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Guest Editors: Ben W.-L. Jang, Roger Gläser, Chang-jun Liu and Mingdong Dong

Depolymerization of lignocellulosic biomass to fuel precursors: maximizing carbon efficiency by combining hydrolysis with pyrolysis

Jungho Jae,[a] Geoffrey A. Tompsett,[a] Yu-Chuan Lin,[a] Torren R. Carlson,[a] Jiacheng Shen,[b] Taiying Zhang,[b] Bin Yang,[c] Charles E. Wyman,[b] W. Curtis Conner[a] and George W. Huber*[a]

In this paper we study the carbon efficiency of combining hydrolysis and pyrolysis processes using maple wood as a feedstock. A two-step hydrolysis of maple wood in batch reactors, that consisted of a thermochemical pretreatment in water followed by enzymatic hydrolysis, achieved an 88.7 wt% yield of glucose and an 85 wt% yield of xylose as liquid streams. The residue obtained was 80 wt% lignin. A combination of TGA and pyroprobe studies was used for the pyrolysis of pure maple wood, hemicellulose-extracted maple wood, and the lignin residue from the hydrolysis of maple wood. Pyrolysis of raw maple wood produced 67 wt% of condensable liquid products (or bio-oils) that were a mixture of compounds including sugars, water, phenolics, aldehydes, and acids. Pyrolysis of hemicellulose-extracted maple wood (the solid product after pretreatment of maple wood) showed similar bio-oil yields and compositions to raw maple wood while pyrolysis of the lignin residue (the final solid product of enzymatic hydrolysis) produced only 44.8 wt% of bio-oil. The bio-oil from the lignin residue is mostly composed of phenolics such as guaiacol and syringol compounds. Catalytic fast pyrolysis (CFP) of maple wood, hemicellulose-extracted maple wood, and lignin residue produced 18.8, 16.6 and 10.1 wt% aromatic products, respectively. Three possible options for the integration of hydrolysis with pyrolysis processes were evaluated based on their material and carbon balances: Option 1 was the pyrolysis/CFP of raw maple wood, option 2 combined hemicellulose extraction by hydrolysis with pyrolysis/CFP of hemicellulose-extracted maple wood, and option 3 combined the two-step hydrolysis of hemicellulose and cellulose sugar extraction with pyrolysis/CFP of the lignin residue. It was found that options 1, 2, and 3 all have similar overall carbon yields for sugars and bio-oils of between 66 and 67%.

Introduction

Lignocellulosic biomass is a low-cost feedstock that is uniquely suited for production of sustainable liquid fuels.[1] The first step in

[a]Department of Chemical Engineering, University of Massachusetts, 159 Goessmann Laboratory, Amherst, MA 01003, USA. E-mail: huber@ecs. umass.edu; Tel: +4135450276
[b]Center for Environmental Research and Technology (CE-CERT), Chemical and Environmental Engineering Department, Bourns College of Engineering, University of California, Riverside, CA 92507, USA
[c]Center for Bioproducts and Bioenergy, Washington State University, Richland, WA 99354, USA

any biomass-to-fuel conversion process is deconstruction of the solid lignocellulosic material into reactive intermediates that can be used as building blocks for fuels and chemicals. There are two major pathways to deconstruct lignocellulosic biomass: low-temperature hydrolysis and high-temperature thermal deconstruction. Hydrolysis-based pathways involve depolymerization of sugar polymers using either acids or enzymes, with the products from hydrolysis being sugar solutions that can be fermented to alcohols[2] or converted into alkanes or alcohols by liquid-phase processing.[3] Thermal depolymerization of biomass can be achieved by pyrolysis. Pyrolysis is of interest because of its low cost

Broader context

Due to its low cost, renewability and abundance lignocellulosic biomass is being studied worldwide as a feedstock that can be used to produce renewable liquid biofuels. The major impediment to the utilization of our biomass resources is the lack of efficient and economical processes for the deconstruction of biomass. The first step in any biomass-to-fuel conversion process is the deconstruction of the solid lignocellulosic material into reactive intermediates that can be used as building blocks for synthesis fuels and chemicals. There are two major pathways to deconstruct lignocellulosic biomass: low-temperature hydrolysis and high-temperature thermal deconstruction such as pyrolysis and catalytic fast pyrolysis. In this paper, we show how hydrolysis and pyrolysis can be combined to decompose the maximum amount of biomass to reactive intermediates that can be easily upgraded. We report on material and carbon balances for application of these two operations to maple wood. It was found that combining hydrolysis and pyrolysis showed a similar carbon yield to pyrolysis alone, suggesting that the choice of technology for biomass deconstruction will likely depend on the options available for upgrading these intermediates to products.

and relative simplicity in directly heating raw biomass to produce a liquid product called pyrolysis oil or bio-oil. The current challenge with pyrolysis oils is that processes for upgrading these compounds into marketable products are not commercially available.[4]

The chief impediment to the utilization of cellulosic biomass resources is overcoming the recalcitrant nature of the biomass.[5] The objective of this paper is to study how hydrolysis and pyrolysis could be combined in an integrated biorefinery to help overcome this barrier. We perform both fast pyrolysis and catalytic fast pyrolysis (CFP) on pure solid maple wood and solid maple wood samples after two different hydrolysis treatments. We have chosen maple wood as a candidate lignocellulosic biomass feedstock to represent this concept. Thermochemical hydrolysis was employed in stage 1 to remove most of the hemicellulose, while much of the remaining cellulose was removed in stage 2 by enzymatic hydrolysis of the solids from stage 1. We calculated material balances before and after each hydrolysis and pyrolysis treatment to track the fate of overall materials and carbon. The most efficient process will be the process that converts the most carbon of the biomass into usable fuel precursors.

