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Thermochemical Behavior of Alkali Pretreated Biomass – a Thermogravimetric and Py-GC/FID study

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ABSTRACT

The acidity of biomass pyrolysis oils (bio-oils) is problematic and may contribute to coking and catalyst deactivation during hydrotreating, reducing catalyst performance and the extent of hydrodeoxygenation. Clogging of trickle bed hydrotreatment reactors due to coke formation is the main hurdle that needs to be addressed to refine pyrolysis oils. Acetic acid is the highest concentration acid found in bio-oils and is a product of hemicellulose pyrolysis. By applying an alkali biomass pretreatment, commonly used in the pulp and paper industry for eliminating hemicellulose from lignocellulosic biomass, acetic acid production can be significantly reduced during pyrolysis. The extracted portions can be used as high-value co-products such as bio-fiber gum for use in food and non-food industries. To reduce bio-oil acidity, this study investigated the pyrolysis behavior of parent and alkali pretreated biomasses using thermogravimetric (TG) analyses and Py-GC/FID analyses. The TG results were analyzed with the aid of Friedman kinetics. Four energy crops and crop residues were studied: switchgrass, sorghum biomass, corn stover, and barley straw. The TG analysis shows significant differences associated with the removal of the hemicellulose fraction. However, similar overall activation energies associated with depolymerization reactions, mainly of cellulose and lignin, were observed for the parent and pretreated biomasses for all of the biomasses except sorghum. For sorghum, the parent biomass required a higher activation energy for thermal decomposition than the alkali pretreated sorghum, which was attributed to its high protein content. The Py-GC/FID results showed a significant decrease in acetic acid concentrations after alkali extraction, which was attributed to the lower hemicellulose concentration in the biomass after the extraction process. The alkali biomass pretreatment studied is a promising approach for reducing bio-oil acidity, however, further analysis is needed to determine the carbon efficiency of bio-oils produced using this approach.

Keywords: alkali extraction, pretreatment, acetic acid, pyrolysis, hydrotreating

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1. Introduction

As a renewable alternative to petroleum liquids, the use of bio-oil, a liquid product of biomass pyrolysis, as a hydrocarbon feedstock for industrial chemical/fuel production can help decarbonize the chemical industry. Generally, bio-oils are highly oxygenated and corrosive and require upgrading to improve their stability and chemical properties before co-refining in existing petroleum refining infrastructure [1, 2]. Fast pyrolysis followed by hydrotreating is one approach to deoxygenate bio-oils and improve their stability during storage and transport. However, the acids compete for catalytic active sites reducing the rate of hydrogenation. Addition, aromatization, and polycondensation reactions, which are responsible for coke formation also compete with hydrogenation. Coke formation gradually decreases catalyst reactivity over time, contributes to clogging, and increases the pressure drop in trickle bed reactors [3]. In addition, acidic compounds in the bio-oil are particularly recalcitrant to hydrotreating, which is an important technical limitation that will be addressed in this study. During pyrolysis, acids are mainly recovered in the aqueous phase; however, due to the wide composition of organics and the high water content, the valorization of organics from the aqueous phase is energy intensive and therefore the aqueous phase is often treated as wastewater [4]. To maximize the recovery of valuable products from biomass and to avoid the process challenges associated with acids, new approaches are needed to reduce the bio-oil acidity.

The chemical conversion mechanisms of bio-oil functional groups during upgrading have been previously studied [5]. Compared to other oxygenated functional groups like aldehydes, ketones, and phenols, the difficulty of carboxylic acid, namely acetic acid, to be converted during hydrotreating has been reported by multiple authors. Choi et al. studied hydrotreating reactions over a 5 wt. % Ru/C catalyst and found that aldehydes and ketones were directly hydrogenated to alcohols. In contrast, acetic acid was removed via esterification with alcohols, resulting in less acid conversion with the tested catalyst [3]. For effective conversion of all oxygenated compounds, the authors suggest both a hydrogenation catalyst and an acid/base catalyst for esterification may be required, adding cost to the process. This observation was consistent with results reported by Stankovikj et al, who also found less conversion extent of acetic acids during hydrotreating using a Ru/C catalyst [5]. Guitierrez-Rubio et al (2019) also observed a reduction in deoxygenation of guaiacol in the presence of acetic acid [6]. Goodwin et al (2015) studied the hydrodeoxygenation of bio-oil model compounds and free fatty acids and also found a decrease in hydrodeoxygenation reactivity with increasing free fatty acid concentration in the feed [7]. Poissonier et al (2022) studied the competitive adsorption and reactivities of oxygenated compounds with different functionality and chain length effects during hydrodeoxygenation with NiMo and CoMo [8]. The authors found that compounds with aldehyde had higher reactivities. The presence of carboxylic acids in feed mixtures shifted conversion to higher temperatures due to the competitive adsorption of carboxylic acids on active sites. This is one of the major technical challenges of this bio-oil stabilization approach that has not been adequately addressed. Many studies have investigated different catalyst formulations or have proposed multi-step upgrading approaches attempting to eliminate acids from bio-oils; however, few studies have suggested removal of the acid-forming components from the biomass prior to pyrolysis.

Acetic acid is typically the most concentrated acidic component of bio-oils and is largely a product of hemicellulose pyrolysis. Removal of hemicellulose from biomass prior to pyrolysis can minimize formation of acetic acid leading to a less acidic bio-oil that can be more easily hydrotreated. Hemicelluloses are easily hydrolyzed from the cell wall compared to cellulose and lignin and, therefore, can be easily extracted from lignocellulosic biomass for various food (e.g. emulsifier [9], non-caloric food ingredient [10]) and non-food (e.g. ethanol [11], adhesives [12], films [13], hydrogels [13]) applications. It is also a potential animal feed as a supplement to grains as hemicellulose is easily digested by livestock compared to whole lignocellulosic biomass. These value-added uses of hemicellulose could help improve the economics and justify the cost of biomass pretreatment prior to pyrolysis and upgrading.

