adsorbed enzymes as well as the C=C bonds of the aromatic compounds. Amide II vibrations were also observed at 1530 cm^{-1} . The peaks at 800–1200 cm^{-1} were assigned to the C–C, C–O, C–O–H, and C–O–C bonds of the sugar residues and ester moieties.

The FT-IR spectra of the residues after treatments II and III exhibited larger IR absorption bands because of the presence of sugars, indicating the insufficient removal of the cellulosic and hemicellulosic polysaccharides. Treatment IV was effective in removing the sugars, especially for *E. crassipes*, *S. canadensis*, *M. sinensis*, and the bagasse. Additionally, the peaks arising from the alkyl chains at 2900 cm^{-1} were strengthened, indicating the enriched concentration of plant cuticles in the residue (IV-1). The subsequent methanolysis treatment resulted in a reduction in these alkyl absorptions, indicating sufficient fractionation of the plant cuticles (IV-2). These results suggested that the hydrothermal treatment effectively fractionates the sugars and concentrates the cutin present in the residue. Cutin was subsequently recovered by the continued methanolysis treatment.

3.4. Higher heating value (HHV) of bio-oils

The bio-oil yields obtained by MW treatments II–IV are presented in Fig. 3(A). The methanolysis treatment using HCl (treatment II) afforded the largest bio-oil yield, followed by that using NaOMe (treatment III). These results were attributed to the greater enhancement of aromatic compound and protein removal by HCl over that by NaOMe as observed in the FT-IR spectra (Fig. 2). On the other hand, the bio-oil yield obtained from treatment IV was only ~10%. However, the bio-oil HHV improved to values $\leq 32 \text{ kJ kg}^{-1}$ (bagasse), which are comparable to the theoretical value of linoleic acid methyl ester [$\text{C}_{18}\text{H}_{32}\text{O}_2 = 32.07 \text{ MJ kg}^{-1}$, Fig. 3(B)]. The larger bio-oil HHVs were attributed to their higher C and H contents and lower O content (Table S1). Gas chromatography (GC) of the bio-oil obtained from bagasse (treatment IV) afforded a relatively high proportion of hydroxylated and epoxylated fatty acids from the plant cuticles (Fig. S2). Although not all the GC peaks could be clearly identified due to the complicated chromatograms, the bio-oils from treatments II and III appear to be contaminated with oxygenated compounds generated by the degradation of the polysaccharides and lignin-like polyphenols, thereby resulting in lower