Lignocellulosic biomass is the most prevalent form of renewable carbon on Earth. It is primarily composed of three polymeric components: cellulose, hemicellulose, and lignin.[1] Cellulose is a glucose polysaccharide whose long chains are arranged in a highly crystalline structure. Hemicelluloses are amorphous polysaccharides made up of three hexoses (galactose, glucose, and mannose), two pentoses (xylose and arabinose), and other compounds such as acetyl groups. Lignin is a complex network of different phenyl propane units (p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol). All three of these biomass building blocks have different rates of depolymerization to release a complex mixture of sugars, degradation compounds, and other products, with the distribution depending on the reaction system applied.

Hot water or dilute acid thermochemical pretreatments or enzymatic hydrolysis can be employed to convert hemicellulose and cellulose into sugars.[6] Hot water and dilute acid pretreatments are favored for recovering sugars from hemicellulose with high yields at low costs. These pretreatments however cannot match the high yields of glucose from cellulose with enzymes. However, some type of pretreatment is needed prior to enzymatic hydrolysis in order to realize high-glucose sugar yields (i.e. 90%).[7] Furthermore, crystallinity, accessible surface area, enzyme effectiveness, enzyme inhibition, and other factors impede the rate of sugar release, and high loadings of enzymes are required to achieve high yields in reasonable times.[8,9] As we will show in this paper the remaining lignin-rich solids can then be pyrolyzed to obtain a pyrolysis oil that has a large fraction of aromatic products.

Pyrolysis is the thermal decomposition of solid materials and is the first step in any thermochemical conversion process. Pyrolysis involves a number of parallel and series reaction pathways. High heating rates, temperatures ranging from 400–600 °C, and short residence times are required to maximize the yield of pyrolysis liquids.[10,11] The pyrolysis vapors can be condensed to form a liquid fuel typically called bio-oil. Zeolite catalysts can be added into a pyrolysis reactor to convert the pyrolysis vapors

directly into aromatics.[12–20] This approach called catalytic fast pyrolysis (CFP) is a single-step process for the conversion of solid biomass (or other organic materials) directly into liquid fuels in a single reactor. High heating rates, high catalyst-to-feed ratios, and proper catalyst selection are required to produce aromatic selectively.[21]

Experimental

Hydrolysis of biomass

Biomass feedstock. Mascoma Corporation provided the red maple wood feedstock used in these experiments. The wood was ground to a small particle size (<2 mm) using a laboratory mill (model 4, Arthur H. Thomas Company, Philadelphia, PA) and an internal sieve. The composition (carbohydrates, lignin, and ash) of the raw maple wood was analyzed following NREL standard procedures,[22–24] and the results are shown in Table 1. Prior to feeding to the reactor systems, the milled maple was stored in plastic bags in a freezer at −18 °C.

Hot water pretreatment (extraction of hemicellulose). Tubular batch reactors (Hastelloy C-276, ½ "O.D. × 0.035" wall thickness × 6″ length) or a 1 L stirred Parr pressure reactor (Hastelloy C, Parr Instruments, Moline, IL) were used for pretreatment. The tubular reactors were employed to test time–temperature combinations to optimize pretreatment conditions for maximum hemicellulose release. The Parr reactor was then applied to treat larger quantities of maple wood at the combination of time and temperature to give the highest sugar yields with the tubes. Both types of reactors were heated in 4 kW fluidized sand baths (Model SBL-2D, Techne Co., Princeton, NJ), and their internal temperature was monitored with a K-type thermocouple probe (Omega CASS-18U-12, Omega Engineering Co., Stamford, CT). The heat-up time to the target temperature was about 3–4 min (not included in stated reaction times).[25]

The milled red maple was presoaked in water overnight at a solid loading of 10 wt% for use in both the tubular reactors and the Parr reactor. The slurry containing water and maple in the reactors was sealed. Temperatures of 160 °C, 180 °C, and 200 °C were tested at different pretreatment times. The pressures in the Parr reactor during water treatment were about 620–1517 kPa, depending on temperature (620 kPa for 160 °C, 979 kPa for 180 °C, and 1517 kPa for 200 °C). The reactor contents were quickly cooled at the end of the reaction time by immersing the reactors in a water bath, and the reactors cooled down to a temperature of 40 °C in approximately 40 s, with further hydrolysis stopping well before that. The maple residues were filtered, and the liquid fraction was collected. The pretreated solid fraction was thoroughly washed to remove solubles from the solid residues.

