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16. Abstract

Pongamia seedpods are recognized as a potential feedstock for sustainable aviation fuel production due to the relatively high oil content of the seeds. Pongamia pods are byproduct residues available after seed separation. Pods have high chlorine and potassium content that may be problematic in thermochemical energy conversion systems. Leaching experiments were performed to remove inorganic constituents of pods and thereby reduce the potential for fouling, slagging, and agglomeration. A 23 factorial design determined the impacts of process operating parameters (i.e. rinse water temperature (25 ◦ C vs. 75 ◦ C), rinse duration (10 min vs. 2 h), and particle size (<2 mm vs. whole pod)) on the composition and physicochemical properties of the pods and the water. The higher heating value of the pods was found to increase from 16 to 18–19 MJ/kg after leaching, while the ash content was reduced from 6.5% to as low as 2.8%wt, with significant removal of sulfur (S), chlorine (Cl), and potassium (K). The chemical oxygen demand, non-purgeable organic carbon, and total nitrogen of the postexperiment leachates were all found to increase with the rinse water temperature and rinse duration but decrease with the increase of particle size. Leached pods were further processed via torrefaction and the targeted mass and energy yields, ~70% and 85%, respectively, were reached at a process temperature of 270 ◦ C. The S, Cl, and K contents of the leached, torrefied pods were found to be lower than that of the raw pods. The reuse of leachate on successive batches of fresh pods showed that ash removal efficiency was reduced after three cycles, although some removal was possible through 15 cycles.

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Water leaching for improving fuel properties of pongamia Pod: Informing process design

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ABSTRACT

Pongamia seedpods are recognized as a potential feedstock for sustainable aviation fuel production due to the relatively high oil content of the seeds. Pongamia pods are byproduct residues available after seed separation. Pods have high chlorine and potassium content that may be problematic in thermochemical energy conversion systems. Leaching experiments were performed to remove inorganic constituents of pods and thereby reduce the potential for fouling, slagging, and agglomeration. A 2^3 factorial design determined the impacts of process operating parameters (i.e. rinse water temperature (25 °C vs. 75 °C), rinse duration (10 min vs. 2 h), and particle size (<2 mm vs. whole pod)) on the composition and physicochemical properties of the pods and the water. The higher heating value of the pods was found to increase from 16 to 18–19 MJ/kg after leaching, while the ash content was reduced from 6.5% to as low as 2.8%wt, with significant removal of sulfur (S), chlorine (Cl), and potassium (K). The chemical oxygen demand, non-purgeable organic carbon, and total nitrogen of the post-experiment leachates were all found to increase with the rinse water temperature and rinse duration but decrease with the increase of particle size. Leached pods were further processed via torrefaction and the targeted mass and energy yields, ~70% and 85%, respectively, were reached at a process temperature of 270 °C. The S, Cl, and K contents of the leached, torrefied pods were found to be lower than that of the raw pods. The reuse of leachate on successive batches of fresh pods showed that ash removal efficiency was reduced after three cycles, although some removal was possible through 15 cycles.

1. Introduction

Interest in biorefineries to produce biofuels and chemicals as an alternative and/or supplement to fossil fuels is growing worldwide [1–4]. In Europe and North America, biomass has been serving as fuel in power plants for several decades [5–7]. Boilers, however, may experience fouling, slagging, and agglomeration owing to the presence of inorganic constituents in biomass, e.g. chlorine, sulfur, and alkali and alkaline earth metals [5,6,8–11]. Deposition reduces heat transfer, and if severe may require boiler shutdown and manual removal [5,9,12]. Furthermore, biomass with high ash content is susceptible to incomplete combustion and may lead to emission-related problems [12]. These operational problems, however, can be effectively mitigated by reducing the content of these undesirable inorganic compounds in biomass via biomass pretreatment.

Water washing/leaching techniques have been regarded as an efficient and cost-effective pretreatment method for biomass [10,12]. It lowers the biomass ash content via removing water-soluble metal ions, e.g. potassium (K), sodium (Na), chlorine (Cl), and sulfur (S), yields a significant increase in ash fusion temperatures, and consequently reduces the fouling and slagging potential [12–14]. Previous studies have found water-leaching can effectively reduce the ash content of biomass [5,10,12,14–17] with three main factors contributing to the effectiveness of the treatment: time, temperature, and particle size. All three factors affect pretreatment cost and therefore final system design. In general, decreased particle size and increased treatment time and temperature all improve the removal of ash from biomass, with the consensus being that the most cost-effective treatment is at a higher temperature for a shorter period [5,12]. A concern associated with the leaching process, the required volume of water [18], can be addressed by processing system designs that consume less water (e.g. leachate recycling or reuse, or reverse osmosis employed for biomass leachate treatment and nutrient recovery [18,19]) or are able to manage leachate use (e.g. mechanical irrigation systems [20]. The fate of leachate will

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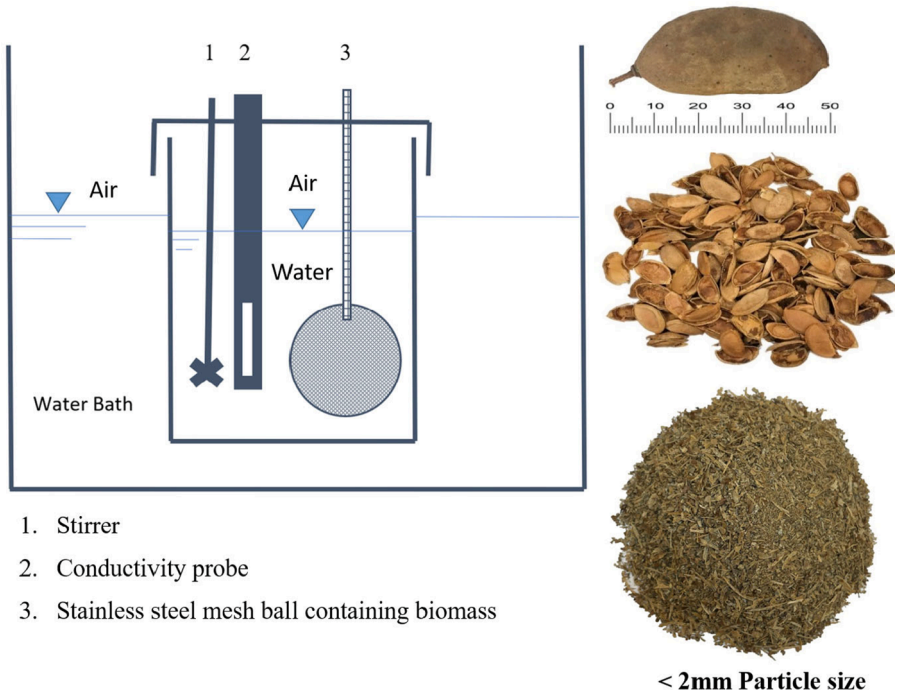

Fig. 1. Diagram of leaching test equipment and pongamia pods (whole and < 2 mm).

necessarily depend on the location of the processing facility and its surrounding agricultural, regulatory, cultural, and environmental landscape.

Millettia pinnata, commonly known as pongamia, is a leguminous, medium-sized, fast-growing tree that grows in humid tropical and subtropical environments, and thrives in traditionally non-usable land ranging from sandy and stony to clay [21]. Pongamia is a robust crop, is naturally pest-resistant, and can survive drought, heat, frost, and salinity, all while having little need for fertilizers [21]. Trees can produce seedpods in as little as 3 years and have a production life of over 40 years [21]. Pongamia seed is a potential feedstock for sustainable aviation fuel production owing to its high oil content [21–23], whereas the application of the fibrous byproduct pods is very limited [24–26]. Thermochemical conversion of the pods for heat, electricity, or value-added chemical products is regarded as a potential application. A previous study investigated the impact of torrefaction processes on the fuel characteristics of the pods for potential use in thermochemical conversion applications. Fuel properties of the pods were found to be improved but were accompanied by elevated potassium and chlorine contents [26]. An efficient and cost-effective pretreatment process, therefore, is required to reduce the concentration of these problem elements and improve the fuel properties of pongamia pods.

The present work investigates the impact of water leaching on the fuel characteristics of pods collected from pongamia trees grown on the

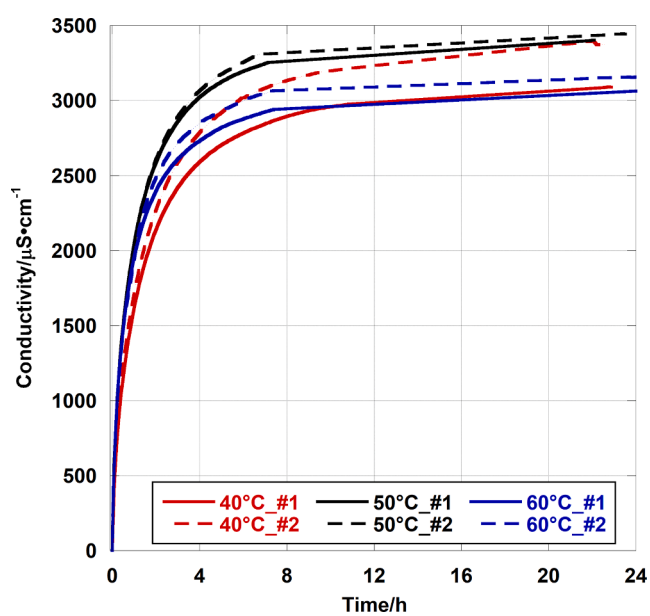

Fig. 2. Conductivity of leachate during the leaching process of whole pods at 40, 50, and 60 °C, small-scale test system. #1 and #2 are two repetition runs.