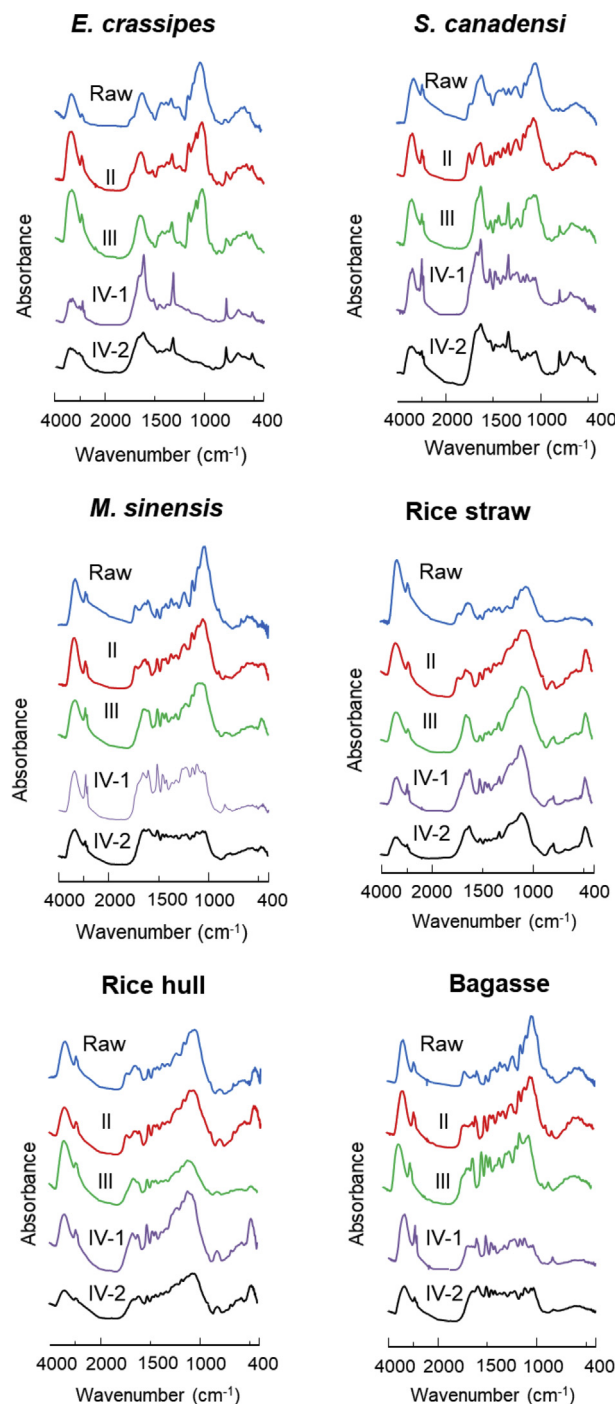


Fig. 2. Fourier transform infrared (FT-IR) spectra of six types of soft biomass after the microwave (MW)-assisted methanolysis, hydrothermal, and enzymatic treatments (Raw) raw biomass (II) MW-assisted methanolysis (HCl) + enzymatic hydrolysis (III) MW-assisted methanolysis (NaOMe) + enzymatic hydrolysis (IV-1) hydrothermal pretreatment + enzymatic hydrolysis, and (IV-2) hydrothermal pretreatment + enzymatic hydrolysis + MW-assisted methanolysis.

HHVs. Hydrothermal pretreatment and enzymatic hydrolysis effectively removed the polysaccharides and polyphenols (FT-IR data, Fig. 2). Thus, an increase in the plant cuticle concentration in the residual material was observed after these treatments. These results confirmed that hydrothermal pretreatment and enzymatic hydrolysis effectively purified the plant cuticles and afforded bio-oils with higher HHVs.

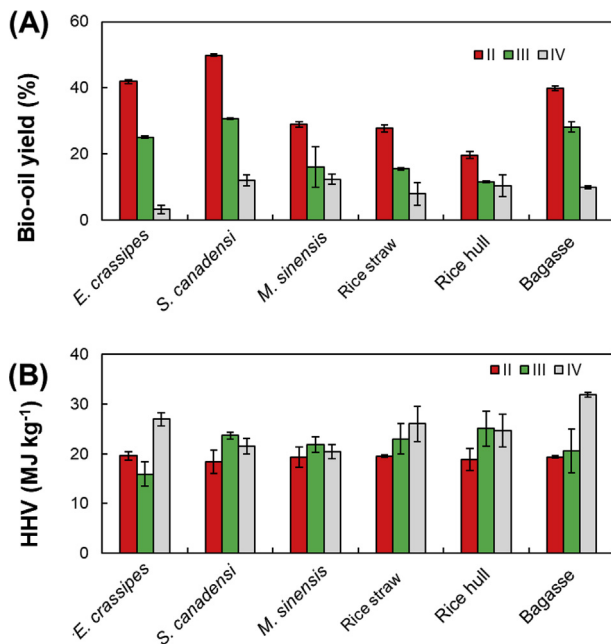


Fig. 3. (A) Bio-oil yields obtained from six types of soft biomass after microwave (MW)-assisted methanolysis treatments II, III, and IV (II) MW-assisted methanolysis (HCl) + enzymatic hydrolysis (III) MW-assisted methanolysis (NaOMe) + enzymatic hydrolysis (IV) hydrothermal pretreatment + enzymatic hydrolysis + MW-assisted methanolysis (B) Higher heating values (HHVs) of the bio-oils afforded from each methanolysis treatment. The CHNO contents are listed in Table S1. The error bars indicate the standard deviations ($n = 3$).

