

Combination of Torrefaction and Leaching Treatments on the Solid Biofuel Characteristics of Fast-Growing Timbers Species and Oil Palm Biomass

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The potential of integrating acid acetic leaching and torrefaction processes was studied to create an enhanced solid biofuel from lignocellulosic biomass. The focus was on evaluating the impact of these combined methods on ash removal efficiency and the melting characteristics of the treated biomass. Two possible strategies were considered: implementing torrefaction first followed by leaching, or conducting leaching first followed by torrefaction. By incorporating both leaching and torrefaction treatments, regardless of order, a solid biofuel with improved properties was attained, especially in terms of higher heating value yield and ash melting temperature compared to individual treatment (either only torrefaction or only leaching). Depending on the sequencing of the leaching treatment, there was a reduction in ash yield from raw biomass ranging between 60% and 86%, while for torrefied biomass it was between 47% and 68%. Leaching treatment before torrefaction treatment was determined to be a more effective combination.

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INTRODUCTION

Biomass pretreatment has been recognized as a potential key step that can affect both logistics and handling. Torrefaction and leaching have been introduced in numerous studies to enhance the solid biofuel characteristics of lignocellulosic biomass (Chen *et al.* 2017, 2020; Zhang *et al.* 2018; Ma *et al.* 2019; Li *et al.* 2020). Both pretreatments have been customized to increase the fuel quality of respective lignocellulosic biomass. Biomass pretreatment through torrefaction enhances its calorific value and shows potential for transforming low-grade biomass into a solid biofuel with higher energy density and reliable chemical and physical characteristics. Although torrefaction has been demonstrated to enhance the properties of biomass fuel by resulting in a high-energy-density fuel, a persisting challenge is the substantial retention of alkali metals in the char, and the metals have adverse impact on the heat transfer and corrosion rates in the boiler (Chin *et al.* 2013; Haddad *et al.* 2017). The leaching method significantly reduces the ash content and improved the ash sintering characteristic of biomass (Chin *et al.* 2020). However, only a slight increment in heating value was observed due to total ash reduction; leaching does

not essentially increase the heating value as in using torrefaction method (Chin *et al.* 2015; Chen *et al.* 2019). In general, both torrefaction and leaching benefit in one respective factor, *i.e.* heating value or ash sintering characteristic, but neglected the other factor.

Nature offers a wide range of biomass with varying properties. Employing torrefaction followed by leaching, or the reverse sequence, shows promise in improving the efficiency of converting biomass to energy and addressing logistical challenges in large-scale sustainable energy systems, better energy density and combustion efficiency. A combination of leaching and torrefaction may be an ideal pretreatment method for both biofuels and biopower. The previous work in this area is sparse, Cen *et al.* (2021), Chen *et al.* (2017, 2019) and Ma *et al.* (2019) examined the bio-oil yield from the effect of torrefaction and leaching combination treatment and was not focusing on the effect of the treatment on solid biofuel characteristics. Su *et al.* (2021) investigated the superiority of CO₂ washing before torrefaction pretreatment on rice husk but did not include the effect of the process sequence from the integration of leaching and torrefaction process. Zhang *et al.* (2018) reported that ash forming elements were difficult to be leached out from the straw char from pyrolysis treatment under high heating temperature. Torrefaction, a thermal treatment using lower temperature than pyrolysis might induce a different outcome when integrated with leaching treatment.

Numerous studies have also indicated that rinsing lignocellulosic biomass before the torrefaction process can enhance the qualities of the fuel and remove a majority of ash-forming components from the raw biomass (Chen *et al.* 2017; Zhang *et al.* 2018; Kasim *et al.* 2019). However, some reports have indicated that pre-treatment leaching before torrefaction may not always improve fuel characteristics. This is because the catalytic effects of inorganic species, particularly K and Na, have been shown to lower the initial decomposition temperature of the torrefaction process (Cen *et al.* 2016; Shoulaifar *et al.* 2016), thus, the absence of these inorganic compounds from the leaching process may necessitate an increase in torrefaction severity to achieve similar results compared to the unleached samples. Saleh *et al.* (2013) also discovered that even a small presence of inorganic compounds, particularly potassium (K), resulted in improved grindability of the torrefied biomass.

Water can be regarded as a low-cost leaching agent; however, lignocellulosic biomass contains higher non-water-soluble elements that cannot be easily removed by water. It was reported by Abelha *et al.* (2019) that pre-washing low-grade biomasses such as road-side grass, miscanthus, wheat straw, and spruce bark with water, has minor impact on the slagging propensity of the fuel. Chin *et al.* (2015) stated that after acetic acid leaching treatment, biomass showed a significant reduction in ash content and a positive effect on the ash melting characteristics. Compared to water leaching, acid leaching can remove higher amounts of non-water soluble elements. For less damaging washes, organic acids such as acetic acid are suggested as alternatives to straight mineral acid use.