Table 1
Summary of analysis results for whole pods from 24-hour tests at three temperatures.

	Raw	40 °C	50 °C	60 °C	40 °C(Lg)
Kinetic parameters					
C_s(μS cm^{-1})		3396	3445	3169	3361
k(cm μS^{-1}h^{-1})		2.94E-04	4.63E-04	5.92E-04	3.30E-04
h(μS cm^{-1}h^{-1})		3391	5496	5950	3733
R^2		0.99	1.00	1.00	1.00
Physicochemical Properties					
HHV(MJ kg^{-1})	16.2 ± 0.1	18.3 ± 0.1	18.7 ± 0.1	18.8 ± 0.1	18.8 ± 0.1
C% wt	42.7 ± 0.09	46.97 ± 0.04	47.67 ± 0.03	47.90 ± 0.02	48.29 ± 0.03
H% wt	5.95 ± 0.03	6.01 ± 0.01	5.91 ± 0.01	5.88 ± 0.00	5.85 ± 0.00
N% wt	1.10 ± 0.01	0.96 ± 0.01	0.92 ± 0.01	0.92 ± 0.02	0.97 ± 0.00
O% wt [4]	43.68	43.33	42.77	42.64	41.96
H/C	1.67	1.53	1.49	1.47	1.45
VM % wt [2]	72.6 ± 0.11	75.46 ± 0.09	75.41 ± 0.10	75.77 ± 0.07	75.62 ± 0.18
Ash % wt [2]	6.54 ± 0.02	2.73 ± 0.04	2.73 ± 0.06	2.66 ± 0.04	2.93 ± 0.04
FC% wt [2,3]	20.8 ± 0.11	21.81 ± 0.11	21.86 ± 0.13	21.58 ± 0.07	21.45 ± 0.21
Na/ppm	650 ± 37	216 ± 17	266 ± 30	217 ± 50	261 ± 18
Mg/ppm	1,163 ± 28	1,307 ± 27	1,257 ± 41	1,287 ± 28	1,417 ± 34
Si/ppm	222 ± 13	196 ± 24	198 ± 20	156 ± 16	192 ± 17
P/ppm	388 ± 10	148 ± 6	91 ± 5	83 ± 11	117 ± 10
S/ppm	1,323 ± 27	648 ± 11	633 ± 8	597 ± 16	632 ± 17
Cl/ppm	5,793 ± 83	387 ± 12	391 ± 15	368 ± 13	409 ± 17
K/ppm	33,050 ± 455	11,300 ± 179	12,067 ± 175	11,300 ± 141	12,050 ± 105
Ca/ppm	4,297 ± 96	4,988 ± 71	4,720 ± 130	4,798 ± 125	4,898 ± 58
ΣXRF oxide/% [6]	6.23 ± 0.38	2.72 ± 0.19	2.70 ± 0.13	2.56 ± 0.04	2.71 ± 0.02

Note: (1) HHV is higher heating value; (2) VM, and FC are volatile matter and fixed carbon contents, respectively, and VM and FC are on dry bases; (3) FC was calculated by subtracting VM and ash percentages from 100; (4) O content was calculated by subtracting C, H, N and ash content from 100; (5) Element concentrations were calculated with $C_6H_{10}O_5$ matrix as the mean ± standard error of six analyses (3 pellets and 2 sides); (6) ΣXRF oxide is sum of all XRF elemental values as oxides.

island of Oahu, Hawaii, USA. Preliminary studies were conducted with the whole pods under various leaching temperatures and duration (up to 24 h). Release rates of sulfur, chlorine, and potassium from the pods to the leachate were monitored. A factorial 2^3 experimental design was employed to determine the effectiveness of particle size, rinse water temperature, and time for the removal of ash forming elements, as well as the improvement of essential fuel properties for thermochemical conversion. Leached pods were torrefied and their characteristics compared with that of the raw pods. Leachate reuse to reduce water and energy consumption was also evaluated.

2. Materials and methods

2.1. Test materials

Pongamia seed pods were provided by TerViva Inc. and collected in May 2016 from Hawaii Agriculture Research Center, Kunia, HI (21°22′58.9″N, 158°02′21.8″W) (TerViva Planting). The seed pods were hand-harvested from trees then 1.) soaked in a chlorine/water solution for 1 min, 2.) placed on a mesh screen and dried in full sun for 2–3 h, and 3.) stored in an air-conditioned room at ~ 21 °C in loosely woven mesh bags. The pods were hand separated from the seeds. A subsample of the pods was milled to < 2 mm particle size using a Fritsch Universal Cutting Mill "Pulverisette 19" (Idar-Oberstein, Germany).

2.2. Processing steps and experimental design

Water leaching tests were performed with both a small-scale and a large-scale water bath system. The torrefaction tests of the leached pods were performed with a macro TGA (TGA801, LECO Corporation, St. Joseph, MI), and experimental details are described in a previous publication [26].

2.2.1. Small-scale test system

The small-scale system consisted of 500 g of leaching water in an 800 mL glass beaker placed in a heating bath (Buchi B-100, Cat. No. 11061894). With leaching water stabilized at the target temperature, a stainless-steel, hollow, 0.42 mm mesh sphere (75 mm internal diameter) containing 25 g pods (equilibrium moisture content, ~5%wt) was immersed in the leach water and mechanically agitated over the test duration (Fig. 1). A conductivity/temperature probe (Orion™ DuraProbe™ 4-Electrode Conductivity Cells, Cat. No. 13005MD) and meter (Orion A222, Cat. No. STARA2220) were used to monitor process conditions. Data were recorded every 10 sec. After the prescribed contact time, the sample was removed and drained of free leachate, and particulate matter was separated from the leachate by filtration. Residual solids were oven-dried at 105 ± 1 °C overnight.

2.2.2. Large-scale test system

Large-scale leaching tests were performed with 200 g pods (equilibrium moisture content, ~5%wt) in a stainless-steel 1 mm mesh container; the top of the container was covered by nylon, 0.6 mm mesh bags (Part No. 11311, Trimaco, Morrisville, NC, USA) to keep the pods immersed in the leach water. The covered sample container was placed into the bath containing 4 L of heated water (Buchi B-100, Cat. No. 11061894). After stabilizing at the temperature setpoint, the water was continuously circulated through the sample with a submersible pump over the test duration. After the prescribed contact time, the solid sample was removed and drained of free leachate and dried in an oven at 105 ± 1 °C overnight.

The resulting leached solids (<2 mm particle size) were torrefied using a macro thermogravimetric analyzer (TGA801, LECO Corporation, St. Joseph, MI, USA): (1) heating rate of 20 °C/min from 40 °C to target temperature, (2) 60 min residence time, and (3) 60 min cooling period. The N_2 flow rate was set at 10 L/min during the heating, holding, and cooling process. Details on the torrefaction process were described in a previous publication [26].

2.2.3. Factorial experiment

The impacts of three factors, i.e. temperature (A), rinse duration (B), and particle size (C), at two levels (2^3 factorial design) were evaluated using the small-scale test system. Three replicate tests were performed at