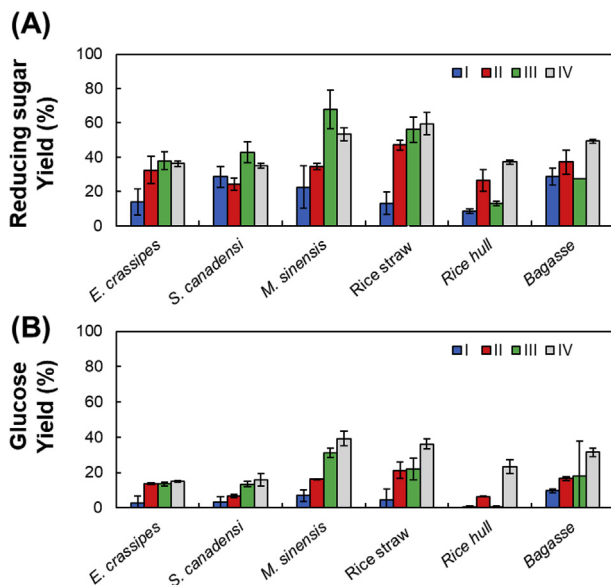


Fig. 4. Yields of (A) reducing sugars and (B) glucose after combined treatments of microwave (MW)-assisted methanolysis combined with hydrothermal pretreatment and enzymatic hydrolysis (II) MW-assisted methanolysis (HCl) + enzymatic hydrolysis (III) MW-assisted methanolysis (NaOMe) + enzymatic hydrolysis (IV) hydrothermal pretreatment + enzymatic hydrolysis + MW-assisted methanolysis. The error bars indicate the standard deviations ($n = 3$).

3.5. Reducing sugars yields

The amount of produced sugars after MW treatment and enzymatic hydrolysis were subsequently determined to test the efficacy of the proposed process for the co-production of sugar and plant-cuticle compounds. The amount of generated reducing sugars and glucose during

enzymatic hydrolysis and hydrothermal pretreatment were determined using the DNS method and mutarotase-GOD assay. Fig. 4 illustrates the amount of reducing sugars and glucose generated by treatments I–IV. The reducing sugars indicate the degree of polysaccharide hydrolysis during hydrothermal pretreatment and enzymatic hydrolysis. The carbohydrate-rich *M. sinensis* (34.6–67.5%) and rice straw (47.0–59.5%) biomass samples exhibited relatively higher reducing sugar and glucose yields. Conversely, the glucose yields from the *E. crassipes* (32.45–37.8%), *S. canadensis* (24.1–42.7%), and rice hull samples (12.8–37.1%) were relatively low. Among the tested treatments, the MW-assisted hydrothermal pretreatment (treatment IV) afforded the best glucose yields (15–39%). The trends in the amounts of generated reducing sugars were consistent with the degree of polysaccharide removal indicated in the FT-IR spectra. These results confirmed that the proposed cascading treatments co-produce reducing sugars and bio-oils originating from plant cuticles.

4. Conclusions

The combination of MW-assisted methanolysis with hydrothermal pretreatment and enzymatic hydrolysis treatments were used to fractionate plant cuticles as bio-oils from six soft biomass types (*E. crassipes*, *S. canadensis*, *M. sinensis*, rice straw, rice hull, and bagasse). MW-assisted hydrothermal pretreatment was the most effective for enzymatic saccharification of the tested samples and plant cuticle concentration in the residual materials. Plant cuticles were further recovered as bio-oils comprising FAME mixtures by the methanolysis treatment. The highest HHV (32 kJ/kg), which is near-identical to the theoretical HHV of methyl linoleate, was attained from bagasse. Additionally, reducing sugars were produced by hydrothermal pretreatment and enzymatic hydrolysis. This work demonstrated that the residues produced after the hydrolysis of soft biomass show great potential as bio-oil sources originating from plant cuticles. The proposed process opens a new way of utilizing plant cuticles in the same process used in sugar platform biorefineries.