Various chemical pretreatment methods have been developed for hemicellulose extraction from biomass including liquid hot water, acid, alkali, organic acid, and ionic liquid pretreatments [14], and a few studies have studied the effects of biomass pretreatment methods on pyrolysis products. For example, hot water treatment has been previously shown to reduce biomass hemicellulose and reduces bio-oil acidity after pyrolysis [15, 16]. Alkali pretreatment using dilute sodium hydroxide is an effective and inexpensive process commonly used in the paper and pulp industry for hemicellulose removal and disruption of lignin structure, however, few works have studied pyrolysis of alkali pretreated biomass as an approach to reduce bio-oil acidity. In one study, alkaline pretreatment using NaOH led to similar but marginally greater bio-oil yield than acidic pretreatment after pyrolysis at an optimized temperature of 350 °C [17], while others have reported lower yields after alkali pretreatment compared to acid or hot water treatments [18]. These differences are likely due to discrepancies between pretreatment conditions and pyrolysis conditions between studies. By removing hemicellulose from lignocellulosic biomass, alkali pretreated biomass has the potential to reduce bio-oil acidity compared to whole-biomass pyrolysis, which could reduce the catalytic burden of subsequent bio-oil upgrading processes.

It is known that alkali pretreatment alters the biomass chemical composition by partial hemicellulose removal, partial lignin degradation, and cellulose crystallinity alteration [19]. Alkali cleaves lignin-carbohydrate ester linkages, which effectively hydrolyzes hemicellulose and breaks down lignin to various degrees, depending on biomass type [20]. In herbaceous biomass, such as those considered in the present study, some lignin-carbohydrate bonds are alkali-labile, such as ester, while alkali-stable bonds also exist, such as glycosidic and ether linkages [20]. As a result, the degree of hemicellulose hydrolysis and delignification varies depending on biomass composition. While alkali and other chemical extractions have been widely studied as a pretreatment to improve biochemical conversion processes, few have studied chemically pretreated biomass as a feedstock for pyrolysis. This study investigates the effect of alkali pretreatment on the thermochemical decomposition behavior during fast pyrolysis, by analyzing the pyrolysis reaction kinetics and pyrolysis product composition from alkali pretreated biomass. Four different herbaceous biomasses were investigated using kinetic and analytical (Py-GC/FID) methods before and after alkaline pretreatment. Comparison of pyrolysis reaction kinetics during biomass decomposition is useful for design and optimization of a pyrolysis process while analytical pyrolysis studies can help determine selectivity of products from the parent and pretreated biomasses.

2. Methods

2.1 Materials

Herbaceous biomass representing energy crops (switchgrass and sorghum biomass) and agricultural crop residues (corn stover and barley straw) were selected for this study. The parent biomass samples were used as-received while the pretreated samples were prepared by alkali extraction.

Preparation of alkali-extracted biomass samples was carried out according to the procedure described by Yadav et al. [21], Qiu et al. [22], and Yadav and Hicks [10], which is summarized by the schematic in Figure 1. First, dried and milled biomass (20 mesh) was de-oiled by hexane extraction. The de-oiled material was de-starched by treatment with heat-stable α-amylase (Termamyl®) at 85 °C with mechanical stirring for 1 hour. Then the pH of the slurry was raised to 11.5 by adding 50% sodium hydroxide and stirred using a mechanical stirrer at 85 °C for an additional 30 minutes. During the reaction, pH was maintained at 11.5 by adding 50% NaOH and the reaction volume was maintained by adding water as needed to compensate water loss due to evaporation. The hot slurry was immediately sheared using a high speed Polytron (PT 10/35 GT) equipped with 12 mm probe (Kinematica Inc., Bohemia, NY) at 10,000 rpm for 30 minutes. The solid residue was separated from the reaction mixture by centrifugation at 14,000 X g for 10 minutes, suspended in 2 L boiling water and stirred using a mechanical stirrer for 5 minutes. The hot suspension was again sheared at 10,000 rpm for 5 minutes. The sheared material was allowed to cool at room temperature and centrifuged at 14,000 X g for 10 minutes to separate the solid cellulosic residue. The hot water washing and shearing cycles of the cellulosic residue were repeated until a clear supernatant was obtained. The final solid cellulosic residue was collected, suspended in water, and dried by drum drying technique. The supernatants from all centrifugation steps, which contained hemicelluloses were discarded. The weight percent of the components present in the studied biomass is presented in Table 1. Protein content (N X 6.25) was determined following AACC Approved Method 46-30.01 [23], using Flash 2000 protein Analyzer (CE Elantech, Inc., Lakewood, NJ). The alkali extracted cellulosic residue contains mainly cellulose and lignin and is referred to as the alkali-pretreated or alkali extracted biomass throughout this paper.

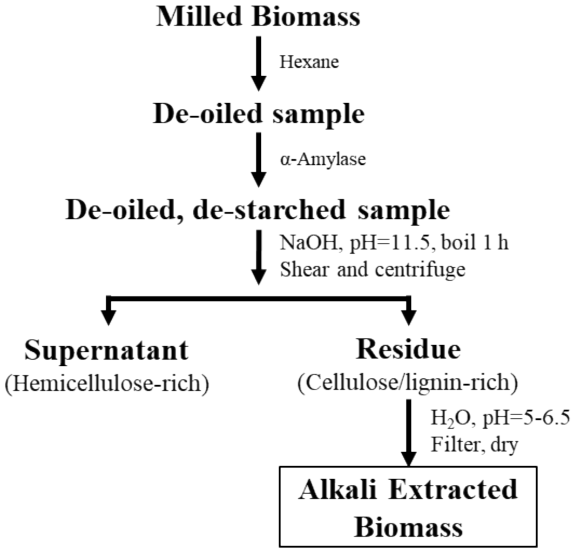

Figure 1: Schematic of the alkali extraction procedure used to prepared the alkali extracted biomass.