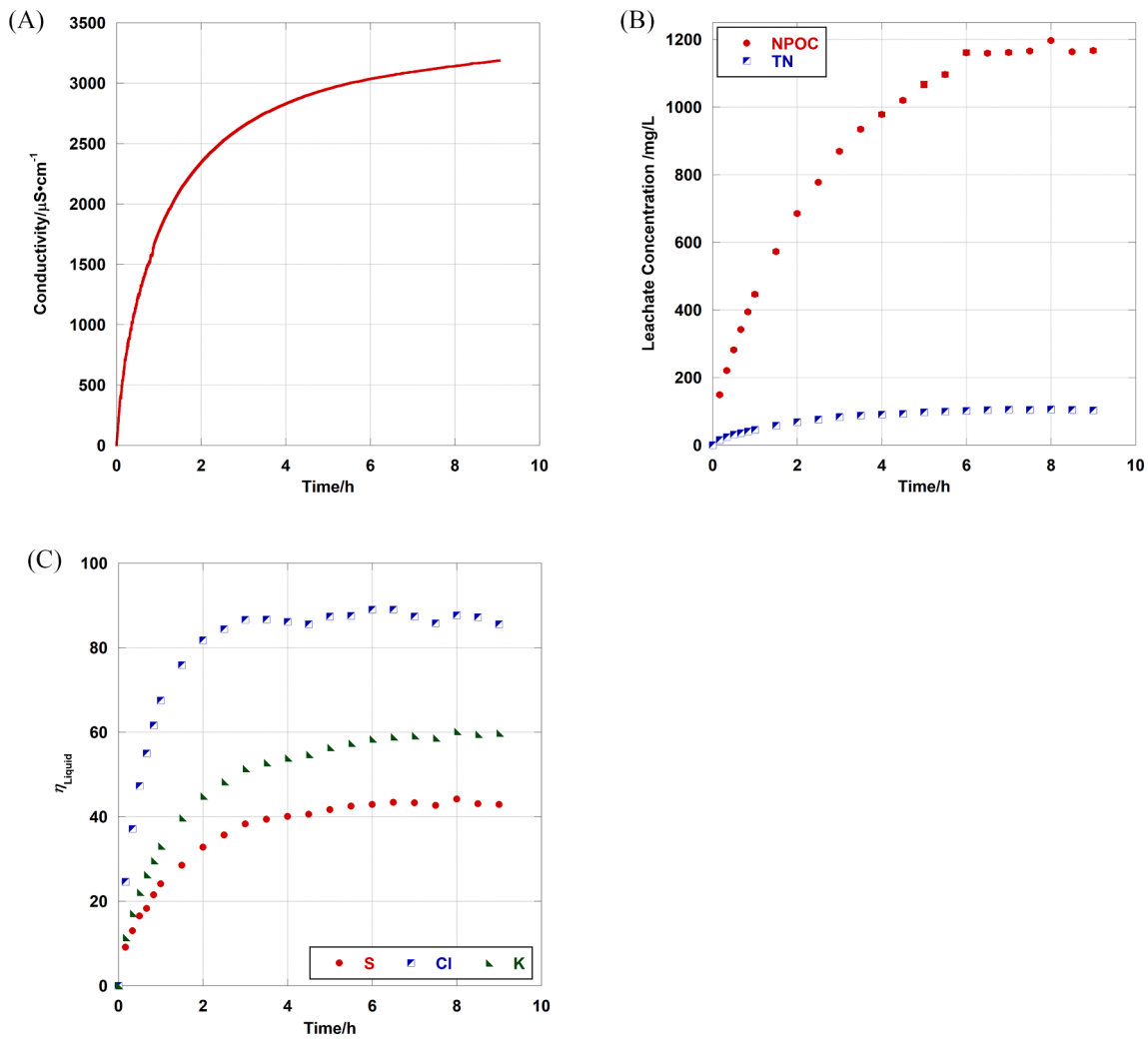

Fig. 3. Leachate analysis of 24 h whole pod leaching test at 40 °C using large-scale test system: (A) conductivity; (B) NPOC and TN; (3) S, Cl, and K removal efficiency.

each condition. The leaching tests were performed with tap water (Honolulu Board of Water Supply). The two levels were assigned negative (-) and positive (+) designations as follows. Process conditions [15] included two treatment temperatures (25 °C (-) and 75 °C (+)), two rinse durations (10 min (-) and 2 h (+)), and two particle sizes (<2 mm (-) and whole pods (3–6 cm long and 1–2 cm wide) (+)).

2.2.4. Leachate reuse

The reuse of leachate was evaluated using the small-scale test system in section 2.2.1 with 25 g, < 2 mm particle size, and 500 g water at 75 °C for 10 min. A 7 mL leachate sample was removed after each test for liquid analysis. Clean water was added to the mass of leachate in the beaker to bring the total to 500 g prior to the following leaching test. The maximum reuse of the water was reached when no significant change was observed between the final conductivities of two consecutive tests.

2.3. Property determination

The raw and leached pongamia pods were milled to < 0.2 mm particle size using an ultra-centrifugal mill (Retsch ZM200, Düsseldorf, Germany) for property and composition analysis.

2.3.1. Leachate analysis

Major ion (potassium (K^+), calcium (Ca^{2+}), chloride (Cl^-), and sulfate (SO_4^{2-})) concentrations in the leachate samples were determined using a ThermoFisher Scientific dual Dionex ICS-1100 Ion Chromatograph (Waltham, MA, USA) operated at ambient temperature. Anions were separated on a Dionex IonPac AS14A column with 8 mM Na_2CO_3/1 mM $NaHCO_3$ eluent. Cations were separated on a Dionex IonPac CS12A column with 20 mM CH_3SO_3H eluent. The flow rate was 1.0 mL/min, with detection by suppressed conductivity. The non-purgeable organic carbon (NPOC) and total nitrogen (TN) of the leachate were measured by catalytic oxidation using a TOC-V Analyzer (Shimadzu, Kyoto, Japan) equipped with a TNM-1 module. Chemical oxygen demand (COD) of leachate was measured using COD vials (Hach, Cat. No. 97009–592 and 97009–592) and a spectrophotometer (Hach D6000, Loveland, CO, USA), following United States Environmental Protection Agency (US EPA) 5220D standard method [27]. The leachate was filtered with Millipore 0.45 μm syringe filter before ion content, NPOC, TN, and COD analyses. The ion, NPOC, and TN leachate analyses were conducted by the Water Resources Research Center at University of Hawaii at Manoa, Honolulu, HI, USA.

2.3.2. Elemental composition of solids

Quantitative elemental analysis of the solid pod samples was performed using a Bruker S8 TIGER XRF spectrometer (Bruker Corp., Billerica, MA) to determine concentrations of the ash-forming elements, Na, Mg, Si, P, S, Cl, K, and Ca. Details on pellet preparation and XRF system

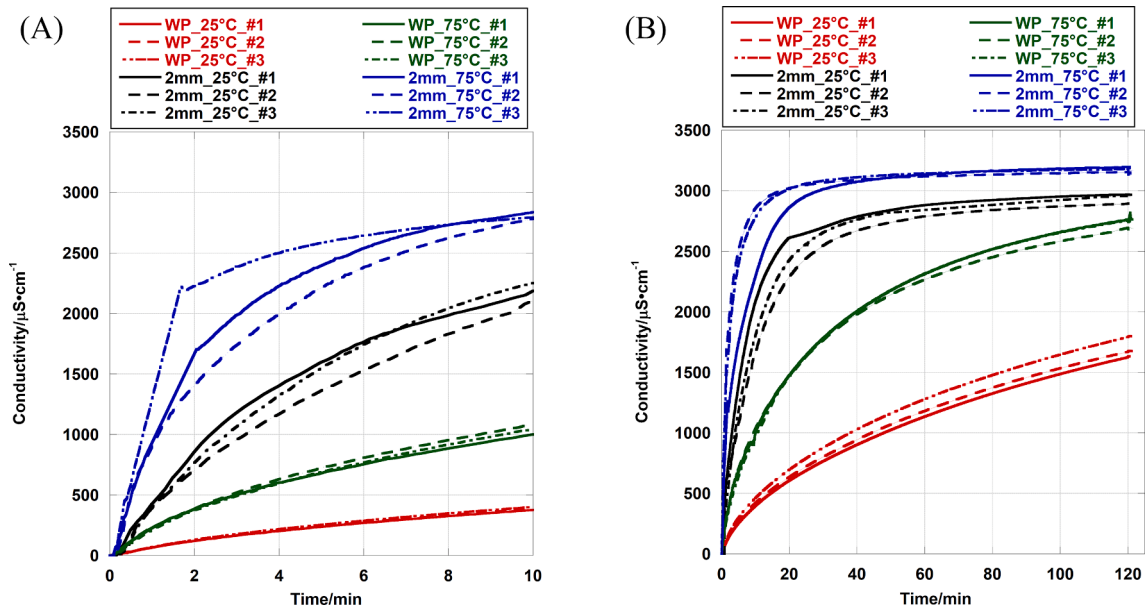

Fig. 4. Conductivity during the leaching processes from 2^3 factorial experiments: (A) 10 min analysis; (B) 2 h analysis. #1–3 are three repetition runs.

parameters are described elsewhere [26,28]. Spectrum recording and evaluation were performed with the Quant-Express software using the best detection mode (Bruker AXS).

2.3.3. Thermogravimetric analysis of solids

Reactive characteristics of the raw and leached pods were investigated with a micro-thermogravimetric analyzer (micro-TGA) (TA Instruments SDT Q600, Delaware, USA). The micro-TGA experiments were performed under atmospheric pressure with 100 mL/min argon flow. A 6–10 mg sample was evenly loaded into an alumina sample cup (TA Instruments, 960070.901). The micro-TGA system was programed with 1) start temperature of 50 °C and heating rate of 10 °C/min; 2) a 30 min isothermal hold at 110 °C to remove moisture from the sample; and 3) a heating rate of 10 °C/min to a final temperature of 800 °C.

2.3.4. Other physicochemical characterization of solid materials

(1) A Parr 6200 Isoperibol Calorimeter (Parr Instrument Company, Moline, IL) was used to measure the heat of combustion based on ASTM D4809-18 [29] and reported as the high heating value (HHV).

(2) Infrared spectra were generated and recorded using an FTIR equipped with attenuated total reflectance (ATR) sampling accessory (Thermo Scientific Nicolet iS 10, Massachusetts, USA). Approximately 1–2 mg of milled sample (<0.2 mm particle size) was pressed against a diamond crystal using a spring-loaded press and all the spectra were obtained over the wavenumber range from 4000 to 650 cm^{-1} with 64 scans at 2 cm^{-1} resolution.

(3) The proximate analysis was performed using a macro thermogravimetric analyzer (TGA801, LECO Corporation, St. Joseph, MI) based on ASTM E1756, E872, and E1755 for moisture, volatile matter, and ash content determination, respectively [30–32].

(4) A LECO CHN628 (LECO Corp., St. Joseph, MI) was employed to determine the carbon, hydrogen, and nitrogen content of the materials, method details in https://knowledge.leco.com/app-notes/application-note-chn-in-biomass-using-the-chn628-510/viewdocument.