Based on these findings, two potential pre-treatment combination approaches were suggested in this research: implementing torrefaction first followed by acid acetic leaching, or vice versa – applying the acid acetic leaching method first followed by torrefaction. The study investigated the prospect of merging torrefaction and leaching processes to create a more potent solid biofuel from fast-growing timber species and oil palm biomass that would result in higher energy density and lower ash content. The experiments assessed both treatment sequences: (i) torrefaction preceding leaching, or (ii) leaching preceding torrefaction, with regards to their impact on higher heating value, ash removal efficiency, and the ash melting characteristics of the treated lignocellulosic biomasses. It is essential

to evaluate each case individually when selecting the treatment sequence for these combined processes, as the results heavily depend on the influence of the initial treatment and its effects when combined with different lignocellulosic biomasses having varied chemical compositions. The selection of the torrefaction and leaching parameters for each respective biomass species in the combination treatment process was adapted from the optimum results obtained by (Chin *et al.* 2013, 2015). The studies were conducted to develop a method to produce commercial quality of clean biomass solid biofuel. This study aimed to create a procedural series for the combined treatment of torrefaction and leaching to produce solid biofuel with improved qualities, such as reduced ash content and higher heating value.

EXPERIMENTAL

Materials

Logs (including bark) from four rapidly growing types of timber (*Acacia* spp., *Paraserianthes falcataria*, *Macaranga* spp. and *Endospermum* spp), empty fruit bunch and oil palm trunk were processed into chips with a thickness of less than 3 mm and diameters ranging from 1 to 15 mm. The lignocellulosic biomasses were oven-dried at 105 °C for 24 h and kept in a conditioning room for later use.

Methods

Combined treatment process

Two distinct combination treatments were employed: torrefaction preceding leaching and leaching preceding torrefaction. Table 1 shows the process sequences of the combination treatment. For the AB combination treatment, the biomass was torrefied before undergoing leaching treatment (torrefaction - leaching). For the BA combination treatment, the dried samples were leached followed by torrefaction treatment. Table 2 summarises the experimental conditions for each lignocellulosic biomass applied in this study. The temperature and reaction time for these treatments were varied for each lignocellulosic biomass based on the optimum conditions adapted from the publications by Chin *et al.* (2013) for torrefaction and Chin *et al.* (2015) for leaching.

Table 1. Summary of the Combination Treatment Process Sequences

OPTION 1: Torrefaction – Leaching (AB) Combination Treatment		
No.	Sequence	Remarks
1.	Size reduction	Logs (including bark) from fast-growing timber species and oil palm biomass were chipped, ground, and sieved.
2.	Drying process	The lignocellulosic samples were dried at 105 °C for 24 h.
3.	Torrefaction	10 g of dried samples were placed in a furnace and torrefied in a tube furnace controlled by a continuous nitrogen flow rate (0.5 to 1.0 L/min) under the selected reaction time and temperature (as shown in Table 2).
4.	Leaching	After cooling process, the torrefied samples were soaked and submerged in 1M acetic acid (liquid-solid ratio of 10 mL/g) under selected leaching conditions (as shown in Table 2).
5.	Filtering and washing	After acetic acid leaching, the treated samples were filtered and washed with distilled water.
6.	Drying	The treated samples were oven-dried at 105 °C for 24 h.

OPTION 2: Leaching – Torrefaction (BA) Combination Treatment		
No.	Sequence	Remarks
1.	Size reduction	Logs (including bark) from fast-growing timber species and oil palm biomass were chipped, ground, and sieved.
2.	Drying process	The lignocellulosic samples were dried at 105 °C for 24 h.
3.	Leaching	10 g samples of dried samples were soaked and submerged in 100 mL of 1M acetic acid under selected leaching conditions (as shown in Table 2).
4.	Filtering and washing	After acetic acid leaching, the leached samples were filtered and washed with distilled water.
5.	Drying	The leached samples were dried at 105 °C for 24 h before proceeded to torrefaction treatment.
6.	Torrefaction	The dried leached samples were torrefied in a tube furnace controlled by a continuous nitrogen flow rate (0.5 to 1.0 L/min) under the selected reaction time and temperature (as shown in Table 2). After torrefaction, the treated samples were left to cool in desiccators.