Table 1: Isolated components of switchgrass, sorghum biomass, corn stover, and barley straw[a] (reported in wt. % on a dry basis)

Samples	Ash	Protein	Hemicelluloses	Cellulosic residue	Others[b]	Total[c]
Switchgrass	2.8 ± 0.2	2.8 ± 0.1	25.0 ± 0.1	57.4 ± 0.2	7.6	95.6
Sorghum biomass	12.4 ± 1.0	19.0 ± 1.9	23.0 ± 1.8	39.4 ± 3.1	0.0	93.8
Corn stover	9.5	4.4 ± 0.1	35.7	52.2	3.9	105.7
Barley straw	2.4 ± 0.0	2.3 ± 0.1	27.1 ± 0.1	59.6 ± 0.2	3.9	95.3

[a] Weight percent based on the de-oiled biomass samples.

[b] Isolated fractions including hot water extract, oligosaccharides, starch, and acid insoluble lignin are denoted as “others”.

[c] Yields were not corrected for moisture content of the isolated fractions leading to slight overestimation of yields and the reason for a total >100%.

2.2 TG/DTG

Thermogravimetric analysis (TGA) of each parent and alkali pretreated biomass sample was carried out on a Q500 TGA (TA Instruments) for proximate analysis and kinetic modeling. For each analysis, approximately 10 mg of sample was loaded onto a tared platinum pan and heated from 25 to 700 °C under a N_2 atmosphere, then heated to 900 °C under an air atmosphere to combust the residual char. TGA experiments were repeated for four different heating rates: 5, 10, 20, and 30 °C/min. Estimates of volatile matter, fixed carbon, and ash were obtained based on the average of the TGA mass loss data from each heating rate.

The concentration of hemicellulose, cellulose, and lignin in the parent and alkali extracted biomasses were approximated by deconvolution of the DTG curves (10 °C/min) for each biomass, similar to the method described by Saldarriaga [24]. The DTG spectrum was fitted using three gaussian peaks and the fitting was optimized using the Solver analysis tool in Microsoft Excel by minimizing the sum of squares error between the measured and modeled DTG spectrum. For sorghum, a fourth peak centered around 200 °C was observed, attributable to protein in sorghum biomass, and it was accounted as an additional peak during the DTG spectrum fitting. The DTG curve fits for each biomass are presented in Figure S1. The relative peak areas were used to estimate the concentration of hemicellulose, cellulose, and lignin.

2.3 Kinetic modeling

To model the decomposition kinetics of each parent and alkali pretreated biomass sample, the Friedman method was used, which has been shown to provide accurate activation energies for lignocellulosic biomass pyrolysis reactions compared to other methods [25]. TGA mass loss data from 150 to 600 °C were considered in the kinetic analysis. The Friedman method is an isoconversional method, where the degree of conversion is assumed to be constant and the reaction rate is dependent on the reaction temperature. The conversion level, α, is defined as the mass loss at a given temperature over the final overall mass loss according to Equation 1:

$$\alpha = \frac{x_0 - x}{x_0 - x_f} \qquad [1]$$

where x is the sample mass at a given temperature, and the subscript 0 and f represent the initial and final temperature, respectively. The Friedman model is expressed by Equation 2:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left[A * f(\alpha)\right] - \frac{E}{RT} \qquad [2]$$

where $f(\alpha)$ is the conversion function, which is assumed to be constant (i.e., $f(\alpha) = \alpha$), t is the reaction time (s), A is the preexponential factor (s^{-1}), E is the activation energy in (J mol^{-1}), R is the universal gas constant (8.3145 J mol^{-1} K^{-1}), and T is the temperature (K). For a given conversion level, the plot of $ln(d\alpha/dt)$ versus $1/T$ gives a line with the slope $-E/R$.

2.4 Py-GC/FID

A Frontier Labs micropyrolyzer connected with a with a gas chromatograph (Shimadzu GC2010) coupled to a catalytic microreactor (Polyarc, Activated Research Company) that converts all organic compounds to methane before detection by a flame ionization detector (FID) was used to quantify the pyrolysis volatile composition. Separate identical experiments using Py-GC/MS (Frontier Laboratories, Shimadzu) were used to identify the compounds. For a typical analysis, an approximately 500 µg sample was weighed into a steel cup and loaded into the auto sampler of the instrument. The auto sampler dropped the sample cup into a 550 °C micropyrolyzer (Multi-Shot Pyrolyzer EGA/PY 3030D, Frontier Laboratories Ltd), which was connected inline to a GC. The GC inlet temperature was held at 280 °C and a 2.5 mL/min flow of helium was used as a carrier gas. The pyrolysis gases were separated by means of a 0.25 mm I.D. x 60 m length midpolarity column (Restek RTX-1701) with a 0.25 µm film thickness and a split ratio of 30:1 was used. The column oven was held at 45 °C for 4 minutes, then heated to 280 °C at a rate of 3 °C/min and held at 280 °C for 20 minutes. After the GC, the Polyarc reactor heated to 300 °C converted the carbon atoms of the organic molecules to methane via oxidation and reduction reactions, then compounds were detected by an FID with detector temperature of 300 °C, H_2 flow rate of 1.5 mL/min, and air flow rate of 350 mL/min. Py-GC/FID analysis was performed for each biomass in triplicate to ensure repeatability. The FID spectra peaks were assigned to compounds previously identified by Py-GC/MS of the same biomass samples by comparison of their mass spectra to the NIST library.

For quantification, integrated peak areas from the FID spectra of the unknown analytes were quantified relative to the integrated peak area of external standard o-cresol. Using a separate analysis of the external standard, the FID response (peak area) was correlated to the carbon concentration in the sample. As the Polyarc reactor enables uniform FID sensitivity of all organic molecules, the correlation established for the external standard was then applied to the FID responses of the unknown analytes to quantify the compounds. Yields of each compound were calculated according to the following equation:

$$C_A = C_s\left(\frac{Area_A}{Area_S}\right)\left(\frac{MW_A}{MW_S}\right)\left(\frac{\#C_S}{\#C_A}\right) \qquad [3]$$

where C, Area, MW, and #C are the mass concentration, integrated peak area, molecular weight, and carbon number, respectively, and the subscripts A and S represent the analyte and standard, respectively. For the alkali pretreated biomasses, the compound yields were normalized to the mass fraction of biomass residue recovered after the pretreatment, which varied from 35-55 wt% of the original biomass (Table 1). The reported component yield values are an average of triplicate analyses for each sample and reported error bars represent +/- one standard deviation.