Declarations

Author contribution statement

Shuntaro Tsubaki: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Kiriyo Oono: Performed the experiments; Analyzed and interpreted the data.

Ayumu Onda: Conceived and designed the experiments; Wrote the paper.

Funding statement

This work was supported by the Program to Disseminate the Tenure Tracking System of the Ministry of Education, Culture, Sports, Science and Technology of Japan (Kochi University), JSPS Grant-in-Aid for Young Scientists (B) 15K18814, JSPS Grant-in-Aid for Young Scientists (A) 17H05049, and Grant for Environmental Research Projects from the Sumitomo Foundation.

Competing interest statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at <https://doi.org/10.1016/j.heliyon.2019.e01887>

References

- Azuma, J., Tanaka, F., Koshijima, T., 1984. Enhancement of enzymatic susceptibility of lignocellulosic wastes by microwave irradiation. *J. Ferment. Technol.* 62, 377–384.
- Belding, R.D., Blankenship, S.M., Young, E., Leidy, R.B., 1998. Composition and variability of epicuticular waxes in apple cultivars. *J. Am. Soc. Hortic. Sci.* 123, 348–356.
- Benítez, J.J., García-Segura, R., Heredia, A., 2004. Plant biopolyester cutin: a tough way to its chemical synthesis. *Biochim. Biophys. Acta Gen. Subj.* 1674, 1–3.
- Buschhaus, C., Herz, H., Jetter, R., 2007. Chemical composition of the epicuticular and intracuticular wax layers on the adaxial side of *Ligustrum vulgare* leaves. *New Phytol.* 176, 311–316.
- Gaudino, E.C., Cravotto, G., Manzoli, M., Tabasso, S., 2019. From waste biomass to chemicals and energy via microwave-assisted processes. *Green Chem.* 21, 1202–1235.
- Hendriks, A.T.W.H., Zeeman, G., 2009. Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresour. Technol.* 100, 10–18.
- Heredia, A., 2003. Biophysical and biochemical characteristics of cutin, a plant barrier biopolymer. *Biochim. Biophys. Acta Gen. Subj.* 1620, 1–7.
- Heredia-Guerrero, J.A., Heredia, A., García-Segura, R., Benítez, J.J., 2009. Synthesis and characterization of a plant cutin mimetic polymer. *Polymers* 50, 5633–5637.
- Heredia-Guerrero, J.A., Heredia, A., Domínguez, E., Cinalonai, R., Bayer, I.S., Athanassiou, A., Benítez, J.J., 2017. Cutin from agro-waste as a raw material for the production of bioplastics. *J. Exp. Bot.* 68, 5401–5410.
- Holloway, P.J., Deas, A.H.B., 1971. Occurrence of positional isomers of dihydroxyhexadecanoic acid in plant cutins and suberins. *Phytochemistry* 10, 2781–2785.
- Järvinen, R., Silvestre, A.J.D., Gil, A.M., Kallio, H., 2011. Solid state ¹³C CP-MAS NMR and FT-IR spectroscopic analysis of cuticular fractions of berries and suberized membranes of potato. *J. Food Compos. Anal.* 24, 334–345.
- Johnson, E.J., Dorot, O., Liu, J., Chefetz, B., Xing, B., 2007. Spectroscopic characterization of aliphatic moieties in four plant cuticles. *Commun. Soil Sci. Plant Anal.* 38, 2461–2478.
- Kolattukudy, P.E., Purdy, R., 1973. Identification of cutin, a lipid biopolymer, as significant component of sewage sludge. *Environ. Sci. Technol.* 7, 619–622.
- Meher, L.C., Sagar, D.V., Naik, S.N., 2006. Technical aspects of biodiesel production by transesterification—a review. *Renew. Sustain. Energy Rev.* 10, 248–268.
- Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M., Ladisch, M., 2005. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour. Technol.* 96, 673–686.