Table 2. Optimum Conditions of Torrefaction and Leaching Treatments

Lignocellulosic Biomass	Optimum Treatment Condition			
	Torrefaction (A)		Leaching (B)	
	Temp (°C)	Time (min)	Temp (°C)	Time (min)
<i>Acacia spp.</i>	260	40	30	95
<i>Paraserianthes falcataria</i>	220	45	40	30
<i>Macaranga spp.</i>	280	40	40	70
<i>Endospermum spp.</i>	220	45	40	65
EFB	230	40	40	55
OPT	300	45	40	70

Evaluation

Mass loss

For each combination treatment, the mass loss of the treated samples was obtained using the following expression,

$$W_L = [(M_I - M_D) / M_I] \times 100$$

where W_L is the mass loss (%), M_I is the initial oven-dried mass of the lignocellulosic sample before combination treatment process, and M_D is the oven dried mass of the lignocellulosic sample after the combination treatment.

Determination of ash content

The ash content was determined by heating the dried sample (2 g) in a muffle furnace at 575 ± 25 °C until constant weight was obtained (5 h). This procedure enabled the estimation of ash quantity, expressed as the percentage of remaining residue following the dry oxidation of biomass. The experiments were replicated three times, and the mean values were documented.

Determination of major elements (ash forming elements)

Following the CEN/TS 15290 standard, the chemical compositions of primary elements like aluminum, silicon, calcium, potassium, magnesium, and phosphorus were

examined for all samples. The digestion involved using a closed vessel with H₂O₂ (30%), HNO₃ (65%), and HF (40%) at a temperature of 190 °C for 30 minutes. After cooling, the sample was neutralized with H₃BO₃ (4%) and reheated for an additional 15 minutes. Following this process, the digest was analysed using an ICP-OES (inductively coupled plasma optical emission spectrometer). All analyses were conducted in triplicate and the means were reported.

Determination of higher heating value (HHV)

Following the BSI standard EN 14918, the higher heating value was measured using a bomb calorimeter, where 0.5 g of dried biomass was burned completely in an oxygen atmosphere at a pressure of 3000 kPa. All tests were conducted three times, and the average results were reported.

Ash sintering characteristic at different combustion temperature

In actual power plants, biomass combustion is carried out in high temperature combustion chambers operating at around 800 to 1000 °C. One of the major categories in ash deposition mechanism which often occur in the actual combustion is initiated by the ash fragments in the molten or semi-molten state. These ash fragments flow with the flue gas into the heated surface and bound together, then develop continuously in the heating surface of high temperature combustion region. The direct risk is the dramatic decrease of energy conversion efficiency due to the slagging formation on heat exchange components surfaces. Obviously, seeking an appropriate method to reduce or prevent the heating surface deposition is important to ensure high combustion efficiency and extensive utilization of various types of lignocellulosic biomass as solid biofuel.

Treated lignocellulosic biomass specimens were transformed into ash to determine their melting characteristics. Approximately 10 g of the treated lignocellulosic biomass were placed into crucibles, and then heated for 6 h in a muffle furnace at 550 °C to obtain low-temperature ash. Low-temperature ash samples weighing 0.2 g were placed in small ceramic crucibles and then subjected to heating in a muffle furnace at specific combustion temperatures (700, 800, 900, and 1000 °C) for two hours. After reaching the specified temperature, the furnace was allowed to cool down to below 500 °C before removing the crucibles. Once cooled, the crucibles were weighed after placing them in desiccators. The resulting ash for each sample were categorized into one of the four ash sintering severity index and sintering classes according to a classification structure outlined in Table 3 which were adapted from Chin *et al.* (2015) and Chin *et al.* (2018) with modification. This classification of ash sintering characteristics considers both macroscopic and microscopic features; microscopic characteristics are determined by observing the ash appearance using a stereo microscope at magnifications of up to 40X.

Data analysis

Statistical analyses were performed using SPSS for Windows, version 16.0 (SPSS, Chicago, IL, USA). This software was utilized to assess the impacts of two different combination treatments on the ash content, mass loss, and higher heating value (HHV) data of lignocellulosic biomass samples. The obtained data from the two treatment groups were compared using a t-test. The effects were considered to be not statistically significant when the p-value was higher than 0.05 at the 95% confidence level.

Table 3. Ash Sintering Severity Index and Sintering Classification According to Macroscopic and Microscopic Features

Ash Sintering Severity Index	Ash Sintering Class	Ash Sintering Characteristics
1	Loose	Macroscopic: Loose ash, no signs of fusion. Stereo microscope: Preserved organic structure, with few or no small melted vesicles visible.
2	Slightly sintered	Macroscopic: Ash is slightly fused and breaks apart easily upon manual disintegration. Stereo microscope: Organogenic structure remains intact, with surfaces partially or fully fused, and larger melted vesicles are observable.
3	Strongly sintered	Macroscopic: The ash is densely fused and highly resistant to manual disintegration. Stereo microscope: Most of the ash has melted, but the organic structure remains clearly visible, and the ash overall porosity persists.
4	Molten	Macroscopic: The ash is melted and cannot be manually broken apart. Stereo microscope: There are minimal or no remnants of organic structure visible, and the compacted ash contains a large amount of molten material that has flowed into the original structure's pores.