Table 1 Compositions of the red maple wood

Klason lignin (%)	Glucan (%)	Xylan (%)	Arabinan (%)	Ash (%)	Moisture (%)
24.9 ± 0.2	41.9 ± 0.3	19.3 ± 0.1	0.81 ± 0.1	0.95 ± 0.05	6.67 ± 0.02

Enzymatic hydrolysis (extraction of cellulose). Washed pretreated maple solids were hydrolyzed at pH 4.8 and 50 °C in duplicates by following a modified NREL LAP procedure.[26] Spezyme (SP) (activity 58.2 FPU/ml, protein content 116.0 mg ml^{-1}, Genencor, Rochester, NY) and Novozymes 188 (β-glucosidase, acitivity 665.0 CBU/ml, protein content 125.0 mg ml^{-1}, Franklinton, NC) were used at 2% biomass solid loadings, with the latter added to give a filter paper unit (FPU) to β-glucosidase activity ratio (FPU:CBU) of 1 : 4. A high enzyme loading of 60 FPU/g total glucan plus xylan in the pretreated solid was applied to determine the maximum possible sugar release. Samples were taken at selected time intervals.

Sugar analysis. Sugar monomers in the liquid portion were analyzed quantitatively by a Waters HPLC model 2695 system equipped with a 2414 refractive detector and a Waters 2695 autosampler using Millenium32 chromatography manager 3.2 software (Waters Co., Milford, MA). A Bio-Rad Aminex HPX-87P column (Bio-Rad Laboratories, Hercules, CA) was employed for separating the different sugars. The total xylose, glucose, galactose, arabinose, and mannose concentrations in the liquid fractions were measured after post-hydrolysis of each liquid sample with 4 wt% sulfuric acid at 121 °C for 1 h according to NREL Laboratory Analytical Procedure,[22,27,28] and concentrations of xylose oligomers in the liquid were calculated as the difference between the total xylose concentration after post hydrolysis and the monomeric xylose concentrations measured prior to post hydrolysis.

Pyrolysis in a thermogravimetric analyzer

Thermogravimetric analysis (TGA) was performed with a Q600 TGA system (TA Instruments). For a typical run approximately 5 mg of powdered sample was used for biomass pyrolysis. Prior to all trials, samples were preheated to 110 °C for 30 min, under helium flow to remove physically adsorbed water. Pyrolysis under helium was then carried out from 50 °C to 800 °C with a heating rate of 15 °C min^{-1}.

Pyrolysis and catalytic fast pyrolysis in a pyroprobe reactor

Catalytic fast pyrolysis experiments were conducted using a Pyroprobe-GC-MS system (CDS Analytical Inc.), following the experimental methods reported previously.[21] All reactions were carried out at the following reaction conditions: catalyst-to-feed ratio of 19 (wt/wt%), reaction temperature 600 °C, heating rate 1000 °C s^{-1}, and reaction time 240 s. Prior to reaction, ZSM-5 catalyst (Zeolyst, $SiO_2/Al_2O_3 = 30$) was calcined at 550 °C in air for 5 h. Carbon yields reported here are in terms of molar carbon where the moles of carbon in the product are divided by the moles of carbon in the reactant. The aromatic selectivity reported is defined as the moles of carbon in an aromatic species divided by the total moles of aromatic species carbon. Carbon on the spent catalyst was quantified by elemental analysis (performed by Galbraith Laboratories using combustion, GLI method # ME-2).

An in-house designed condenser trap was coupled with the pyroprobe to trap pyrolysis vapors from the pyrolysis experiments. The trap consisted of a 25 mL pyrex vial, a screw-tight frame with plug-valve controlled gas inlet and outlet, and the pyroprobe pyrolyzer. A 1/4 inch channel allowed the pyroprobe pyrolyzer to be inserted from the top of frame into the center of the vial. Prior to each trial, the vial was flushed with ultra-high-purity helium at 50 mL min^{-1} flow rate for 10 min. After purging, the vial was made gas-tight by closing the outlet and inlet valves. The trap was then transferred to a Dewar flask in a liquid nitrogen bath at 77 K, which allowed rapid quenching of any volatiles evolved during the reaction. After reaction the condensed products on the walls of the vial were quantitatively removed with 1 mL of methanol. The methanol solution was then analyzed using a GC-MS (Shimadzu GC-2010 and QP2010S, analytes separated by Restek RTX-VMS column). Once the peaks were confirmed, GC-FID (Agilent) was used to quantify each species. The carbon content of the bio-oils was determined using a Total Organic Carbon analyzer (TOC-V$_{CPH}$). For these measurements, the condensed products in the vial were dissolved in 20 mL of deionized water, while gaseous species, including CO and CO_2 were identified using the Py-GC-MS system. The weight of the final char was estimated by weighing the sample before and after pyrolysis using a Mettler Toledo microbalance with sensitivity of 0.001 mg. The carbon content of the final char was quantified by elemental analysis performed by Galbraith Laboratories.