2.5 Char yield determination

The micropyrolyzer unit of the Py-GC/FID analyzer was used to pyrolyze the biomass samples and char yields were determined gravimetrically. For a typical analysis, a pre-weighed stainless-steel cup was charged with ~1 mg biomass sample and placed at the end of a plunger apparatus which was used to transfer the sample-containing cup into the center of the 550 °C micropyrolyzer. After the sample was pyrolyzed, it was cooled and weighed. The char determination method was repeated three times for each sample to ensure repeatability and the values reported are an average of triplicate char yield determinations. The char yields were used as a component of the mass balance.

3. Results

3.1 Proximate and ultimate analysis

Compared to the parent biomass, the alkali-extracted biomass had a greater volatile matter composition for each of the biomasses except corn stover, which had a slightly less (by 1%) volatile matter after pretreatment (Table 2). The ash composition of the switchgrass and sorghum biomasses decreased after pretreatment by 68% and 59%, respectively, while pretreated corn stover and barley straw had a higher ash composition with an increase of 22% and 50%, respectively, after pretreatment. On net, some ash was removed from all biomasses after extraction when the amount of material extracted is considered.

Based on the estimates for hemicellulose, cellulose, and lignin, about 50-60% of hemicellulose was removed from each of the parent biomasses after alkaline pretreatment. For all biomasses, cellulose concentration increased after pretreatment. According to the lignin estimates, the alkali pretreatment removed the biomass lignin by varying degrees, depending on biomass type, with a decrease of 39.2%, 58.7%, 44.0%, and 71.8% for switchgrass, sorghum, corn stover, and barley straw after alkali extraction. After alkali pretreatment, some lignin is removed while some lignin remains firmly associated with alkali extracted residues due to the presence of both alkali-labile and alkali-stable lignin-carbohydrate ester bonds. High ash composition may inhibit delignification during alkali pretreatment as the alkali reaction with silica to produce silicate is more kinetically favorable than ester bond cleavage [20]. For barley straw, the comparatively large 71.8% decrease in lignin may be due to the low ash content of the parent biomass, suggesting greater selectivity for ester bond cleavage during alkali pretreatment compared to the other biomasses. The large lignin decrease also corresponds to a decrease by about half in fixed carbon for pretreated barley straw as lignin is the main contributor to fixed carbon.

Table 2: Compositional analysis of parent and alkali extracted biomass (SWG: switchgrass, SG: sorghum biomass, CS: corn stover, BS: barley straw). Values in parentheses represent the overall concentration of each component in the alkali extracted biomass.

	SWG	Alk. Ext. SWG	SG	Alk. Ext. SG	CS	Alk. Ext. CS	BS	Alk. Ext. BS

Proximate analysis, %wt, dry basis								
Moisture	6.4 ± 0.1	7.7 ± 0.2	7.2 ± 0.3	7.6 ± 0.2	8.3 ± 0.4	6.9 ± 0.7	8.2 ± 0.2	8.2 ± 0.3
VM	87.7 ± 2.9	89.3 ± 2.3	73.1 ± 2.9	81.8 ± 2.4	83.7 ± 3.0	82.7 ± 1.7	86.7 ± 2.4	91.7 ± 2.7
FC	9.3 ± 2.9	9.7 ± 2.4	17.8 ± 2.5	14.5 ± 2.5	10.7 ± 1.8	10.6 ± 2.0	11.9 ± 2.5	6.1 ± 2.9
Ash	3.1 ± 0.5	1.0 ± 0.1	9.1 ± 1.3	3.7 ± 0.3	5.5 ± 1.5	6.7 ± 0.3	1.4 ± 0.2	2.1 ± 0.2
Ultimate analysis, %wt, dry basis								
C	43.8 ± 0.4	44.2 ± 0.7	40.6 ± 0.4	40.9 ± 0.2	42.9 ± 0.8	42.8 ± 0.2	44.9 ± 0.0	44.6 ± 0.5
H	4.7 ± 0.1	5.8 ± 0.2	4.2 ± 0.3	4.5 ± 0.2	4.7 ± 0.4	4.7 ± 0.7	6.0 ± 0.2	3.7 ± 0.4
N	0.5 ± 0.1	0.4 ± 0.0	1.1 ± 0.0	0.3 ± 0.0	0.8 ± 0.1	0.1 ± 0.1	1.1 ± 0.1	1.4 ± 0.2
O[a]	47.9 ± 0.7	48.7 ± 0.8	44.9 ± 1.4	50.7 ± 0.4	46.1 ± 1.8	45.7 ± 0.8	46.7 ± 0.3	48.2 ± 0.7
Biochemical composition, %wt, dry basis								
Extracted fraction	N/A	38.1	N/A	60.6	N/A	47.8	N/A	40.8
Hemicellulose	49.1	19.4 (33.5)	38.7	19.2 (46.8)	50.3	23.0 (41.0)	52.1	24.9 (41.2)
Cellulose	25.5	24.4 (42.1)	18.3	9.1 (22.1)	24.2	18.0 (32.2)	21.9	27.4 (45.3)
Lignin	22.2	13.5 (23.3)	27.1	11.2 (27.3)	20.0	11.2 (20.0)	24.6	6.9 (11.5)