RESULTS AND DISCUSSION

Ash Removal

The statistical t-test revealed significant differences between the two groups studied: Torrefaction-Leaching (AB) and Leaching-Torrefaction (BA). For each test, the level of probability that was set at $p < 0.01$ revealed statistically significant differences in ash content for different combination treatments for all the lignocellulosic biomasses used in this study. Table 4 shows that generally the ash content of the various samples was reduced by incorporating the acetic acid leaching technique in the torrefaction treatment. The ash content yield of treated lignocellulosic biomass from AB combination (torrefaction – leaching) ranged 0.65 to 1.52% and for the BA combination treatment (leaching – torrefaction) the ash content ranged 0.38 to 1.05%. The ash generated from a combined AB treatment was significantly reduced compared to untreated or torrefaction and leaching alone. As expected, leaching followed by torrefaction (BA combination) generated an acceptably low ash content, ranging from 0.38 to 1.05%. These values however are still higher when compared with those recorded for when using leaching alone, 0.21 to 0.82%. Cen *et al.* (2021) conducted an experiment by combining leaching, torrefaction, and pyrolysis treatment. The research by Cen *et al.* (2021) revealed that the decrease in total ash content is attributable to both the initial leaching pretreatments and subsequent reduction through devolatilization, where inorganic elements like chlorine, phosphorus, potassium, and sulfur are vaporized during torrefaction and pyrolysis.

Table 4. Ash Content of Lignocellulosic Samples after Combination Treatment

Lignocellulosic biomass	Ash Content (%)					p-value
	Untreated	Torrefaction (A)	Leaching (B)	Torrefaction-Leaching (AB)*	Leaching-Torrefaction (BA)*	
<i>Acacia</i> spp.	1.71	2.18	0.39	0.89b	0.52a	<0.001
<i>Paraserianthes falcataria</i>	1.46	1.98	0.23	0.74b	0.42a	<0.001
<i>Macaranga</i> spp.	2.10	3.42	0.39	1.52b	1.05a	<0.001
<i>Endospermum</i> spp.	1.27	1.78	0.21	0.75b	0.38a	<0.001
EFB	5.96	6.36	0.82	2.04b	0.96a	<0.001
OPT	1.33	2.05	0.53	1.08b	0.63a	<0.001

Note: *Means followed by the different letter in the same row of a species are significantly different at $P \leq 0.05$

Table 5. Mass Loss of Lignocellulosic Samples After Combination Treatment

Lignocellulosic biomass	Mass Loss (%)				p-value
	Torrefaction (A)	Leaching (B)	Torrefaction-Leaching (AB)*	Leaching-Torrefaction (BA)*	
<i>Acacia</i> spp.	10.12	2.09	13.58 ^b	13.78 ^a	<0.05
<i>Paraserianthes falcataria</i>	6.18	2.19	8.63 ^b	9.16 ^a	<0.05
<i>Macaranga</i> spp.	13.41	3.08	15.84 ^b	15.94 ^a	<0.05
<i>Endospermum</i> spp.	9.73	1.96	10.53 ^b	10.73 ^a	<0.001
EFB	9.55	10.41	19.31 ^b	20.29 ^a	<0.001
OPT	14.94	14.97	27.63 ^b	28.95 ^a	<0.001

Note: *Means followed by the different letter in the same row of a species are significantly different at $P \leq 0.05$

Table 6. Higher Heating Value of Lignocellulosic Biomass After Combination Treatment

Lignocellulosic biomass	Higher Heating Value (MJ/kg)					p-value
	Untreated	Torrefaction (A)	Leaching (B)	Torrefaction-Leaching (AB)*	Leaching-Torrefaction (BA)*	
<i>Acacia</i> spp.	18.28	25.96	18.75	25.54b	25.98a	<0.001
<i>Paraserianthes falcataria</i>	18.01	19.13	18.12	18.86b	19.08a	<0.05
<i>Macaranga</i> spp.	17.94	27.19	18.15	25.64b	25.78a	<0.05
<i>Endospermum</i> spp.	18.35	19.79	18.43	19.42b	19.68a	<0.05
EFB	18.06	23.08	18.47	22.55b	22.82a	<0.001
OPT	17.18	22.22	16.53	22.13a	22.50b	<0.05

Note: *Means followed by the different letter in the same row of a species are significantly different at $P \leq 0.05$