Results

Hydrolysis of biomass feedstock

Pretreatment of biomass is needed to overcome the natural recalcitrance of the lignocellulosic biomass structure.[6] For example, use of just water, steam, or dilute acids will release sugars from hemicellulose. Pretreatment also alters the crystalline structure of cellulose and promotes access to enzymes for hydrolysis. In the present study, hot water alone was used to pretreat maple wood biomass and no other chemicals were added, thereby simplifying both pretreatment as well as the downstream neutralization and conditioning operations. The solid residues left after pretreatment were primarily comprised of cellulose and lignin as a result of the release of xylan, other sugars, and other compounds from hemicellulose into the liquid stream of the process. Then, cellulase and β-glucosidase enzymes could be applied to hydrolyze the cellulose in the remaining solids to glucose. The combination of the two steps, pretreatment and enzymatic hydrolysis, can provide high yields of sugars from hemicellulose and cellulose.[7] The residue obtained after pretreatment and enzymatic hydrolysis contains up to ~80 wt% lignin.

It was determined that the optimal pretreatment conditions for maximum sugar recovery from maple wood was 200 °C and 10 min reaction time based on a series of experiments with raw maple using hot water at temperatures of 160 °C, 180 °C, and 220 °C and treatment times between 5 and 40 min. A high enzyme loading (60 FPU/g total glucan plus xylan) was used in the enzymatic hydrolysis at known optimal digestion conditions of 50 °C and pH 4.8, to remove the glucan from the pretreated maple wood. The mass balances of each stream from pretreatment and enzymatic hydrolysis of maple wood are shown in Fig. 1. The mass balances are adjusted to a basis of 100 kg of total maple feed (note: the glucan and xylan in the solid in Fig. 1 have been

Conversion of Maple to Sugars by Water
Pretreatment Followed by Enzymatic Hydrolysis
• Parr reactor, ~10% solids
• 200 °C, 10 min
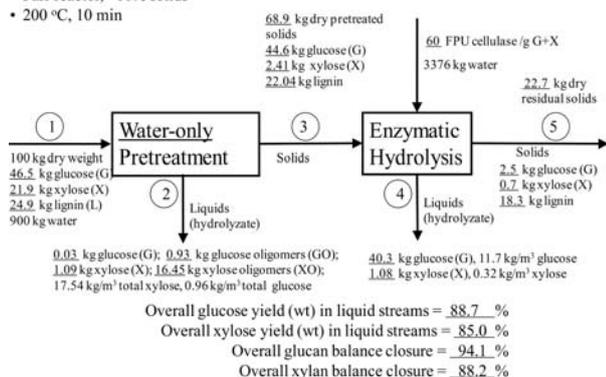
Fig. 1 Mass balance of hydrolysis of maple wood with water pretreatment and enzymatic hydrolysis adjusted to a basis of 100 kg of dry maple wood feed.

converted into glucose and xylose with conversion factors of 0.90 and 0.88, respectively). Thus, 100 kg of maple wood would produce 17.54 kg of total xylose (mono-xylose plus xylo-oligomer, 17.54 kg m^{-3} of total xylose concentration in stream 2), 0.96 kg total glucose (mono-glucose plus gluco-oligomer, 0.96 kg m^{-3} of total glucose concentration in stream 2), and 68.9 kg of residual solid from the pretreatment step (stage one). The corresponding theoretical glucose and xylose yields expressed as a percent of the maximum amount that could be obtained from maple were 2.1% and 80.1%, respectively, in pretreatment.

It should be noted that we were not able to account for 12.6 kg of the solid biomass lost in water only pretreatment, and 17.42 kg of the solid biomass lost in the combined pretreatment and enzymatic hydrolysis, which resulted in 5.9% and 11.8% deviations in the glucan and xylan closure calculations. These deviations might result from three factors. First, the solid particles could be lost in the suspension after hot water pretreatment because the filter paper used could not capture the finer particles in suspension after hot water pretreatment. Second, not all of the solid could be recovered after filtration as some solids were adsorbed in the filter paper and funnel wall during filtration. Third, some components of hemicellulose and cellulose were likely degraded into unknown compounds that could not be identified by HPLC. After pretreatment of 100 kg of maple wood in stage 1, enzymatic hydrolysis (stage 2) would produce 40.3 kg of glucose (11.7 kg m^{-3} of glucose concentration) and 1.08 kg of xylose (0.32 kg m^{-3} of xylose concentration) in the liquid stream 4, and 22.7 kg of solid, containing mostly lignin, in stream 5, again as shown in Fig. 1. The corresponding glucose and xylose yields as a percent of the theoretical maximum possible based on the composition of raw maple for the combined operations of pretreatment and enzymatic hydrolysis were 88.7% and 85.0%, respectively. In this second step only 4.82 kg of the original 100 kg of solid maple wood could not be accounted for as a result of the high selectivity of enzymes.

Pyrolysis of biomass components

Pyrolysis of biomass samples in TGA. The pyrolysis characteristics, both thermogravimetric (TG, in wt%) and differential

thermogravimetric (DTG, in wt%/°C) curves of the raw maple wood, hemicellulose-extracted maple wood, and lignin residue are shown in Fig. 2. We were able to volatilize over 95 wt% of both the raw maple wood and the maple wood after hemicellulose extraction. However, we were only able to volatilize 70 wt% of the lignin residue. This indicates that the lignin residue most likely undergoes repolymerization reactions during the hydrolysis steps. These repolymerization reactions make it harder to volatilize the raw lignin forming "hard coke".