- Naik, S.N., Goud, V.V., Rout, P.K., Dalai, A.K., 2010. Production of first and second generation biofuels: a comprehensive review. *Renew. Sustain. Energy Rev.* 14, 578–597.
- Nuissier, G., Bourgeois, P., Grignon-Dubois, M., Pardon, P., Lescure, M.H., 2002. Composition of sugarcane waxes in rum factory wastes. *Phytochemistry* 61, 721–726.
- Pereira, S.I., Freire, C.S.R., Neto, C.P., Silvestre, A.J.D., Silva, A.M.S., 2005. Chemical composition of the epicuticular wax from the fruits of *Eucalyptus globulus*. *Phytochem. Anal.* 16, 364–369.
- Pollard, M., Beisson, F., Li, Y.H., Ohlrogge, J.B., 2008. Building lipid barriers: biosynthesis of cutin and suberin. *Trends Plant Sci.* 13, 236–246.
- San-Miguel, M.A., Oviedo, J., Heredia-Guerrero, J.A., Heredia, A., Benítez, J.J., 2014. Biomimetic polymers of plant cutin: an approach from molecular modelling. *J. Mol. Model.* 20, 2329.
- Stewart, D., 1996. Fourier transform infrared microspectroscopy of plant tissues. *Appl. Spectrosc.* 50, 357–365.
- Takahashi, Y., Tsubaki, S., Sakamoto, M., Watanabe, S., Azuma, J., 2012. Growth-dependent chemical and mechanical properties of cuticular membranes from leaves of *Sonneratia alba*. *Plant Cell Environ.* 35, 1201–1210.
- Tsubaki, S., Azuma, J., 2013b. Total fractionation of green tea residue by microwave-assisted alkaline pretreatment and enzymatic hydrolysis. *Bioresour. Technol.* 131, 485–491.
- Tsubaki, S., Iida, H., Sakamoto, M., Azuma, J., 2008. Microwave heating of tea residue yields polysaccharides, polyphenols, and plant biopolyester. *J. Agric. Food Chem.* 56, 11293–11299.
- Tsubaki, S., Sakamoto, M., Azuma, J., 2010. Microwave-assisted extraction of phenolic compounds from tea residues under autohydrolytic conditions. *Food Chem.* 123, 1255–1258.
- Tsubaki, S., Ozaki, Y., Yonemori, K., Azuma, J., 2012. Mechanical properties of fruit-cuticular membranes isolated from 27 cultivars of *Diospyros kaki* Thunb. *Food Chem.* 132, 2135–2139.
- Tsubaki, S., Sakamoto, S., Uemura, N., Azuma, J., 2013a. Compositional analysis of leaf cuticular membranes isolated from tea plants (*Camellia sinensis* L.). *Food Chem.* 138, 286–290.
- Tsubaki, S., Azuma, J., Yoshimura, T., Maitani, M.M., Suzuki, E., Fujii, S., Wada, Y., 2016. Microwave-induced biomass fractionation. In: Mussatto, S. (Ed.), *Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery*. Elsevier, pp. 103–126.
- Vicente, G., Martinez, M., Aracil, J., 2004. Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresour. Technol.* 92, 297–305.
- Villena, J.F., Domínguez, E., Heredia, A., 2000. Monitoring biopolymers present in plant cuticles by FT-IR Spectroscopy. *J. Plant Physiol.* 156, 419–422.
- Walton, T.J., Kolattukudy, P.E., 1972. Determination of the structures of cutin monomers by a novel depolymerization procedure and combined gas chromatography and mass spectrometry. *Biochemistry* 11, 1885–1896.
- Yin, C.Y., 2011. Prediction of higher heating values of biomass from proximate and ultimate analyses. *Fuel* 90, 1128–1132.
- Yusuf, N.N.A.N., Kamarudin, S.H., Yaakub, Z., 2011. Overview on the current trends in biodiesel production. *Energy Convers. Manag.* 52, 2741–2751.
- Zhang, B., Uyama, H., 2016. Biomimic plant cuticle from hyperbranched poly(ricinoleic acid) and cellulose film. *ACS Sustain. Chem. Eng.* 4, 363–369.