2.4. Data processing and evaluation

2.4.1. Mass balance and removal efficiency

The initial and final weight of pods and water was recorded, and the estimated material mass loss (MML) based on the solids measurements, mass balances (α_i), and removal efficiency (η_i) of element (i) were calculated by the following equations,

$$MML = \frac{m_{final}}{m_{inital}} \times 100\% \tag{1}$$

$$\alpha_i = \frac{\left(Q_{i,final}\right)_{solid} + \left(Q_{i,final}\right)_{liquid}}{\left(Q_{i,initial}\right)_{solid} + \left(Q_{i,initial}\right)_{liquid}} \tag{2}$$

$$\eta_{\mathrm{i-Solid}} = \frac{\left(Q_{i,initial}\right)_{solid} - \left(Q_{i,final}\right)_{solid}}{\left(Q_{i,initial}\right)_{solid}} \times 100\% \tag{3}$$

$$\eta_{\mathrm{i-Liquid}} = \frac{\left(Q_{i,final}\right)_{liquid} - \left(Q_{i,initial}\right)_{liquid}}{\left(Q_{i,initial}\right)_{solid}} \times 100\% \tag{4}$$

where m_{inital} and m_{final} are the mass of the solid pods before and after the leaching tests, respectively; $Q_{i,intial}$ and $Q_{i,final}$ are the mass of an analyzed quantity (i: mass or element) in a liquid or solid before and after the leaching tests, respectively. The removal efficiency (η_i) can be determined by measuring the element content in the final solid or liquid samples, depending on the availability of sample analysis.

2.4.2. Ash fouling and slagging index

Three empirical formulas were employed for evaluating the effectiveness of water leaching on reducing the fouling and slagging propensity in thermochemical conversion processes [33]. The base/acid ratio and fouling and slagging indexes are expressed as,

- Base/acid (B/A) ratio

$$\frac{B}{A} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + P_2O_5}{SiO_2 + Al_2O_3 + TiO_2} \tag{5}$$

- Fouling index, F_u

$$F_u = \frac{B}{A}(K_2O + Na_2O) \tag{6}$$

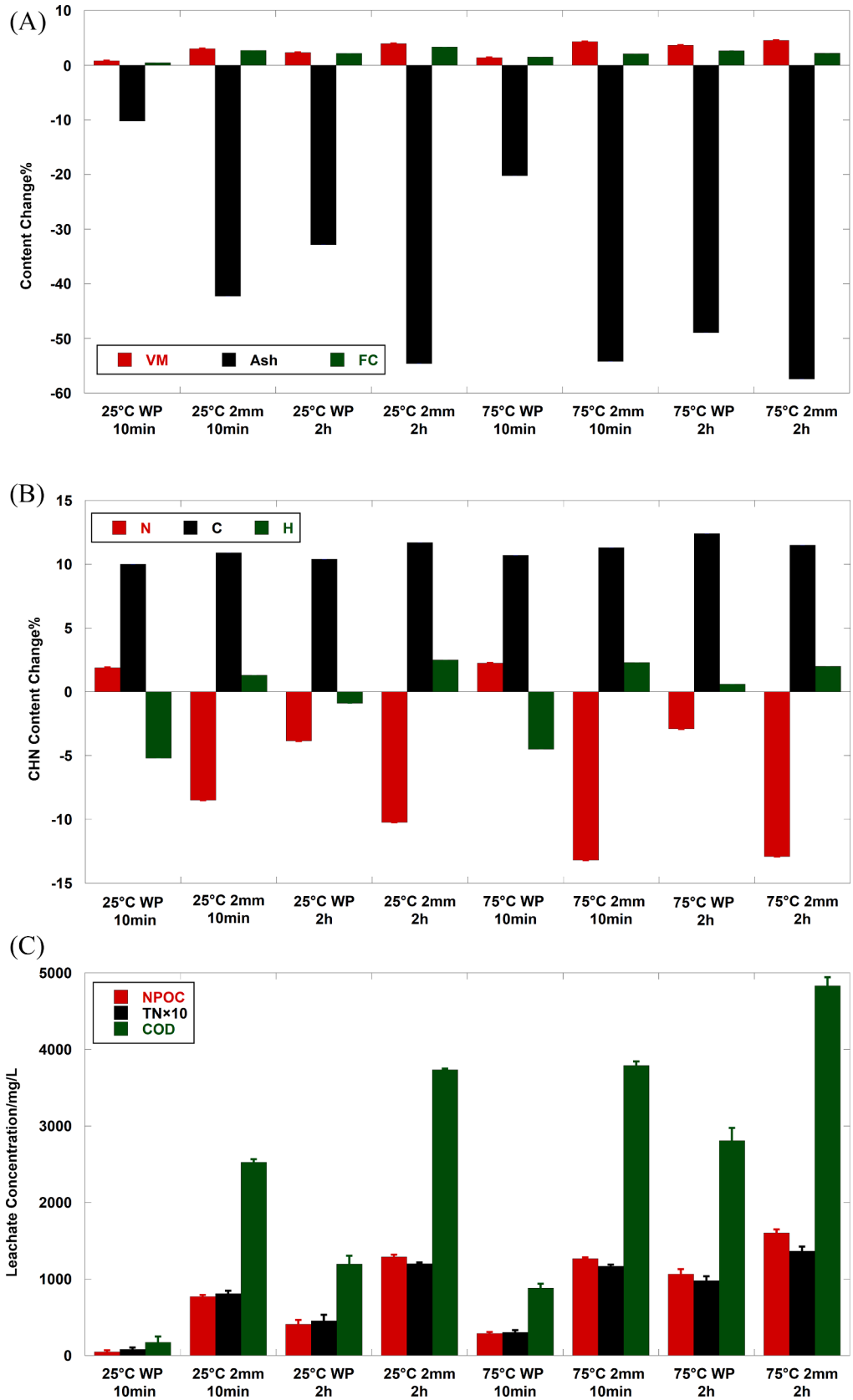

Fig. 5. Property of leached pods and leachates from 2^3 factorial experiments: (A) change of volatile matter, fixed carbon, and ash content of leached pods; (B) change of carbon, hydrogen, and nitrogen content of leached pods; (C) NPOC, TN, and COD of leachates; (D) changes of S, Cl and K content of the leached pods.

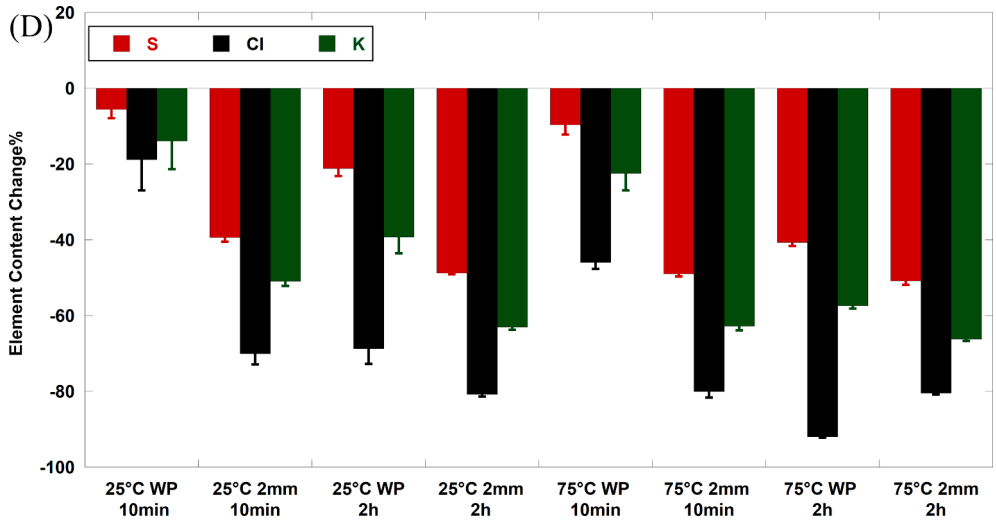

Fig. 5. (*continued*).

- Slagging index, R_s

$$R_s = dry\,S\% \times \frac{B}{A} \tag{7}$$

where Fe_2O_3, CaO, MgO, K_2O, Na_2O, P_2O_5, SiO_2, Al_2O_3, and Ti_2O are the percentage concentrations of the metal oxides in the pod samples, and S % is the percentage concentration of sulfur. These values were determined by XRF analysis.

2.4.3. Factorial experiment: Data reduction and analysis

A 2^3 factorial experimental design was used to determine the effects of the three independent variables (temperature, time, and particle size) and their interaction. Each set of test conditions was replicated three times for a total of 24 tests [34]. The response variables selected were the ash content and the removal efficiencies of S, Cl, and K. The effect of each factor, their interactions, and standard error (SE) were calculated [34].

3. Results and discussion

3.1. Whole pod leaching study

A preliminary study was performed with whole pod samples to investigate the leaching performance. Fig. 2 shows the leachate conductivity in the small-scale test system during a 24 h test period with a pod to water mass ratio of 1:20. The change of conductivity is due to the leaching and transport of water-soluble compounds from the pod to the liquid. A rapid increase in conductivity is evident in the first 1 to 2 h, followed by a slower increase thereafter. The conductivity reached a plateau of 3100–3400 μS cm^{-1} after 6–8 h depending on the operating temperature. The ion removal during the biomass leaching process can be described by a combination of two first-order kinetics, one fast and one slow [35], and the initial rapid leaching is attributed to the high ion concentration gradient between solid and freshwater [36]. The composite kinetics of the leaching process can be described by the pseudosecond-order model in equations (8) to (10) [12,36],

$$\frac{dC_t}{dt} = k(C_S - C_t)^2 \tag{8}$$

$$\frac{t}{C_t} = \frac{1}{kC_S^2} + \frac{t}{C_S} \tag{9}$$

$$h = kC_S^2 \tag{10}$$

where k is the second-order leaching rate constant (cm $\mu S^{-1}h^{-1}$), C_s the leaching capacity at the final conductivity plateau (μS cm^{-1}), C_t is the conductivity of the leachate at time, t (h), and h is the initial leaching rate (μS $cm^{-1}h^{-1}$).