From the DTG curves, it can be seen that the maple wood undergoes decomposition processes at several different temperatures. The maple wood first starts to decompose at a temperature of 250–300 °C. Once the hemicellulose fraction is removed from the maple wood this low-temperature peak is no longer present. This indicates that this low-temperature peak from 250–300 °C is most likely from the hemicellulose fraction of the biomass. It has been reported that DTG peaks for hemicellulose and cellulose occur at around 268 °C and 355 °C, respectively.[29] The majority of the maple wood and the hemicellulose-extracted maple wood sample decompose at a temperature range from 300–400 °C. Pure cellulose decomposes in this same temperature range.[30] This peak in the 300–400 °C range is mainly due to cellulose pyrolysis. This is the largest peak and most abundant species present in the maple wood.
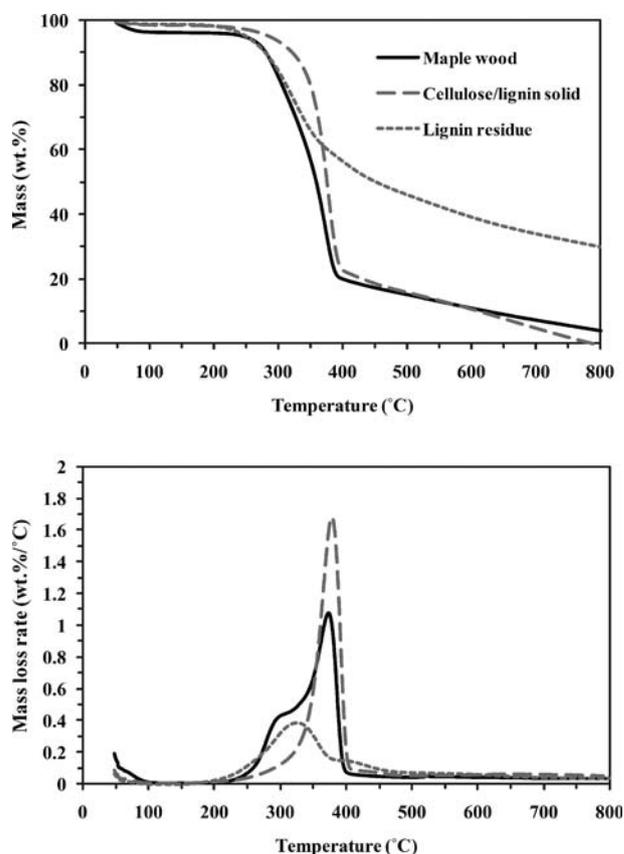
Fig. 2 TGA and DTG curves of raw maple wood (solid or black), solid residue after hemicellulose extraction (cellulose/lignin solid, dash dot or grey), and solid residue after hemicellulose and cellulose extraction (lignin residue, short dot or light grey) with a heating rate of 15 °C min^{-1} from 50 °C to 800 °C.

The solid lignin residue shows three major temperature regimes for pyrolysis including: a first peak from 250–350 °C, a second peak from 350–450 °C, and a broad peak from 350–800 °C. About 40 wt% of the lignin decomposes in this first temperature regime from 250–350 °C. The lignin residue only contains 10 wt% sugars so this first temperature peak has to contain lignin compounds. These results suggest that the lignin residue contains at least three different structures that decompose at significantly different temperatures. This is consistent with results which indicate that lignin has no specific structure and is formed from free radical polymerization reactions.[1] This also indicates that it is difficult to convert the lignin residue into fuels or chemicals because it does not have a well-defined structure. Based on the results presented in Fig. 2 this lignin structure most likely undergoes changes during the hydrolysis processing of the biomass.

Pyrolysis of biomass samples in pyroprobe. Table 2 shows the weight and carbon yield of gases, bio-oil, and char from the pyrolysis of biomass fractions at 600 °C for 4 min with a heating rate of 1000 °C s^{-1} in the pyroprobe reactor. Pyrolysis in the pyroprobe reactor typically produces more coke than pyrolysis in the TGA system. This is because a higher concentration of vapors is present in the pyroprobe reactor, and these thermally unstable pyrolysis vapors react with one another to form coke. On a weight yield basis, the yield of condensable liquids or bio-oil is around 67 wt% for both maple wood and cellulose/lignin solid. For the lignin residue the yield of the bio-oil is only 45 wt%. All three samples have similar gas yields of 20–23 wt%. However, the lignin residue produces significantly higher amounts of coke than the other two samples. These results are consistent with the TGA results. The amount of bio-oil produced is known to be a function of the reactor, reaction conditions, and feedstock.[4,31,32] It has been reported that fast pyrolysis processes of woody biomass typically produce yields of 60–75 wt% of liquid bio-oil.[10,33] This indicates that the yields obtained from our pyroprobe reactor are similar to yields in other types of fast pyrolysis reactors. Also in Table 2 we report the carbon yields of the various products. The estimated carbon contents of the bio-oils were 45 wt% for maple wood, 48 wt% for cellulose/lignin solid and 53 wt% for the lignin residue. We have higher CO and CO$_2$ yields than have been obtained in a fluidized sand bed reactor.[4,33] Piskorz and Scott