[a] by difference

3.2 Kinetic modeling

TG and DTG curves were obtained at heating rates of 5, 10, 20, and 30 °C/min for parent and alkali pretreated biomasses. There are clear differences between the DTG curves of the parent and alkali extracted biomasses (Figure 2). The parent biomass DTG has two distinct mass loss regions attributed to hemicellulose decomposition at lower temperatures (200-325 °C) and cellulose decomposition at higher temperatures (325-415 °C). Hemicellulose is the least thermally stable due to the presence of acetyl groups, while cellulose has a crystalline structure giving it greater thermal stability and fast degradation leading to a sharp DTG peak [24]. Lignin begins its decomposition before or during cellulose decomposition and its decomposition is slow and forms a wide, low intensity peak ranging from 250 to 600 °C [24]. After alkali extraction, the intensity of the hemicellulose peak reduces and the cellulose peak intensity increases, indicating loss of hemicellulose as a result of alkali extraction. For sorghum biomass, a DTG peak is observed at approximately 150-250 °C that is not seen for the other biomasses. This result could be due to the mass loss of proteins in the biomass or the relatively higher ash concentration (9.1%), which is known to lower the decomposition temperature of hemicellulose and lignin [26].

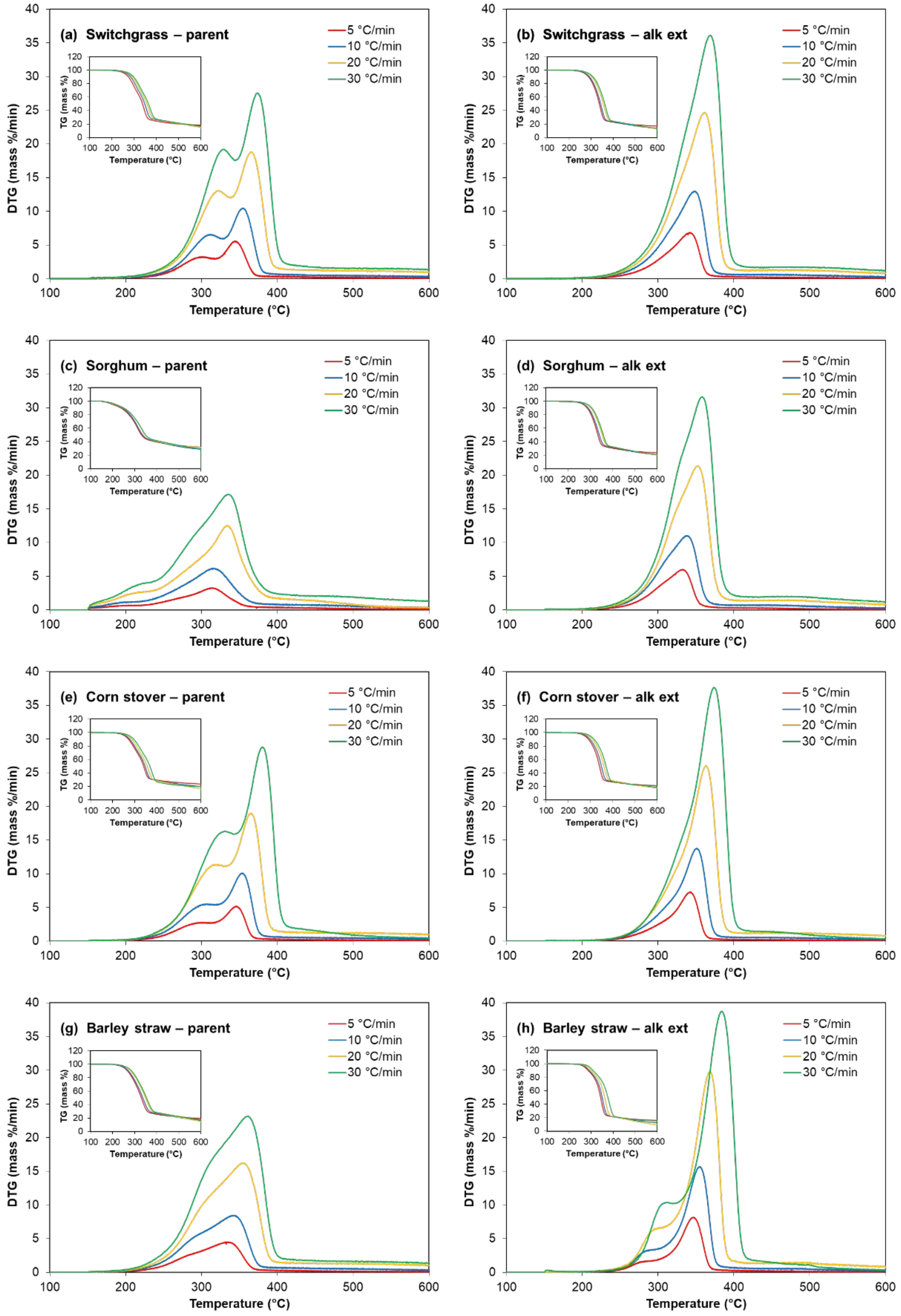

Figure 2: TG (inset) and DTG curves of parent and alkali extracted biomasses obtained at incremental heating rates (5, 10, 20, and 30 °C/min) from 100 to 600 °C.

Activation energies were determined for each conversion level by taking the slope of the Ln(da/dt) vs 1000/T plot (Figure S2). The activation energy of the thermal decomposition of each biomass sample at increasing conversion levels from 0.1 to 0.75 is shown in Figure 3. For switchgrass, corn stover, and barley straw, the activation energy of the parent and alkali extracted biomasses are generally constant across the range of conversion levels from 0.05 to 0.75, with activation energies ranging from 160 to 210 kJ/mol. Sorghum on the other hand exhibits a greater activation energy of the parent biomass (210-280 kJ/mol) and a lower nearly constant activation energy from the alkali-extracted biomass (180-200 kJ/mol). For sorghum, while the extraction resulted in a net loss of hemicellulose on the original biomass basis, the hemicellulose concentration in the residue after extraction was greater than the hemicellulose concentration in the original biomass. Sorghum biomass was the only biomass that had a higher hemicellulose concentration after pretreatment. According to Zong et al (2020), the activation energy of biomass components follows the order of oil > lignin > starch ≈ Hem ≈ protein > cellulose [27]; therefore, the greater hemicellulose content after alkali extraction may have negatively impacted its activation energy. Further, it is expected that sorghum biomass may have a greater oil content than the other biomasses, which may also contribute to the high activation energy of the parent biomass. However, the biomass oil content was not quantified, so this hypothesis was not confirmed. For sorghum, the alkali pretreated biomass resulted in 25% lower (on average) activation energy than the parent biomass, which indicates that less energy is required to decompose the pretreated sample as it has a lower thermal stability. The similar activation energies for the rest of the parent and alkali pretreated biomasses indicates that the biomass maintained its thermal stability after pretreatment.