The extent of leaching became diminished as the biomass underwent thermal treatment prior to leaching in the AB combination treatment (torrefaction followed by leaching). Comparing the ash yield reduction of samples from leaching treatment only (B treatment) and samples from AB treatment, the results revealed higher removal efficiencies using acetic acid were observed from untorrefied samples (raw biomass) compared to torrefied samples. Leaching treatment resulted in an ash yield reduction of 60 to 86% from the leaching of raw biomass, while the ash yield reduction from leaching of torrefied biomass ranged from 47 to 68%. The decrease in effectiveness of removing ash from torrefied biomass may be attributed to the physical and chemical alterations that impact the char matrix, as well as a shift in how ash-forming elements are distributed following thermal degradation. Following torrefaction treatment, the originally leachable ash is most probably transformed into increasingly stable forms such as carbonates and/or oxides, and these shifts reduce the solubility in mild acid. Cai *et al.* (2017) noted that as lignin and hemicelluloses undergo changes during thermal degradation, a molten-phase intermediate results. This intermediate traps the ash components, making it more challenging to remove the ash as char is formed. Madanayake *et al.* (2016) conducted a microscopic examination, which demonstrated that ash-forming components such as potassium become attached to the organic matrix following thermal processing with the potassium is connected to the organic framework. Madanayake *et al.* (2016) also explained that inorganic compounds which remain after torrefaction are heavier and are either attached onto the biomass structure or insoluble in water; thus they are resistant to the leaching process.

Mass Loss

Table 5 illustrates the reduction in mass of the lignocellulosic biomass after undergoing various treatment methods. The statistical t-test demonstrated that the mean values differed significantly for the mass loss value between AB combination treatment and BA combination treatment. The mass loss caused by the leaching treatment either due to the ash forming elements (inorganic) or organic elements removal should not be ignored. Total mass loss was higher than the percentage of ash removed for both combination treatment processes, resulting in a lower solid biofuel yield. This could be due to the continuous chemical and thermal treatments, which created a severe condition leading to the degradation of organic matter. Torrefaction requires the lignocellulosic biomass to be exposed to high heat for a long time, whilst during leaching, the lignocellulosic biomass was soaked in mild acid for quite a time. Such treatments appear to be quite severe irrespective of AB or BA combination treatment, with mass loss ranging from 8.63% to 28.95%. The most affected specimen was OPT, irrespective of the type of treatment used. The most stable material was *Paraserianthes falcataria* wood.

Obviously, using BA combination treatment, *i.e.* leaching followed by torrefaction, degraded the lignocelluloses significantly, as made apparent by the high mass loss. This observation was in agreement with Shoulafar *et al.* (2016), who showed that acid leaching prior to torrefaction led to slight shift in the thermal degradation of hemicelluloses and cellulose to lower temperatures and favor the thermal degradation during torrefaction treatment. Besides, the higher mass loss could be contributed from the higher ash removed using AB combination treatment compared to BA combination treatment. In fact, AB combination treatment resulted with a higher mass loss if the amount of ash content removed is deducted from the total mass loss. This mass loss refers to the loss of organic elements in the lignocellulosic biomass and in a smaller amount as volatile gas during the treatment.

Higher Heating Value (HHV)

By incorporating the torrefaction and leaching treatment, the higher heating value was in the range of 19 to 27 MJ/kg, as shown in Table 6. The determined HHV of the AB and BA combination treatments were compared using a t-test. The p-value was less than 0.05, indicating statistically significant differences between the treatments. Slightly lower heating value was observed for samples treated with combined treatment process compared to torrefied samples. The BA combination treatment resulted in a notably higher HHV for all varieties of lignocellulosic biomass utilised in this study. Thermal pretreatment has been found to result in decomposition of a significant part of the lignocellulosic biomass fraction into soluble and less complex molecules (Cai *et al.* 2017; Zhang *et al.* 2018). In the AB combination treatment process, torrefaction was positioned before the leaching treatment, with most of the ash-forming elements (inorganic materials) having become resistant to the leaching process. This could be due to the physicochemical changes of the organic and inorganic materials during thermal treatment, as reported by Cai *et al.* (2017). This results a higher concentration of inorganic materials that have no contribution to the HHV, and this directly reduced the HHV of the lignocellulosic biomass from AB combination treatment.

Ash Forming Elements Contents

Table 7 shows the contents of ash-forming elements of the treated lignocellulosic samples. The AB combination treatment appeared to be less effective than the BA combination treatment with respect to ash removal. The differences in removal efficiency of ash forming elements was attributed to the variation in leaching treatment; on natural/raw condition (BA combination treatment) or on torrefied condition (AB combination treatment). The ash content of different samples was significantly decreased through the use of acetic acid leaching. The degree to which various elements in the ash are removed depends mainly on how these elements are present in the lignocellulosic biomass samples. Torrefaction might change the bonds between inorganics and the lignocellulosic structure, causing higher concentrations of ash forming elements in the AB combination treatment (torrefaction followed by leaching method). Most of the ash-forming elements were retained in the torrefied material.