Table 3 Carbon molar percentage (%) of products present in the bio-oils

Compound	Formula	Maple wood	Cellulose/lignin solid	Lignin residue
Acetic acid	$C_2H_4O_2$	7.5	2.0	2.1
Hydroxyl acetaldehyde	$C_2H_4O_2$	1.2	0.7	0.3
Hydroxyacetone	$C_3H_6O_2$	1.8	—	—
D-Glyceraldehyde	$C_3H_6O_3$	7.6	1.7	—
Furfural	$C_5H_4O_2$	0.3	0.5	0.2
Catechol	$C_6H_6O_2$	0.3	—	0.5
Guaiacol	$C_7H_8O_2$	—	0.3	3.5
3-Methoxy-1,2-benzenediol	$C_7H_8O_3$	—	—	1.1
4-Methyl guaiacol	$C_8H_{10}O_2$	—	0.5	1.2
Syringol	$C_8H_{10}O_3$	0.8	0.7	6.6
2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	—	—	1.9
1,2,4-Trimethoxy benznene	$C_9H_{10}O_3$	0.7	1.6	2.0
Isoeugenol	$C_{10}H_{10}O_2$	0.6	—	1.3
6-Methoxyeugenol	$C_{11}H_{14}O_3$	1.1	—	0.8
Levoglucosan	$C_6H_{10}O_5$	1.6	9.0	—
Unidentified fraction	—	76.4	83.1	78.7

reported that a 4.83 wt% yield of CO and a 5.36 wt% yield of CO$_2$ were obtained from red maple wood pyrolysis with a 67.3 wt% yield of bio-oil at the reaction temperature 530 °C. We produced greater than a 13 wt% yield of CO and CO$_2$ from maple wood. The difference in the CO and CO$_2$ yield is probably due to the longer vapor residence time in the pyroprobe reactor. It is known that long vapor residence times cause secondary cracking of primary products and favor gaseous products.[11,34]

We attempted to identify the products present in the bio-oil samples. Table 3 shows the detailed chemical composition of the bio-oils from the three biomass samples. We were able to identify approximately 20% of the carbon present in these various samples. It should be noted that almost 80% of the carbon in the bio-oils was present as unidentified fractions of the bio-oils which include unidentified peaks in the GC-MS and high-molecular-weight species (nonvolatile compounds). In fact, bio-oil is a complex liquid composed of over 400 compounds including char particles. However, this analysis shows a clear distinction between the composition of products from the three feedstocks.

The identified chemical species in bio-oils can be classified into the following four categories:

(1) retro-aldol species (acetic acid, D-glyceraldehyde, hydroxyacetone, and hydroxyacetaldehyde),

(2) furfural,

(3) sugars and anhyhdrosugars (primarily levoglucosan)

(4) phenolic compounds (catechol, guaiacol, syringol, isoeugenol, and other methoxybenzene compounds).

The major species of bio-oil from maple wood are retro-aldol species and levoglucosan while bio-oil from cellulose/lignin solid showed primarily levoglucosan rather than retro-aldol species. The bio-oil from lignin residue mainly consists of phenolic compounds, as expected.

Catalytic fast pyrolysis (CFP) of biomass to aromatics

Table 4 shows the weight and carbon yields of gases, aromatics, and coke from catalytic fast pyrolysis of the three solid biomass samples. The same reaction conditions as used in pyrolysis were employed, namely 600 °C for 4 min with a heating rate of 1000 °C s^{-1}. Aromatic carbon yields of 37.9% and 31.5% were

Table 2 Pyrolysis yields for maple wood, hemicellulose-extracted maple wood, and lignin residue in the pyroprobe reactor[a]

Pyrolysis products	Maple wood		Cellulose/lignin solid		Lignin residue	
	Wt (%)	Carbon (%)	Wt (%)	Carbon (%)	Wt (%)	Carbon (%)
CO	9.9	9.3	11.8	10.4	7.0	7.5
CO$_2$	13.4	8.0	11.8	6.6	13.8	9.4
Bio-oil	66.7	65.6	66.6	65.6	44.8	58.8
Char[b]	10.0	4.5	9.8	1.8	34.4	19.5
Unidentified	—	12.6	—	15.6	—	4.7

[a] Bio-oil carbon content: 45 wt% for bio-oils from maple wood, 48 wt% for bio-oils from cellulose/lignin solid, and 53 wt% for bio-oils from lignin residue. Unidentified fraction includes missing carbon. [b] Char is the carboneous solid material produced during pyrolysis.

Table 4 Catalytic fast pyrolysis of maple wood, hemicellulose-extracted maple wood, and lignin residue

CFP products	Maple wood		Cellulose/lignin solid		Lignin residue	
	Wt (%)	Carbon (%)	Wt (%)	Carbon (%)	Wt (%)	Carbon (%)
CO	32.4	30.3	27.6	24.3	11.7	12.5
CO_2	15.6	9.3	11.9	6.6	8.3	5.7
Aromatics	18.8	37.9	16.6	31.5	10.1	23.2
Coke[a] + H_2O	33.2	23.1	44.0	37.6	69.9	58.8