Table 1 lists the saturated leaching capacity (C_s), the leaching rate constant (k), the initial leaching rate (h), and the coefficient of determination (R^2), at the test temperatures. The initial leaching rate and the rate constant were both found to increase with operating temperatures (40–60 °C), from 2280 to 5950 μS $cm^{-1}h^{-1}$, and from 2.94E to 4 to 5.92E-4 cm $\mu S^{-1}h^{-1}$, respectively. A similar result was reported for rice husk (particle size = 1.4–2.8 mm), in which the initial leaching rate increased from 1140 to 1476 μS $cm^{-1}h^{-1}$ when the temperature was increased from 40 to 50 °C [12]. R^2 values were all above 0.99 in this study confirming that the pseudo-second-order kinetic model is suitable to describe the leaching kinetics.

Analyses of pods before and after 24 h tests were performed, and results are presented in Table 1. As expected, the ash contents of the pods significantly decreased from ~ 6.5%wt to ~ 2.7%wt (absolute) (a relative reduction of ~ 58%) after the leaching treatment, resulting in increased volatile matter and fixed carbon contents of the leached pods. The ratio of the summed XRF data in oxide forms (Table 1) to the ash content determined by proximate analysis ranges from 0.92 to 1.00 and provides independent verification of the measurements. Differences can be explained by the presence of elements in the ash unidentified by XRF. The C content of the pods increased from ~ 43%wt to ~ 47–48%wt (absolute), and the HHV increased ~ 13–16% (relative). The increase in heating value cannot be explained by the reduction of ash content alone and the progressive reduction of oxygen content in the samples (from 0.35 to 1.72% absolute) with increasing treatment severity also contributes. The decrease of ash content is mainly associated with the removal of water-soluble inorganic constituents in pods, e.g. Na, S, Cl, and K. Concentrations of the two most abundant inorganic elements, K and Cl, decreased over 60% and 90%, respectively, and were the major contributing factors for the decrease of ash content. Similar K_2O reductions, as high as 95%, were reported for rice husk [12]. Similar to K, the reduction in Na and S concentration were > 60% and > 50%, respectively. As Si and Ca species in biomass usually have low water solubility [12], the impact of hot water treatment on the removal of Ca and Si elements was negligible. The Ca concentration slightly increased after the treatment, likely the result of decreased contents of other inorganic constituents.

The pod leaching behavior was also investigated using the large-scale test system, i.e. ~ 200 g whole pods and ~ 4 kg water, at 40 °C (Table 1). Conductivity was monitored continuously and leachate subsampled in the first 9 h and final measurements after the 24 h. 10 mL

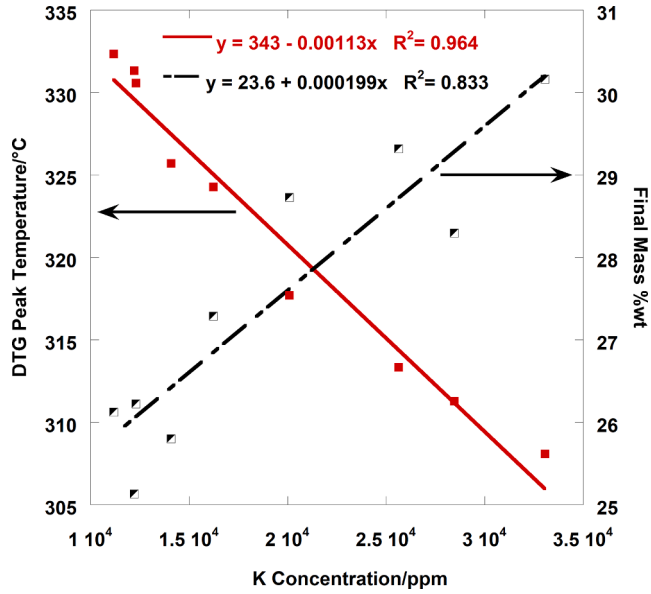

Fig. 6. Relationships between K concentration and DTG peak temperature/final mass from TGA analysis of raw and processed pods from 2^3 factorial experimental design.

leachate subsamples were collected every 10 min in the first hour of the test, and then every 30 min during the following 8 h. Fig. 3 shows the results of leachate analysis in the first 9 h. Results from the physicochemical property analysis of the solid sample after the 24 h test are listed in Table 1. Similar to the results obtained from the small-scale test system, the conductivity of the leachate increases comparably fast in the first 1–2 h and then starts to slow down reaching ~ 3,200 μS cm^{-1} after 9 h (Fig. 3 (A)). The conductivity of the leachate was ~ 3360 μS cm^{-1} after the 24 h tests. The NPOC and TN exhibited similar behavior as the conductivity, i.e. an initial sharp increase followed by a slow increase in the first 9 h (Fig. 3 (B)). The change of NPOC is usually associated with the dissolving of organic constituents from biomass to the leachate, and the increase of TN is related to the increase of Kjeldahl nitrogen (ammonia, organic and reduced nitrogen) and nitrate-nitrite in the liquid phase. The NPOC and TN were found to increase almost linearly with the leaching time in the first 2 h. Fig. 3(C) displayed the removal efficiency of the three major water-soluble inorganic components in pods, i.e. S, Cl, and K. As observed in studies using the small-scale test system, the removal efficiency of Cl is the highest (~90%), followed by K (~60%) and S (~45%) after 9 h. As with NPOC and TN, the S and K concentration in the leachate increased almost linearly with leaching time in the first 2 h of the test, whereas the nearly linear relationships for Cl was only observed in the first hour, indicating that Cl is removed more effectively.

3.2. Factorial experiment results

The leaching process of the inorganic species in the pods was monitored by measuring the conductivity of the leachate shown in Fig. 4. A continuous increase of conductivity was observed for both whole and 2 mm pods at 25 °C and 75 °C over a leaching duration of 10 min (Fig. 4(A)). Both higher temperature and smaller particle size increased the leaching rate of inorganic constituents. The leaching rate for the tests with < 2 mm samples at 25 °C was faster than that of whole pods at 75 °C, indicating the importance of particle size on mass transfer in short-duration treatments. For 2 h tests (Fig. 4(B)), the conductivity reached a plateau at 40 min (~3,100 μS cm^{-1}) and 80 min (2,900 μS cm^{-1}) for the < 2 mm samples at 75 and 25 °C, respectively, whereas the conductivity for the whole pods at 75 °C slowly increased approaching the plateau after 2 h.

The properties of the solid pods and the leachates were analyzed after each test and summarized in Fig. 5, and Tables S1-S4 in the Supplementary Materials. The primary goal of the leaching process is to remove inorganic species and decrease the biomass ash content. Changes in the volatile matter (VM), fixed carbon (FC), and ash contents under different treatment conditions were shown in Fig. 5(A). The decrease of ash content is in a range of 10.2–57.4% (relative), whereas the changes of VM and FC were not appreciable and mainly owing to the reduction in ash content. The impacts of the leaching process on the HHV (Table S1) and carbon content (Fig. 5(B)) of the pods are quite similar across experimental conditions, increasing by 12–15% and 10–12% (relative), respectively. The particle size seems to have more impact on the nitrogen content of the leached pods, and the change of nitrogen is ~ 9–13% (relative) for pod materials (<2 mm). The final leachate samples were also analyzed to investigate the impact of operating conditions (Fig. 5 (C)). As expected, the maximum values for NPOC, TN, and COD all occur under the 75 °C test condition with < 2 mm size pods and 2 h duration.

As observed in the studies of whole pods, the leaching condition has significant impacts on the major water-soluble element contents, i.e. S, Cl, and K (Fig. 5(D)). The maximum reduction in the concentration of S and K, ~66 and 51%, respectively, was realized with < 2 mm size pod at 75 °C for 2-h testing. The lowest Cl, ~1115–1155 ppm, was reached with whole pods at 75 °C and < 2 mm size pods at both 25 °C and 75 °C for 2 h (Table S1). The tests with whole pods at 25 °C for 10 min achieved reductions in Cl, S, and K concentration of < 19%, <6%, and < 14%, respectively, indicating that elevated temperature, particle size reduction, extended test duration, or their combination is needed to increase the efficiency of the leaching process.

Thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses of the raw and leached pods were conducted by micro-TGA, and the results are shown in Figures S1 and S2 in Supplementary Materials. In general, the mass loss has three stages: 1) 1st stage (T < 200 °C) with slightly reduced mass, usually < 10 %wt owing to drying and release of some light volatile species; 2) 2nd stage (200 < T < 500 °C) with a significant drop in mass due to the decomposition of hemicellulose, cellulose, and lignin; 3) 3rd stage (T > 500 °C) with limited weight loss resulting from the degradation of other heavy components (remaining lignin) [37,38]. The final mass percentage (dry basis) from Figure S1 and the temperature of maximum mass loss rate

Table 2
Summary of material mass loss (MML), S, Cl, and K removal efficiencies, and fouling and slagging indices from 2^3 factorial experimental design.