The decrease in ash content was mainly due to the leaching of K. The amount of K was significantly removed from all the pretreated samples. The amount of K in the untreated lignocellulosic biomass was much higher than the torrefied samples. Approximately 64 to 94% of the amount of K was able to be removed *via* leaching (AB combination treatment) from the untreated lignocellulosic biomass. Nonetheless, this percentage was less than the percentage of single leaching treatments; with 93 to 99% of K removed. Lignocellulose biomass treated with BA combination treatment had lower K content than that of treated by AB combination treatment; however, the K content was higher than the acetic acid leached lignocellulosic biomass. During torrefaction, K might have been bound to the biochar matrix or transformed into oxides, thus making it difficult to be leached out. This may lead to higher K concentration in materials of AB combination treatment than that of BA combination treatment. It has been reported that after heat treatment, the potassium is bound much more strongly to the char than in the raw lignocellulosic biomass (Shoulaifar *et al.* 2016; Zhang *et al.* 2018). It was also reported by Shoulaifar *et al.* (2016) that K accelerates the decomposition of biomass during torrefaction, with the rate of mass loss rising as the concentration of K increases. This helps to explain the results of the lower organic decomposition from BA combination treatment,

as much of the K content was removed from the leaching treatment prior to the torrefaction treatment.

Proportions of the element levels relative to each other can have a stronger influence on the ash sintering characteristics than the absolute levels of certain elements (Chin *et al.* 2018; Lebendig and Muller 2022). K is readily accommodated into ash residues rich in silicate melts for lignocellulosic biomass with high K and Si. Due to high availability of K in the lignocellulosic biomass, the Si in the solid biofuel is readily involved in forming of low temperature and high viscous molten K-silicates that initiate ash sintering and slagging. A negative effect of K and a positive effect of Ca and Mg on ash sintering characteristic of lignocellulosic biomass have been previously reported by Chin *et al.* (2018). An increasing K/(Ca + Mg) ratio increased the chances of ash sintering/melting for the lignocellulosic biomass.

Table 7. Major Ash Forming Elements of Lignocellulosic Biomass After Combination Treatment

Ash Forming Elements	Concentration (mg/kg)				
	Untreated	Torrefaction (A)	Acetic acid leaching (B)	Torrefaction – Leaching (AB Combination)	Leaching – Torrefaction (BA Combination)
<i>Acacia spp.</i>					
K	1850	2720	64.8	973	685
Ca	1040	1290	647	984	831
Mg	230	193	9.94	177	46.0
P	58.6	75.8	5.07	25.8	27.2
Si	5.82	6.96	2.83	5.27	4.58
K/(Ca + Mg)	1.43	2.10	0.10	0.84	0.78
<i>Paraserianthes falcataria</i>					
K	1660	1920	30.5	407	248
Ca	1850	2030	863	1390	1080
Mg	406	528	12.6	330	46.0
P	245	296	40.5	102	92.3
Si	1.92	2.73	Not detected	1.28	0.80
K/(Ca + Mg)	0.73	0.75	0.03	0.24	0.22
<i>Macaranga spp.</i>					
K	1860	2100	90.5	935	542
Ca	2660	2790	1450	1050	821
Mg	967	998	59.1	783	325
P	104	105	35.8	60.4	41.6
Si	35.3	30.7	30.4	7.35	5.51
K/(Ca + Mg)	0.51	0.56	0.06	0.51	0.47
<i>Endospermum spp.</i>					
K	1620	3900	10.3	674	364
Ca	1110	1360	458	893	738
Mg	211	266	5.44	96.4	48.2
P	81.8	176	37.3	72.4	56.9
Si	5.91	6.58	3.88	4.97	4.60
K/(Ca + Mg)	1.23	2.41	0.02	0.68	0.46
EFB					

K	12200	15000	124	545	309
Ca	799	854	182	382	363
Mg	1070	1350	27.5	125	87.7
P	409	397	79.5	255	243
Si	71.6	81.5	32.7	48.5	43.3
K/(Ca + Mg)	6.53	6.81	0.59	1.08	0.69
OPT					
K	2000	3080	19.0	389	331
Ca	903	992	71.6	357	384
Mg	735	753	17.4	127	54.8
P	210	232	28.0	63.9	39.4
Si	10.7	10.4	11.8	10.8	10.7
K/(Ca + Mg)	1.22	1.77	0.21	0.80	0.75