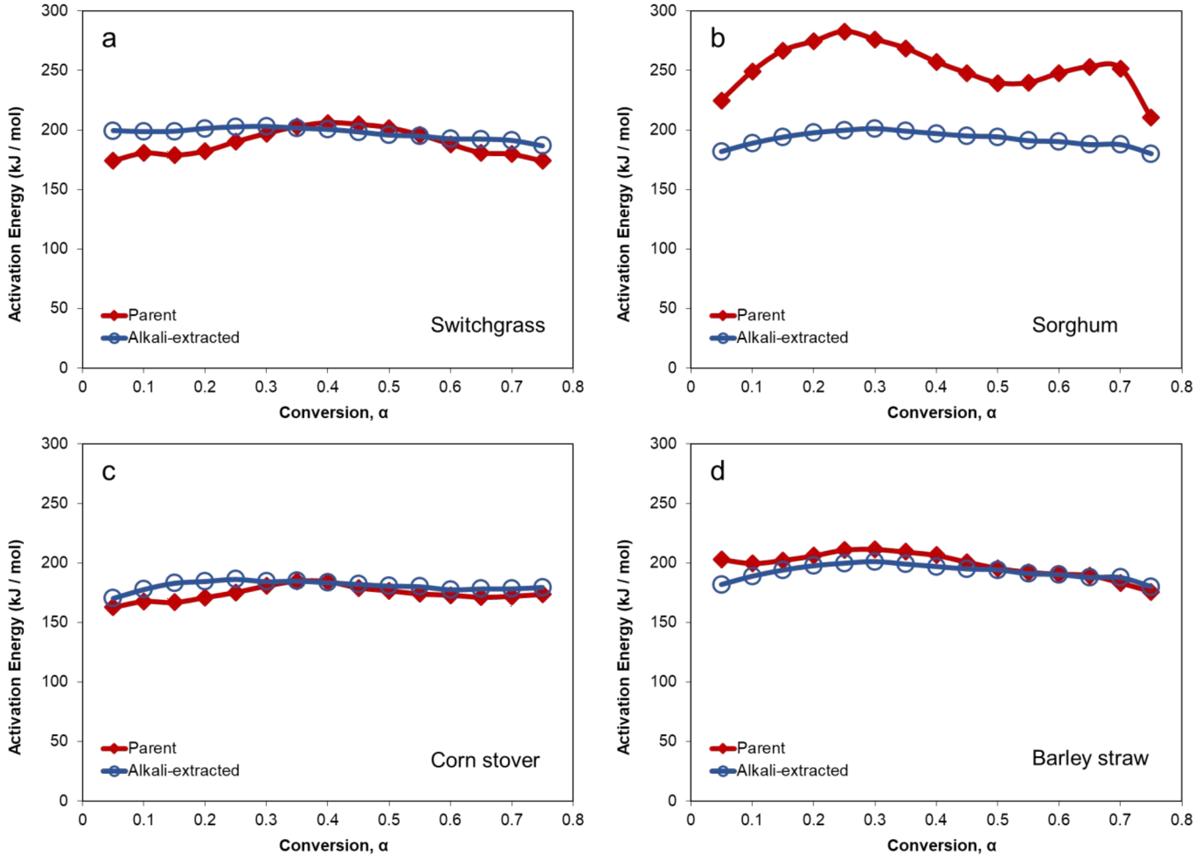

Figure 3: Activation energies of parent and alkali-extracted biomasses as a function of conversion level for switchgrass (a), sorghum (b), corn stover (c), and barley straw (d).

3.3 Mass balance

The mass balance from analytical pyrolysis experiments reveals the differences in overall product yields between the parent and pretreated biomasses (Figure 4). The quantified volatile fraction represents the Py-GC/FID-detectable organic compounds that were included in the quantification (compounds listed in Table S1, S2, S3, and S4). The residual fraction represents the non-quantified Py-GC/FID-detectable volatiles, and non-detectable volatiles including oligomers, water, and non-condensable gases. The relative product yields from the two biomasses are mostly similar, with slightly less char after alkali pretreatment, which could be attributed to lower ash content in the pretreated biomass. The quantified volatile yields from switchgrass, sorghum biomass, and corn stover were similar before and after pretreatment, while pretreated barley straw, on the other hand, had a lower lignin concentration and the greatest increase in cellulose concentration out of all the biomasses leading to the 11% increase in quantified volatiles.