Design Point	Factor			MML%	$\eta_{S\text{-Solid}}$ %	$\eta_{Cl\text{-Solid}}$ %	$\eta_{K\text{-Solid}}$ %	B/A	F_u	R_s
	A	B	C							
Raw								87.4	0.1	3.6
1	–	–	–	18.0 ± 0.1	50.3 ± 0.9	75.5 ± 2.3	59.7 ± 1.0	47.8	0.0	1.0
2	+	+	–	20.3 ± 0.2	59.3 ± 0.6	84.1 ± 1.2	70.3 ± 0.9	41.5	0.0	0.6
3	+	+	–	20.6 ± 0.6	59.3 ± 0.2	84.7 ± 0.4	70.7 ± 0.4	43.8	0.0	0.7
4	+	+	–	22.6 ± 1.6	62.0 ± 1.6	84.9 ± 0.6	73.8 ± 0.9	46.5	0.0	0.7
5	–	–	+	11.4 ± 0.1	16.4 ± 2.1	28.2 ± 7.1	23.8 ± 6.6	77.1	0.1	2.7
6	+	–	+	12.9 ± 0.1	2.2 ± 53.0	1.5 ± 32.5	32.5 ± 3.9	56.5	0.1	1.4
7	–	+	+	14.2 ± 0.2	32.4 ± 1.8	73.2 ± 3.6	47.9 ± 3.8	71.0	0.1	2.3
8	+	+	+	17.9 ± 0.3	51.3 ± 0.6	93.4 ± 0.2	65.0 ± 0.7	45.7	0.0	0.8

Note: (1) factors A, B, and C are temperature, rinse time, and particle size, respectively.

(peak temperature) in Figure S2 were plotted with the K concentration of the corresponding samples, respectively (Fig. 6). As the K concentration is reduced via leaching the DTG peak temperature increases with a corresponding reduction in final mass fraction. Similar phenomena were also observed in previous studies [33,39–41], as K has positive effects on the reactivity of biomass, performs similar to catalysts, and promotes the pyrolysis reaction by decreasing the energy barrier of the reaction.

Table 2 lists material mass losses (MML), S, Cl, and K removal efficiencies, and fouling and slagging indices from the 2^3 factorial experimental design. The MML was calculated based on the mass difference of the pod materials before and after treatment (Eq. (1)). The element mass balances (Table S5) and removal efficiencies were calculated using Eq. (2) and (3), respectively. As expected, the MML increases with the increase of temperature and duration and the decrease of particle size, owing to the loss of water-soluble components. The removal efficiency of Cl can reach ~ 93% in a 10 min test at 75 °C with < 2 mm size pods, and the maximum removals of S (62.0%) and K (73.8%) were reached with an extended test duration (2 h) under the same condition. The base/acid ratio and fouling and slagging indices of pods all decreased after treatment. The lowest B/A and R_s values corresponded to whole pods leached at 75 °C for 2 h, decreasing by > 50% and > 80%, respectively. FT-IR was used to investigate the impact of the leaching process on the chemical structure of the pods (Figure S3), but no changes were observed. The severity of leaching at temperatures < 100 °C and atmospheric pressure is too low to activate chemical reactions or cause structural changes in the lignocellulose.

The average values from Tables S1 and S4 were used to calculate the effect and standard error for each independent variable and their interactions as summarized in Table 3 and Table S6, and Figures S4 and S5. The three variables or factors, i.e., leaching temperature (A), time (B), and particle size (C), all affect the leaching process. The magnitude of their first order impacts are particle size > time > temperature, for the change of ash and the inorganic constituents S and K (Table 3). The increase of solid particle size results in decreased removal of ash and inorganic substances, whereas increased leaching time and temperature exhibited opposite trends. Factor impacts of time and particle size on the change of Cl removal efficiency are comparable but with opposite trends. The interaction between temperature (A) and time (B) is not significant, as the values of AB in Table 3 are<3 times their standard errors. The AC and BC interactions, however, were significant on the change of ash and inorganic constituents S and Cl, and BC has the larger interaction effect. The BC interaction effect was also significant for K removal efficiency. The large, significant 2 and 3 factor interactions limit the interpretation of the results, since all significant impacts (1st, 2nd, and 3rd order) must be jointly considered. Although the particle size reduction clearly impacts the pongamia pod leaching process, it is likely that whole pods (without size reduction) would be used at an industrial scale, and leach water temperature and leaching duration would be available tools to modify fuel properties. Hot water is often available on-site as low-grade waste energy, whereas higher quality energy such as electricity, steam, or diesel would be needed for particle size reduction. Hot water could also offer opportunities for reuse, processing multiple batches of pods, as discussed in section 3.4.

3.3. Torrefaction of water-leached pods

Leaching targets removal of water-soluble inorganic constituents in biomass. Other pretreatment processes may be used to further improve the fuel properties of biomass, e.g. energy density, grindability, and stability [42]. Torrefaction is employed for biomass upgrading to reduce oxygen content and generally results in mass and energy yields of 70 % and 90 %, respectively [42–45]. Previous studies found potassium and chlorine contents of pongamia pods were increased by torrefaction pretreatment, suggesting additional action was needed to avoid deposition and fouling in thermochemical energy conversion applications [26]. Thus, leaching and torrefaction processes were combined here. Pods (<2 mm) leached at 75 °C for 10 min using the large-scale test system (MML = 19.9%) were torrefied with a LECO macro-TGA to evaluate the integrated effects. Performance indicators for the torrefaction process were calculated according to the following equations,

$$M_y(\%) = \frac{m_{tor}}{m_{raw}} \times 100 \tag{11}$$

$$I_{ed} = \frac{HHV_{tor}}{HHV_{raw}} \tag{12}$$

$$E_y(\%) = M_y \times I_{ed} \tag{13}$$

where M_Y and E_Y are mass and energy yields, respectively; I_{ed} is the energy densification index; m is the mass of the material, and HHV is the higher heating value. Subscripts *raw* and *tor* are raw and torrefied biomass, respectively.

Figure 7(A) shows sample mass changes during torrefaction at prescribed temperatures (20 °C/min heating rate, 60 min residence time, and 60 min cooling period). The mass yield of the leached pods decreased with increasing torrefaction temperature and reached a target value of ~ 70 % [43] at a torrefaction temperature of ~ 270 °C, when not considering the mass loss during the leaching process (56.9% when MML is considered). The mass yield of the raw pods at the same conditions is ~ 65%. A similar trend was observed for torrefaction at 255 °C (Figure S6). The lower mass yield of the raw pods may result from elevated K concentration catalytically promoting pyrolytic decomposition reactions [33,39–41]. The HHVs of the pods with and without the leaching treatment after torrefaction at 270 °C were 22.8 ± 0.3 and 23.6 ± 0.1 MJ/kg, respectively, which result in an energy densification index of 1.41 and 1.46, respectively, and an energy yield of 80% and 95%, respectively. Note that this includes the material mass loss due to the leaching process.

The proximate and ultimate analysis results for the torrefied pods are summarized in Table S7. The removal of water-soluble inorganic species

Table 3
Temperature, particle size, and rinse time effects on the properties of solid pod residues from 2^3 factorial experimental design.

Main Effects	Ash decrease % (relative)	$\eta_{S\text{-}Solid}$ %	$\eta_{Cl\text{-}Solid}$ %	$\eta_{K\text{-}Solid}$ %
Temperature (A)	10.2 ± 0.4	8.9 ± 0.8	13.5 ± 1.7	9.9 ± 1.8
Time (B)	16.7 ± 0.4	14.4 ± 0.8	23.9 ± 1.7	17.8 ± 1.8
Particle Size (C)	−24.0 ± 0.4	−27.4 ± 0.8	−20.4 ± 1.7	−26.4 ± 1.8
Two-factor interactions				
AB	−0.7 ± 0.4*	1.9 ± 0.8*	−3.3 ± 1.7*	0.2 ± 1.8*
AC	2.8 ± 0.4	3.0 ± 0.8	9.1 ± 1.7	3.0 ± 1.8*
BC	8.9 ± 0.4	8.6 ± 0.8	18.9 ± 1.7	10.5 ± 1.8
Three-factor interactions				
ABC	3.8 ± 0.4	5.1 ± 0.8	1.0 ± 1.7*	3.9 ± 1.8*

Note: *The effect value is < 3 times the standard error.

reduced the ash content of the torrefied leached pods by ~ 50% (relative) compared to torrefied unleached pods. Fig. 7(B) showed the torrefied pod data overlaid onto a Van Krevelen diagram. As reported in a previous study [26], the element ratios gradually shifted away from biomass toward coal with the increase of torrefaction temperature. The leached and raw pods after torrefaction at 255 °C both fall into the peat area. The leached torrefied materials are all classified in the peat area but the unleached pod values are classified in the lignite area when torrefied at 270 °C. The XRF results for the major ash elements in torrefied pods are summarized in Table S8. They are mostly present in nonvolatile form in the pods, and as expected, their concentrations increase after torrefaction. The concentrations of water-soluble elements (Na, P, S, Cl, and K) in the leached torrefied pods, were lower than the raw pods without any treatments (Table 1). Mg, Si, and Ca concentrations in the leached torrefied pods were comparable to the torrefied raw material owing to the inefficient removal of these elements in the leaching process.