Alkaline earth metals, notably Mg and Ca, can be removed from the raw lignocellulosic biomass through acetic acid leaching, but the extent of leaching diminishes with torrefaction treatment. After torrefaction, the removal efficiency of Ca and Mg through acetic acid leaching was substantially reduced. Following torrefaction, the originally leachable Mg was most probably altered into compounds or organically bound form such as carbonates and /or oxides which are hardly leachable (Zhang *et al.* 2018). Additionally, the partial leaching of Ca, which is the dominant inorganic species in the lignocellulosic biomass, suggests that Ca is largely in insoluble forms such as carboxylates. Madanayake *et al.* (2016) also noted that thermal treatment modified the soluble P into some insoluble minerals (such as apatite or other complex compounds). All of these changes can explain the higher concentration of ash forming elements in treated lignocellulosic biomass AB combination treatment. Although torrefaction treatment will generally increase the ash content of the leached samples (as in BA combination treatment), but due to the large fractions of ash forming elements that had been removed in the first stage (leaching treatment), this mitigated the adverse effects on the ash content from torrefaction treatment in the 2nd stage.

Ash Melting Characteristics

Comparative analysis showed the benefits of combining leaching treatment with the torrefaction process to improve ash melting characteristics in biomass. As shown in Table 8, all lignocellulosic biomass treated with both combination treatments displayed a positive effect on preventing the melt polymerization tendency of the ash at high combustion temperature (>700 °C), compared to lignocellulosic biomass that solely undergone torrefaction.

Torrefied *Acacia* spp., *Endospermum* spp and both oil palm biomasses will cause severe problems during combustion. However, combining leaching and torrefaction treatment (BA combination treatment) had reduced the risk of ash sintering. It is anticipated that lignocellulosic biomass will require pretreatment, and that a combined torrefaction and leaching are now anticipated to pose no issues in terms of fouling when combusted at temperatures below 1000 °C, except for EFB. EFB treated with torrefaction followed by leaching treatment (AB combination treatment) vastly improved the ash sintering but still potentially problematic.

Ashes of all the four fast-growing timber species and OPT were in a loose form even after heated under temperature 1000 °C. Applying the BA combination treatment obviously reduced the sintering degree of the EFB ash. At 1000 °C, EFB treated with the combination of AB resulted in strongly sintered ash, whereas the BA combination treatment produced a slightly sintered ash. This can be partly credited to the retention of ash elements within the char matrix, which are immune to the leaching process in the AB combination treatment. This occurs after a molten phase of EFB is formed during combustion as a result of changes experienced by alkali metals at high temperatures.

Table 8. Ash Sintering Severity Index of Lignocellulosic Biomass Combusted at 700, 800, 900, and 1000 °C

Ash Heating Temperature	Untreated	Torrefaction (A)	Leaching (B)	Torrefaction-Leaching (AB combination)	Leaching-Torrefaction (BA combination)
<i>Acacia</i> spp.					
700	3	3	1	1	1
800	3	3	1	1	1
900	4	4	1	1	1
1000	4	4	1	2	1
<i>Paraserianthes falcataria</i>					
700	1	1	1	1	1
800	1	1	1	1	1
900	1	1	1	1	1
1000	2	2	1	1	1
<i>Macaranga</i> spp.					
700	1	1	1	1	1
800	1	1	1	1	1
900	1	1	1	1	1
1000	1	1	1	1	1
<i>Endospermum</i> spp.					
700	2	3	1	1	1
800	3	4	1	1	1
900	4	4	1	2	1
1000	4	4	1	2	1
EFB					
700	3	4	1	1	1
800	4	4	1	1	1
900	4	4	1	2	1
1000	4	4	2	3	2
700	2	3	1	1	1
800	3	4	1	1	1
900	4	4	1	2	1
1000	4	4	1	2	1

Note: Ash severity index: (1) Loose; (2) Slightly sintered; (3) Strongly sintered; (4) Molten. Refer to Table 3 for the ash sintering classification