[a] Coke is the amorphous carbon produced from either homogeneous gas phase thermal decomposition reaction or heterogeneous reaction on the catalyst.
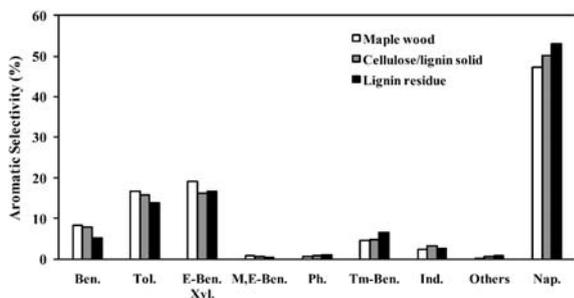
Fig. 3 Aromatic selectivities for CFP from maple wood, cellulose/lignin solid, and lignin residue. Key: maple wood (white), cellulose/lignin solid (grey) and lignin residue (black). Aromatics quantified include: Ben. = benzene, Tol. = toluene, Xyl. and E-Ben. = xylenes, ethylbenzene, M,E-Ben. = methyl-ethyl-benzene, Ph. = Phenols, Tm-Ben. = tri-methylbenzene, Ind. = indanes, Nap. = naphthalenes. Others include ethyl-dimethyl-benzene and tetramethylbenzene.

achieved from raw maple wood and the cellulose/lignin solid, respectively while only 23.2% carbon was produced from the lignin residues. Lignin produced the highest amount of coke (~58.8% carbon). The yields of gases were high in all the samples (18.2–39.6 wt%). In CFP, the oxygen in the biomass is removed by dehydration, decarbonylation and decarboxylation reactions to produce the aromatic hydrocarbon products. The overall reaction converts the biomass into a mixture of aromatics, CO, CO_2 and water. Fig. 3 shows the aromatic selectivities on a molar carbon basis for CFP of the three solid biomass samples. The aromatic distributions are similar to each other regardless of the feedstock. The major aromatic species were naphthalene ≫ xylene > toluene > benzene.

Discussion

As shown in Fig. 4, there are three potential options for combining pyrolysis with hydrolysis to deconstruct biomass. Option 1 is the pyrolysis/CFP of dried maple wood biomass, with the products including: (1) a bio-oil or an aromatics stream, (2) a solid char stream, and (3) a gaseous stream containing CO and CO_2. Option 2 first applies thermal hydrolysis to extract hemicellulose followed by pyrolysis/CFP of the cellulose/lignin rich solid left after hemicellulose hydrolysis. The products for option
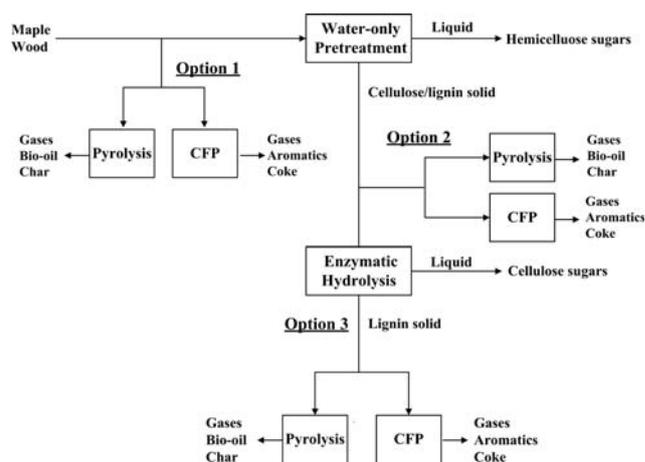
Fig. 4 Integrated process scheme by combining hydrolysis with pyrolysis, including three main routes.

2 include similar products to option 1 plus an aqueous hemicellulose sugar stream rich in C5 sugars and C5 sugar oligomers, plus acetic acid and a small amount of C6 sugars. Option 3 applies thermal hydrolysis of hemicellulose followed by enzymatic removal of most of the cellulose and remaining hemicellulose and then pyrolysis/CFP of the lignin residue. The products from option 3 are thus similar to the products from option 2 plus an additional aqueous glucose stream.

As expected, the amount of bio-oil produced decreased as the number of hydrolysis steps increased. Option 3 produced the largest amount of aqueous sugars, and option 1 did not produce any sugars. It should be noted that the conversion of sugars into fuels by fermentation is already commercially established, whereas technologies for bio-oil conversion into transportation fuels are not yet commercially available.[35] These bio-oil conversion technologies however are moving towards commercial application.

The ideal process will decompose the maximum amount of biomass to products that can be easily upgraded by fermentation,[36–38] aqueous phase processing,[3,39,40] hydrodeoxygenation,[41] or standard petroleum conversion technologies,[35,42] with preservation of the energy content of the feedstock most critical when fuels are desired. We calculated mass and carbon balances as well as the products obtained for each option as shown in Table 5, with the overall mass and carbon efficiencies assuming that sugars, bio-oil and aromatics are useful products that can easily be upgraded. Char and gases are less valuable products because they are more expensive to convert into fuels and chemicals.

Options 1, 2 and 3 all have similar overall carbon yields of between 66–67%. Thus, 66–67% of the carbon of the biomass was converted into products that are easily upgraded. The energy in the products from these three options ranges from 1196 to 1267 MJ per 100 kg of maple wood. Thus, combining hydrolysis with pyrolysis does not produce significantly more usable carbon than pyrolysis alone, for this feedstock. The different options do however produce significantly different reaction intermediates. Therefore, the choice of technology for biomass deconstruction will likely depend on the options available for upgrading these intermediates to products, the capital and operating costs of the overall biomass refining operations, and market preferences.