3.4. Leachate reuse

The reuse of leachate in pod processing was investigated. The original freshwater was recycled repeatedly to process 17 batches of < 2 mm

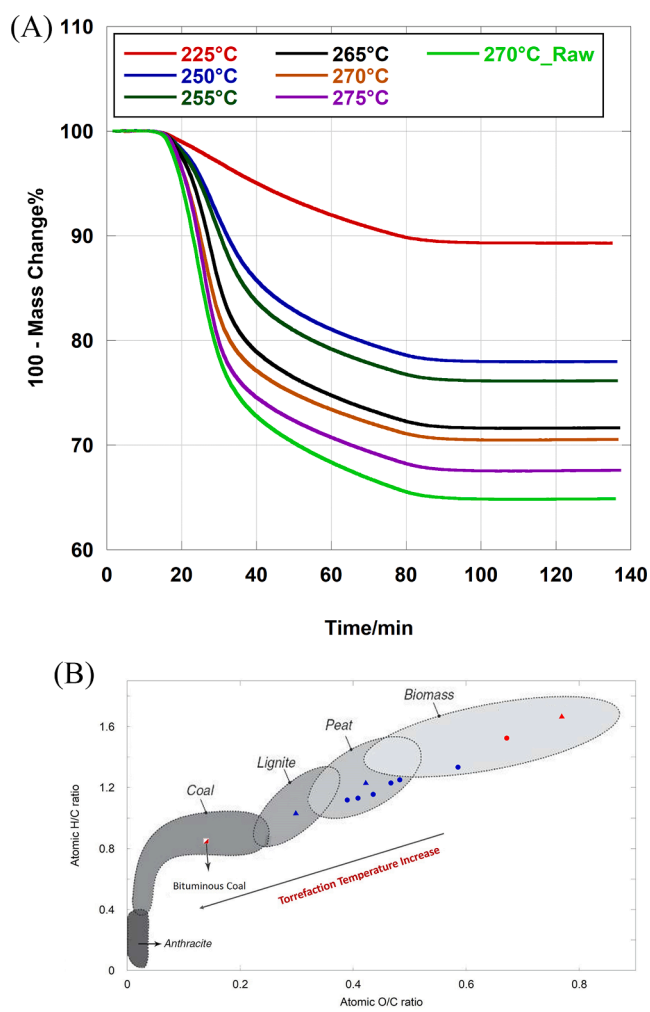

Fig. 7. Pod properties after torrefaction processing: (A) thermogravimetric curves from macro-TGA torrefaction tests using raw and leached pods with 20 °C/min heating rate, 60 min residence time, and 60 min cooling period; (B) Van Krevelen diagram (red color for materials before torrefaction treatment, dot for leached pods, and triangle for unleached pods). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

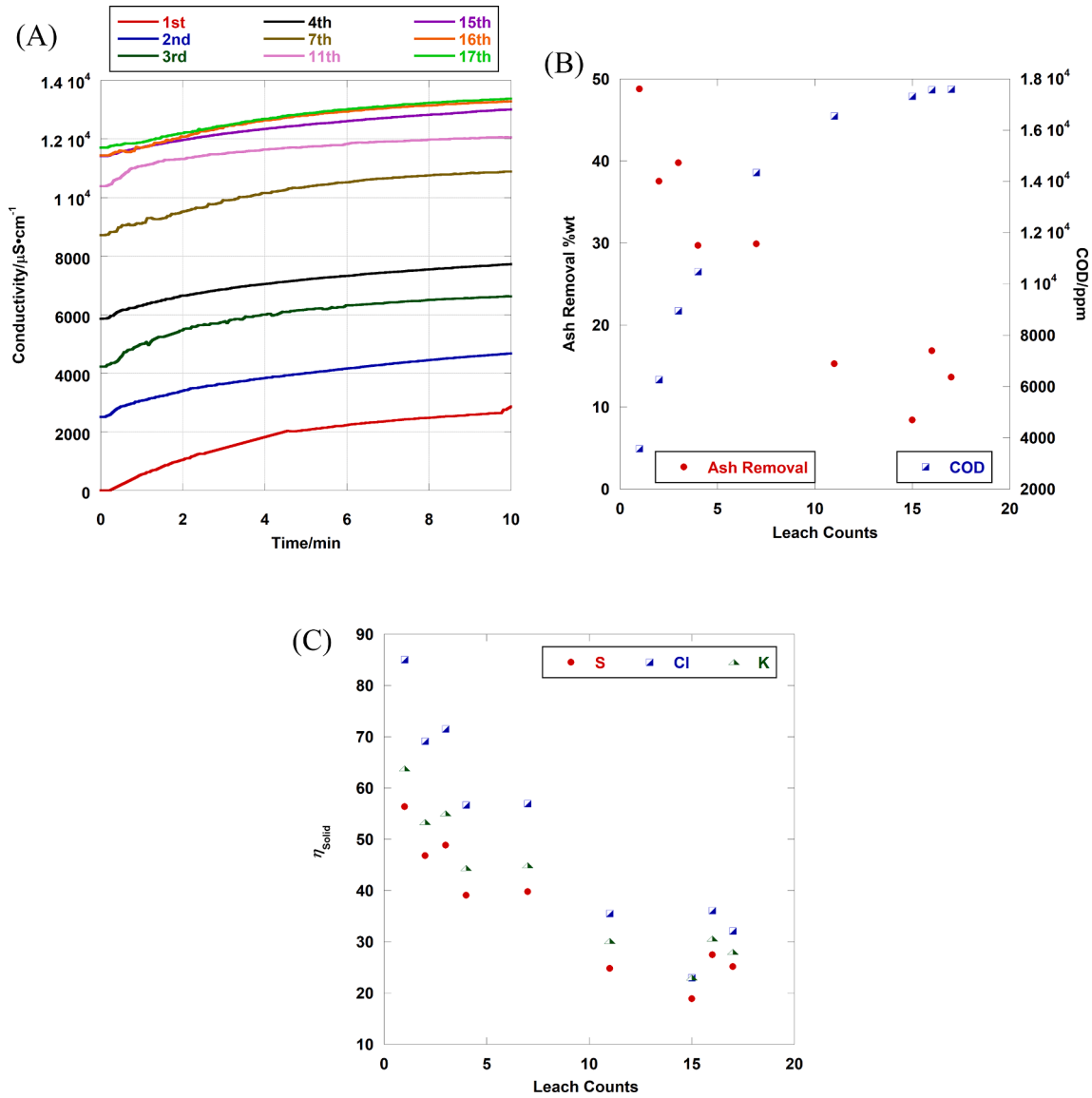

Fig. 8. Results from water reuse analysis: (A) leachate conductivity; (B) ash content and COD; (C) element removal efficiency.

pods at 75 °C for 10 min duration. Approximately 75–80 g freshwater was added to the previous run's leachate to maintain a pod to leachate weight ratio of 1:20. Fig. 8(A) shows the changes in the leachate conductivity during the leaching process. The first run produced an increase in conductivity of 2903 μS cm^{-1} and this increment decreased to 1710 μs cm^{-1} in the 15th run. The final conductivity of the leachate after the 16th and 17th runs are almost identical, 13,540 and 13,860 μs cm^{-1}, respectively, indicating that the leachate has reached maximum reuse and the conductivity change in the 17th run can be attributed to the fresh makeup water added.

The properties of the leached pods and leachate from the reuse experiment are summarized in Tables S9 and S10 in the Supplementary Materials. The conductivity of the leach water and the corresponding percentage decrease in pod ash content and the leachate COD for nine of the 17 successive leach water reuses are presented in Fig. 8(A) and (B), respectively. The increases in conductivity are markedly reduced after the third leachate reuse. The ash content of the leached pods increased from 3.3 % wt after the 1st run to 5.65 % wt after the 17th run (Table S9). The percentage decrease of the ash content declined linearly with leach counts until the 15th run. Correspondingly, the COD of the leachate increases linearly in the first few runs, with smaller increments thereafter, approaching a plateau for the last three runs, i.e. 15th, 16th, and 17th. The leachate reuse has similar influences on the removal efficiency of S, Cl, and K from pods as on ash removal (Fig. 8(C)), decreasing almost linearly with the increase of leachate reuse (X) until the 15th run. As the removal efficiency of Cl is generally higher than that of S and K, the leachate reuse has greater impacts on the Cl removal efficiency, reflected by the higher value of the slope, 4.01 for Cl compared to 2.45 and 2.66 for S and K, respectively. The leachate reuse, however, does not have significant impacts on the HHV of the leached pods, in a range of 17.9–18.7 MJ/kg for the tests (Table S5). The leachate reuse data were verified by replicating the first 4 runs. Results are summarized in Figure S7 and Tables S9 and S10.

4. Conclusion

Leaching experiments were performed on pongamia pods to study the removal of inorganic constituents. A 2^3 factorial experiment was designed and conducted to determine the effects of particle size, rinse water temperature, and rinse duration. Leached pods were characterized for elemental composition and common fuel properties. Analysis of corresponding leachate samples included ion content, water quality parameters, and the extent to which leachate reuse could be implemented while maintaining removal efficiency. A preliminary

investigation was performed to evaluate the combined effects of leaching and torrefaction processes.

Based on the analysis, the following conclusions were drawn:

- 24 h leaching tests effectively removed water-soluble inorganic constituents from whole pongamia pods with removal efficiencies for Cl > 90%, K > 60%, and S > 40%.
- The initial leaching rate and the rate constant increase with operating temperature based on the leachate conductivity analysis.
- The particle size, leaching temperature, and leaching time all have significant influences on the primary performance variables, ash content and K, Cl, and S removal efficiencies, but two and three factor interactions between the variables limit the interpretation of results.
- Whole pods (without size reduction) would be used at an industrial scale and leach water temperature and leaching duration would be available tools to modify fuel properties
- The leaching process at atmospheric pressure and the most severe leaching conditions (75 °C, <2 mm particles, 24 h leach time) did not change the lignocellulosic structure of the pod.
- Removal of potassium by leaching shifted the reactivity of the pod material toward higher temperatures, verifying its catalytic role in promoting pyrolysis.
- Limited testing of combined leaching and torrefaction pretreatments, resulted in improved pongamia pod fuel properties and reduced inorganic content, especially S, Cl, and K.
- The leachate can be reused to treat successive batches of pods, but reduced ash removal efficiency limits this practice to two or three cycles.
- Additional investigation is warranted on the treatment of leachate, recovery of nutrients, and techno-economic assessment of the process.