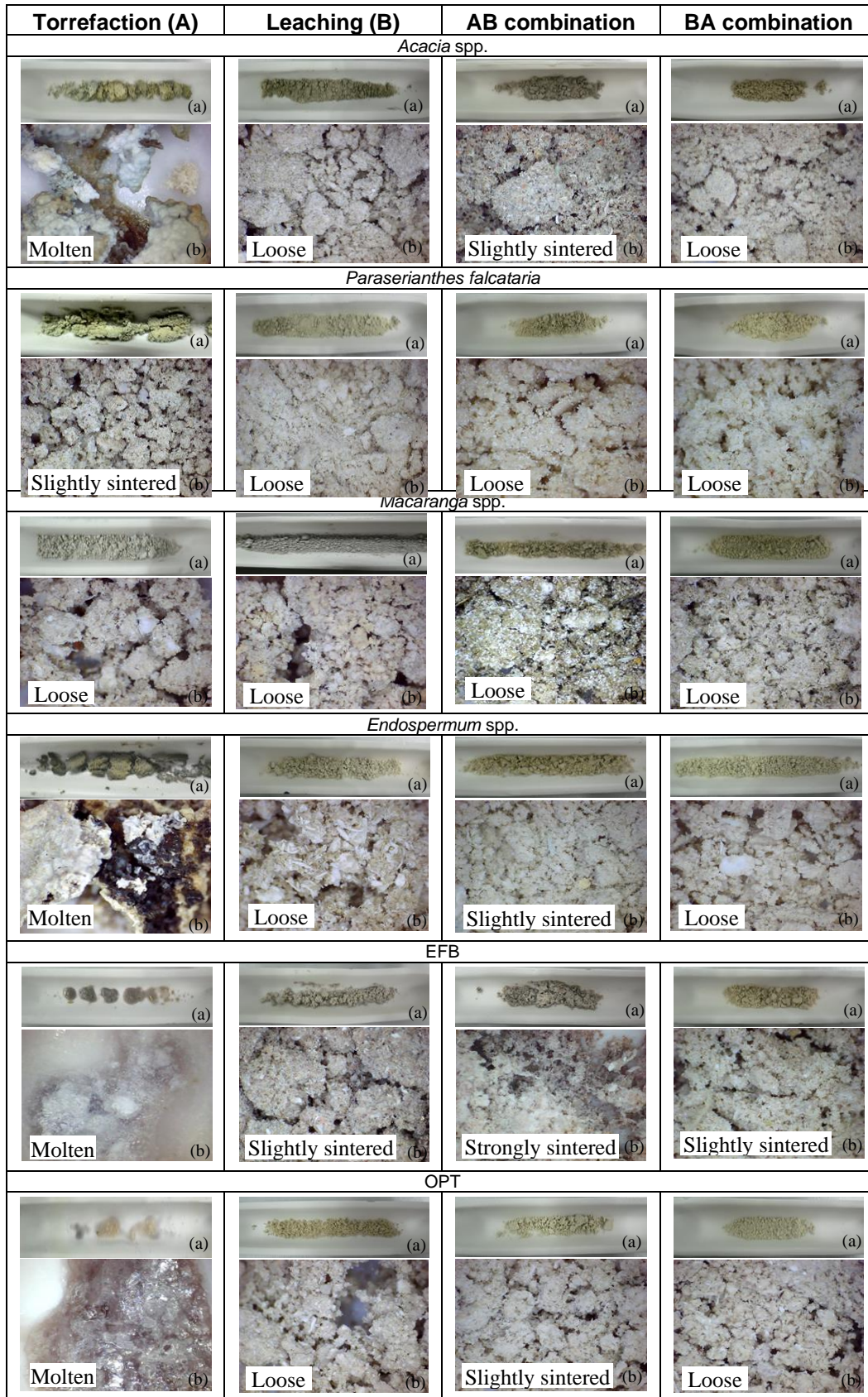


Fig. 1. Macroscopic (a) & microscopic views - 40X (b) of ash formation from biomass at 1000 °C

Further research on the BA combination treatment is needed to optimise the processing parameters with the observed changes in decomposition of organic matters from the torrefaction treatment with the reduction of K from the initial stage of leaching treatment. The practical impact of a lignocellulosic biomass shifting from a high K feedstock to a lower one through leaching treatment at the initial stage is that the subsequent torrefaction temperature or time may need to be adjusted higher than the optimum parameters applied on unleached lignocellulosic biomass in order to optimize the potential for these materials as a direct replacement for coal with comparable performance.

CONCLUSIONS

1. The study showed that by applying leaching procedure followed by torrefaction treatment generated an improved quality biomass solid biofuel, particularly with respect to the higher heating value (HHV), ash content, and ash melting temperature compared to the fuel treated with singular treatment; torrefaction or leaching alone.
2. Leaching gave rise to a remarkable increment in the ash melting temperature of torrefied lignocellulosic biomass. It was particularly beneficial for *Acacia* spp, *Endospermum* spp., empty fruit bunch (EFB) and oil palm trunk (OPT), for which the ash melting temperature increased to over 1000 °C. This suggests that acetic acid leaching is an important treatment for the preparation of torrefied fuels.
3. However, combination treatments process also led to a higher mass loss. The relative HHV loss is inevitable due to the mass loss of the organic matter during torrefaction and leaching treatment. Acetic acid leaching on torrefied lignocellulosic biomass was less effective than on raw lignocellulosic biomass. Most ash forming elements in the torrefied samples may be transformed into increasingly stable forms that are difficult to be leached. Thus, lower ash content was observed on samples undergone leaching followed by torrefaction (BA combination treatment).
4. Prior to torrefaction, leaching was found to be a more effective approach. It led to a considerable increase in the higher heating value of the lignocellulosic biomass and enhanced its ash melting characteristics.

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