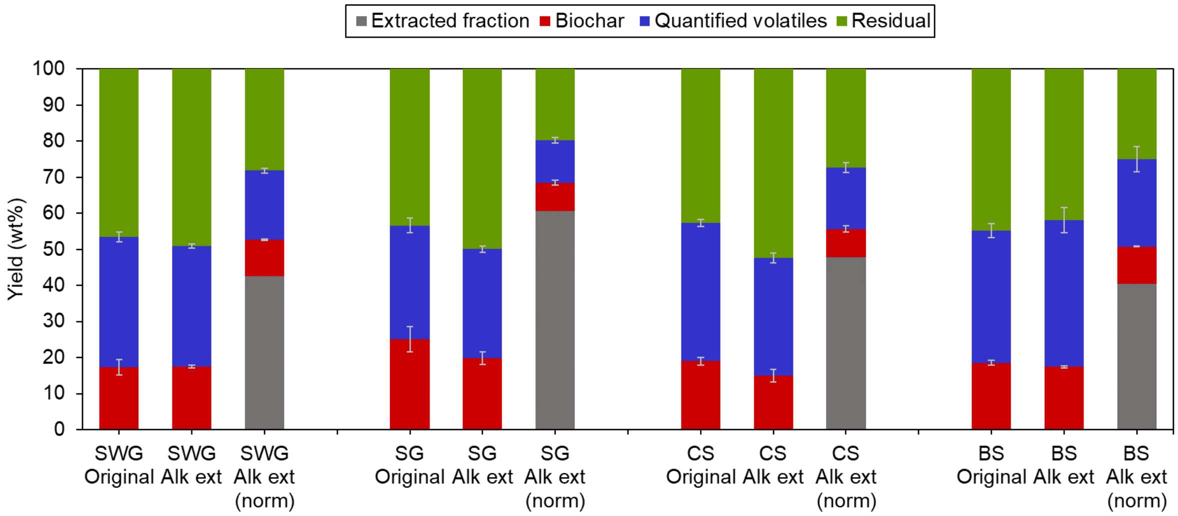

Figure 4: Mass balance of products from analytical pyrolysis experiments with switchgrass (SWG), sorghum biomass (SG), corn stover (CS), and barley straw (BS)

When the extracted fraction is taken into account, the quantified volatiles and biochar yields from alkali pretreated biomass are significantly lower. The total quantified volatile yields on a normalized basis from the pretreated biomasses (SWG: 19.2, SG: 11.9, CS: 17.0, BS: 24.2 g/100 g) were 34 – 62% lower than the quantified volatile yields from the parent biomasses (SWG: 36.0, SG: 31.6, CS: 38.4, BS: 36.6 g/100 g). Similarly, the biochar yields from the pretreated biomasses (SWG: 10.0, SG: 7.8, CS: 7.8, BS: 10.4 g/100 g) were 42 – 69% lower than the biochar yields from the parent biomasses (SWG: 17.4, SG: 25.0, CS: 18.9, BS: 18.5 g/100 g). The lower yields of GC-detectable organics and biochar indicate that the carbon efficiency may be lower for pretreated biomass pyrolysis as the extracted fraction that is removed during pretreatment accounts for 40 – 60% of the original dry biomass.

However, the extracted hemicelluloses may be regarded as a valuable co-product [10, 21, 22] of this conversion approach that may be more valuable than the biochar.

3.4 Py-GC/FID analysis

Pyrolysis products from Py-GC/FID were analyzed by integration of peak areas and the 51 compounds with the greatest peak areas were considered for quantification (Table S1, S2, S3, and S4). The results from quantification are summarized in Figure 5 based on classification of the compounds by their primary functional group. The pyrolysis product distributions were distinctly different between the parent and alkali-extracted biomass samples. The alkali pretreated yields (non-normalized data) represent the direct Py-GC/FID results from the alkali pretreated biomass and can be used to compare the relative pyrolysis product concentrations from the parent and pretreated biomasses. The overall yields from alkali-extracted biomass were similar to the parent biomass (+/- 10%), except for corn stover, which had a 15% lower overall yield for the alkali-pretreated biomass. On the other hand, the normalized data are calculated values representing the yields that would be produced from the same mass of original biomass before pretreatment and the normalized data provides an indication of the yields per mass of original biomass. The lower yield from the normalized alkali-extracted data can be mostly explained by the normalization of the pretreated biomass yields to the original biomass basis.

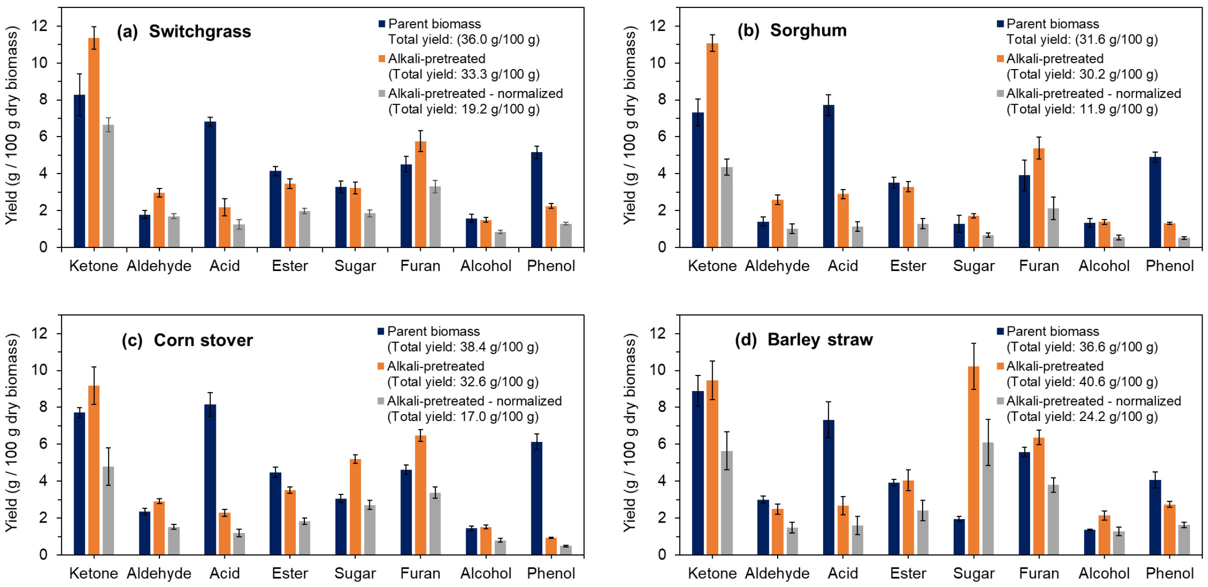

Figure 5: Py-GC/FID quantitative yields of selected compounds (see supporting information) from analytical pyrolysis of parent and alkali extracted biomasses.