Table 5 Mass and carbon balances for the three options of combining hydrolysis with pyrolysis[a]

	Option 1		Option 2		Option 3	
	Wt (%)	Carbon (%)	Wt (%)	Carbon (%)	Wt (%)	Carbon (%)
Hydrolysis						
Glucose			0.03	0.03	40.33	35.27
Xylose			1.09	0.95	2.17	2.85
Glucose oligomer			0.93	0.89	0.93	0.89
Xylose oligomer			16.45	15.83	16.45	15.83
Pyrolysis						
Bio-oil	66.7	65.6	45.9	48.2	10.2	11.7
Gases	23.3	17.3	16.3	12.5	4.7	3.3
Char	10.0	4.5	6.8	1.3	7.8	3.9
CFP						
Aromatics	18.8	37.9	11.4	23.1	2.3	4.6
Gases	48.0	39.7	27.1	22.7	4.5	3.6
Coke	33.2	23.1	30.3	27.6	15.9	11.6
Overall mass and carbon balances						
Pyrolysis + hydrolysis (sugar + bio-oil)	66.7	65.6	64.4	65.9	70.0	66.5
CFP + hydrolysis (sugar + aromatics)	18.8	37.9	29.9	40.8	62.2	59.4
Energy output						
Pyrolysis + hydrolysis (sugar + bio-oil)	1267		1196		1241	
CFP + hydrolysis (sugar + aromatics)	620		701		1124	

[a] Energy output calculation based on higher heating values for glucose and xylose : 17.5 MJ kg^{-1}, bio-oil : 19 MJ kg^{-1}, and aromatics : 33 MJ kg^{-1}.

Combing CFP with hydrolysis produces more sugars and fewer aromatics as shown in Table 5. The carbon yield decreased from 65.6 to 37.9% for pyrolysis and CFP of pure maple wood (option 1 in Table 5), and the carbon yield decreased for all three options using CFP rather than pyrolysis of the biomass. However, the advantage of CFP is in producing a product that can fit into the existing infrastructure which does not require any further upgrading. The overall energy output however for CFP is half that of pyrolysis, and fewer aromatics are produced by CFP after hydrolysis of the biomass. However, combining CFP with hydrolysis allows for the production of sugars along with aromatics, and in this paper we show that CFP is effective for lignin conversion, with the result that CFP can be combined with fermentation technologies to utilize a waste stream to produce aromatics.

As shown in this paper, many options are possible for biomass deconstruction, and many more can be added on for conversion of the intermediates into fuels and chemicals. Although we have provided material balances for maple wood deconstruction to reactive intermediates, more research in the areas of both homogeneous and heterogeneous catalysis combined with process design is needed to optimize the different pathways for converting these intermediates to products and integrate production of the intermediates with downstream operations.

Conclusions

The first step in any biomass refinery is the deconstruction of the solid biomass to reactive intermediates, with hydrolysis and pyrolysis providing two options. In this paper, we report on material balances for application of these two operations to maple wood to release intermediates that can be used for production of fuels and chemicals. Material and carbon balances were developed for three possible options for integration of hydrolysis with pyrolysis: Option 1 was the pyrolysis/CFP of raw maple wood. Option 2 was to combine hemicellulose extraction by hydrolysis with pyrolysis/CFP of hemicellulose-extracted maple wood. Option 3 combined two-step hydrolysis for hemicellulose and cellulose sugar extraction with pyrolysis/CFP of the lignin residue. Pyrolysis of maple wood produced 67 wt% of condensable liquid products (or bio-oils). The bio-oil produced was a mixture of compounds including sugars, water, phenolics, aldehydes, and acids. Pyrolysis of hemicellulose-extracted maple wood (the solid product after pretreatment of maple wood) showed a similar bio-oil yield and composition to the raw maple wood. Pyrolysis of lignin residue (the final solid product of enzymatic hydrolysis) produced only 44.8 wt% of bio-oil. The bio-oil from the lignin residue was mostly composed of phenolic compounds. Catalytic fast pyrolysis (CFP) of maple wood, hemicellulose-extracted maple wood, and lignin residue produced 18.8, 16.6 and 10.1 wt% aromatic products. Two-step hydrolysis of maple wood through pretreatment and enzymatic hydrolysis, achieved a 88.7 wt% yield of glucose and 85 wt% yield of xylose in the liquid stream from the combined streams. The residue obtained after hydrolysis was 80 wt% lignin. Thus, options 1, 2, and 3 were all shown to have similar overall carbon yields for sugars and bio-oils of between 66 and 67%, implying that combining hydrolysis with pyrolysis does not produce significantly more useable carbon than pyrolysis alone. However, it should be noted that conversion of sugars to fuels by fermentation processes is already commercialized whereas the bio-oil upgrading process is still in development. CFP showed a lower carbon yield than pyrolysis in all three options, but CFP produces aromatics that can be directly used for gasoline or

chemicals. Further advances in homogeneous and heterogeneous catalysis combined with process design and process integration are expected to offer economical pathways for biomass conversion into fuels and chemicals.

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