CRediT authorship contribution statement

Jinxia Fu: Conceptualization, Methodology, Investigation, Supervision, Visualization, Writing - original draft. **Gabriel Allen:** Methodology, Investigation, Formal analysis. **Sarah Weber:** Investigation, Formal analysis. **Scott Q. Turn:** Conceptualization, Project administration, Writing - review & editing, Funding acquisition. **William Kusch:** Resources, Writing - review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2021.121480.

References

[1] Kumar B, Bhardwaj N, Agrawal K, Chaturvedi V, Verma P. Current perspective on pretreatment technologies using lignocellulosic biomass: an emerging biorefinery concept. Fuel Process Technol 2020;199:106244. https://doi.org/10.1016/j.fuproc.2019.106244.
[2] Chen H, Liu J, Chang X, Chen D, Xue Y, Liu P, et al. A review on the pretreatment of lignocellulose for high-value chemicals. Fuel Process Technol 2017;160:196–206.
[3] Limayem A, Ricke SC. Lignocellulosic biomass for bioethanol production: current perspectives, potential issues and future prospects. Prog Energy Combust Sci 2012;38(4):449–67.
[4] Reddy N, Yang Y. Biofibers from agricultural byproducts for industrial applications. Trends Biotechnology (Regular ed) 2005;23(1):22–7.
[5] Deng L, Zhang T, Che D. Effect of water washing on fuel properties, pyrolysis and combustion characteristics, and ash fusibility of biomass. Fuel Process Technol 2013;106:712–20.
[6] Baxter LL, Miles TR, Miles TR, Jenkins BM, Milne T, Dayton D, et al. The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences. Fuel Process Technol 1998;54(1-3):47–78.
[7] Knudsen JN, Jensen PA, Dam-Johansen K. Transformation and Release to the Gas Phase of Cl, K, and S during Combustion of Annual Biomass. Energy Fuels 2004;18(5):1385–99.
[8] Michelsen HP, Frandsen F, Dam-Johansen K, Larsen OH. Deposition and high temperature corrosion in a 10 MW straw fired boiler. Fuel Process Technol 1998;54(1-3):95–108.
[9] Jensen PA, Stenholm M, Hald P. Deposition Investigation in Straw-Fired Boilers. Energy Fuels 1997;11(5):1048–55.
[10] Jiang L, Hu S, Sun L-S, Su S, Xu K, He L-m, et al. Influence of different demineralization treatments on physicochemical structure and thermal degradation of biomass. Bioresour Technol 2013;146:254–60.
[11] Library EPaP. Top Value Added Chemicals from Biomass - Volume I, Results of Screening for Potential Candidates from Sugars and Synthesis Gas. United States; 2004.
[12] Bandara YW, Gamage P, Gunarathne DS. Hot water washing of rice husk for ash removal: the effect of washing temperature, washing time and particle size. Renewable Energy 2020;153:646–52.
[13] Ma Q, Han L, Huang G. Evaluation of different water-washing treatments effects on wheat straw combustion properties. Bioresour Technol 2017;245:1075–83.
[14] Jenkins BM, Bakker RR, Wei JB. On the properties of washed straw. Biomass Bioenergy 1996;10(4):177–200.
[15] Cui H, Turn S, Morgan T, Li D. Processing freshly harvested banagrass to improve fuel qualities: Effects of operating parameters. Biomass Bioenergy 2017;105:310–9.
[16] Turn SQ, Kinoshita CM, Ishimura DM. Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching. Biomass Bioenergy 1997;12(4):241–52.
[17] Cui H, Turn SQ, Tran T, Rogers D. Mechanical dewatering and water leaching pretreatment of fresh banagrass, guinea grass, energy cane, and sugar cane: Characterization of fuel properties and byproduct streams. Fuel Process Technol 2015;139:159–72.
[18] Rajabzadeh AR, Ruzich N, Zendehboudi S, Rahbari M. Biomass leachate treatment and nutrient recovery using reverse osmosis: experimental study and hybrid artificial neural network modeling. Energy Fuels 2012;26(12):7155–63.
[19] Jenkins BM, Mannapperuma JD, Bakker RR. Biomass leachate treatment by reverse osmosis. Fuel Process Technol 2003;81(3):223–46.
[20] Guidelines for water reuse, EPA/600/R-12/618U.S. Environmental Protection Agency, Washington, DC, 2012. https://www.epa.gov/sites/production/files/2019-08/documents/2012-guidelines-water-reuse.pdf.
[21] Dwivedi G, Sharma MP. Prospects of biodiesel from Pongamia in India. Renew Sustain Energy Rev 2014;32:114–22.
[22] Bordoloi N, Narzari R, Chutia RS, Bhaskar T, Kataki R. Pyrolysis of Mesua ferrea and Pongamia glabra seed cover: characterization of bio-oil and its sub-fractions. Bioresour Technol 2015;178:83–9.
[23] Morgan TJ, Youkhana A, Turn SQ, Ogoshi R, Garcia-Pérez M. Review of biomass resources and conversion technologies for alternative jet fuel production in Hawai'i and tropical regions. Energy Fuels 2019;33(4):2699–762.
[24] S.A. Patil, S.K. Patil, A.S. Sartape, S.C. Bhise, M.M. Vadiyar, M.A. Anuse, et al. A Pongamia pinnata pods based activated carbon as an efficient scavenger for adsorption of toxic Co(II): kinetic and thermodynamic study, Separat Sci Technol 15.
[25] Ujjinappa S, Sreepathi LK. Production and quality testing of fuel briquettes made from pongamia and tamarind shell. Sadhana-Acad Proc Eng Sci 2018;43(4):7.
[26] Fu J, Summers S, Turn SQ, Kusch W. Upgraded pongamia pod via torrefaction for the production of bioenergy. Fuel 2021;291:120260. https://doi.org/10.1016/j.fuel.2021.120260.
[27] EPA. 5220 CHEMICAL OXYGEN DEMAND (COD) (2017). Standard Methods For the Examination of Water and Wastewater. American Public Health Association; 2018.
[28] Andersen LK, Morgan TJ, Boulamanti AK, Álvarez P, Vassilev SV, Baxter D. Quantitative X-ray fluorescence analysis of biomass: objective evaluation of a

typical commercial multi-element method on a WD-XRF spectrometer. Energy Fuels 2013;27(12):7439–54.
[29] ASTM D4809. Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter (Precision Method). West Conshohocken, PA: ASTM International; 2018.
[30] ASTM E1756. Standard Test Method for Determination of Total Solids in Biomass. West Conshohocken, PA: ASTM International; 2015.
[31] ASTM E1755. Standard Test Method for Ash in Biomass. West Conshohocken, PA: ASTM International; 2015.
[32] ASTM E872. Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels. West Conshohocken, PA: ASTM International; 2019.
[33] Niu Y, Tan H, Hui S. Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. Prog Energy Combust Sci 2016;52:1–61.
[34] Box GEP. Statistics for experimenters: design, innovation, and discovery. 2nd ed. Hoboken, N.J: Wiley-Interscience; 2005.
[35] Conner AH. Kinetic modeling of hardwood prehydrolysis. Part 1. Xylan removal by water prehydrolysis. Wood Fiber; (United States) 1984;16:2.
[36] Ho Y-S, Harouna-Oumarou HA, Fauduet H, Porte C. Kinetics and model building of leaching of water-soluble compounds of Tilia sapwood. Sep Purif Technol 2005;45(3):169–73.
[37] Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 2007;86(12-13):1781–8.
[38] Chen W-H, Kuo P-C. A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. Energy 2010;35(6):2580–6.
[39] Mayer ZA, Apfelbacher A, Hornung A. A comparative study on the pyrolysis of metal- and ash-enriched wood and the combustion properties of the gained char. J Anal Appl Pyrol 2012;96:196–202.
[40] González-Vázquez MP, García R, Gil MV, Pevida C, Rubiera F. Unconventional biomass fuels for steam gasification: Kinetic analysis and effect of ash composition on reactivity. Energy 2018;155:426–37.
[41] Nowakowski DJ, Jones JM, Brydson RMD, Ross AB. Potassium catalysis in the pyrolysis behaviour of short rotation willow coppice. Fuel 2007;86(15):2389–402.
[42] van der Stelt MJC, Gerhauser H, Kiel JHA, Ptasinski KJ. Biomass upgrading by torrefaction for the production of biofuels: a review. Biomass and Bioenergy 2011;35(9):3748-62.
[43] Bergman PCA. Torrefaction for biomass co-firing in existing coal-fired power stations BIOCOAL. In: Energieonderzoek Centrum N, ed.; 2005.
[44] Chen W-H, Peng J, Bi XT. A state-of-the-art review of biomass torrefaction, densification and applications. Renew Sustain Energy Rev 2015;44:847–66.
[45] Niu Y, Lv Y, Lei Y, Liu S, Liang Y, Wang D, et al. Biomass torrefaction: properties, applications, challenges, and economy. Renew Sustain Energy Rev 2019;115:109395. https://doi.org/10.1016/j.rser.2019.109395.