The alkali-pretreated biomass showed significantly lower acid concentration with an acid production of approximately 7-8 g/100 g dry biomass from the parent biomasses while alkali-extracted biomasses produced only approximately 2-3 g/100 g dry biomass. This 62-72% reduction in acidic compounds, depending on biomass type, is mainly attributed to the reduction in hemicellulose concentration after hydrolysis by the alkali pretreatment. A lower bio-oil acidity is beneficial for subsequent hydrotreating by delaying coking and extending catalyst useful life compared to hydrotreating bio-oils from non-pretreated biomass.

The concentrations of ketones, sugars (levoglucosan), and furans, which are typical products of cellulose pyrolysis [28], are higher after alkali pretreatment, as the relative concentration of cellulose is greater in the pretreated biomass. In the case of alkali pretreated barley straw, the selectivity of levoglucosan was significantly improved (a 5-fold increase) relative to the parent biomass, which may be attributed to its increase in cellulose concentration after pretreatment. Barley straw had a 2-fold increase in cellulose concentration, which was the greatest increase of all tested biomasses after pretreatment. In addition, hemicellulose and lignin and known to inhibit levoglucosan production from cellulose during pyrolysis due to interaction effects [29]. Compared to the other biomasses tested, barley straw exhibited the greatest delignification (a 50% decrease in lignin concentration) after alkali pretreatment. Given the inhibitory effect of lignin on levoglucosan yield, this could explain why pretreated barley straw had such a high levoglucosan yield compared to the other pretreated biomasses. Further, alkali and alkaline earth metals (AAEM) in the biomass are known to act as strong ring-fragmentation catalysts, having a negative effect on levoglucosan production [30, 31]. The difference in ash concentration after pretreatment as well as the ash composition may also contribute to the observed differences in levoglucosan yields. Further work is needed to better understand the complex interplay of the feedstock composition and reaction conditions during pyrolysis influencing levoglucosan production. As sugars are a valuable product for conversion to ethanol and other bio-based products, an improved selectivity towards sugar production could offer another important economic benefit to this biomass utilization approach.

Yields of phenols, which are products of lignin pyrolysis, were lower from the alkali pretreated biomass, which could be explained by a couple possibilities. One hypothesis for the reduction in mono-phenols is related to the alteration of lignin structure due to alkali pretreatment. During alkali pretreatment, OH^- can weaken the ester bonds between lignin and carbohydrates, which reduces the degree of polymerization and damages the lignin structure [19]. By this hypothesis, the partially depolymerized lignin may have been primarily converted to oligomeric phenols, which were not quantifiable by the Py-GC/FID methodology. Another possible hypothesis is that the reduced pyrolysis vapor acidity from the pretreated biomass inhibited cracking reactions. Acids produced from biomass pyrolysis may act as a catalyst for cracking and dehydration reactions, thus the lower acidity may inhibit cracking resulting in greater yields of polyphenolics. Understanding the chemical structure of lignin after pretreatment is critical to further understand the role of lignin structure on phenolic production during pyrolysis.

Overall, while the mass yield of GC-detectable organics was lower for the pretreated biomass, the composition of this volatile fraction is less acidic, which may lead to improved bio-oil quality. An improved bio-oil composition may reduce the catalytic burden of hydrotreating and improve the carbon efficiency after upgrading compared to pyrolysis of the original biomass. Further work is needed to evaluate the viability of this pretreatment method based on the overall mass balance and bio-oil composition after pyrolysis and subsequent upgrading. Additionally, a technoeconomic analysis could help weigh the cost of an alkaline pretreatment step and the added value of the extracted hemicellulose fraction on the overall conversion of biomass to the desired end products.

4. Conclusions

Pyrolysis of parent and alkali extracted biomasses was studied via kinetic modeling and analytical Py-GC/FID. Activation energies determined by the Friedman kinetic model were similar for parent and alkali extracted samples for most biomasses studied except sorghum. The similar activation energies for the parent and pretreated switchgrass, corn stover, and barley straw indicate that the biomass maintained its thermal stability after pretreatment. Sorghum had a higher activation energy for the parent biomass and lower activation energy for the pretreated biomass sample, which can be attributed to the greater reduction in cellulose and lignin compared to the other biomasses or the greater oil content of the parent sorghum biomass, which was not quantified in this study. From Py-GC/FID analysis, the acetic acid concentration was greatly reduced by 62 - 72% in the alkali pretreated biomasses, which demonstrates the potential of alkaline pretreatment to reduce bio-oil acidity. During hydrotreating, acids are resistant to deoxygenation, so by eliminating the acid, the catalytic burden of bio-oil upgrading may be reduced. A less acidic bio-oil is expected to improve the catalytic conversion of non-acidic oxygenates such as phenols, ketones, aldehydes into alcohols and esters, which can be easily upgraded via hydrodeoxygenation to hydrocarbon liquids. Hydrotreating reaction studies are required to compare the impact of bio-oils produced from parent and pretreated biomass pyrolysis on product yields, bio-oil composition, and catalyst performance.

In addition, the pretreated biomasses resulted in a generally greater selectivity for levoglucosan, while having a reduced selectivity for mono-phenolics. Based on the results, the chemistry leading to the observed selectivity was not clear, but it is known that biomass lignin concentration and AAEM may have an inhibitory effect on levoglucosan production. With a better understanding of the chemistry leading to the observed selectivity, the pretreatment and/or reaction conditions could be optimized to form the target product, demonstrating the potential of alkali pretreated biomass pyrolysis to be a tunable reaction. A technoeconomic analysis of alkali pretreated biomass pyrolysis followed by upgrading would be useful to evaluate whether it is a justifiable approach for sustainable biomass utilization, particularly considering the valuable co-products such as the extracted hemicelluloses, the levoglucosan, and the low acidity pyrolysis vapor.

5. Conflicts of interest

There are no conflicts of interest to declare.

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6. Disclaimer

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