INL/JOU-21-63600-Revision-0

Pretreatment of Biomass by Selected Type-III Deep Eutectic Solvents and Evaluation of the Pretreatment Effects on Hydrothermal Carbonization

October 2021

Md Tahmid Islam, Al Ibtida Sultana, M. Toufiq Reza, Jordan L Klinger, Nepu Saha

INL/JOU-21-63600-Revision-0

Pretreatment of Biomass by Selected Type-III Deep Eutectic Solvents and Evaluation of the Pretreatment Effects on Hydrothermal Carbonization

Md Tahmid Islam, Al Ibtida Sultana, M. Toufiq Reza, Jordan L Klinger, Nepu Saha

October 2021

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

Pretreatment of Biomass by Selected Type-III Deep Eutectic Solvents and Evaluate the Pretreatment Effects on Hydrothermal Carbonization

Md Tahmid Islam[1], Al Ibtida Sultana[1], Nepu Saha[2], Jordan L. Klinger[2], and M. Toufiq Reza[1,*]

[1]Florida Institute of Technology, 150 W. University Boulevard, Melbourne, Florida, 32901, USA

[2]Energy and Environment Science & Technology, Idaho National Laboratory,750 MK Simpson Boulevard, Idaho Falls, Idaho 83402, USA

*Corresponding Author: email: treza@fit.edu, phone: +1 (321) 674 8578

Abstract

Hydrothermal carbonization (HTC) is a novel thermochemical conversion that converts wet biomass into energy dense solid fuel. Residual moisture under subcritical conditions reacts with lignin-cellulose-hemicellulose matrix with the major reactions being identified as dehydration and decarboxylation. Among other reaction parameters (e.g., temperature, time, pressure), biomass morphology often plays a key role to HTC. The hypothesis of this study was enhancing porous structure of biomass without significantly affecting biopolymer composition would augment hydrothermal carbonization (HTC). To prove the hypothesis, two type-III deep eutectic solvents (DES) namely choline chloride:urea (ChCl:Urea, 1:2 mole/mole) and methyltriphenylphosphonium bromide:ethylene glycol (MTPB:EG, 1:4 mole/mole) were studied to pretreat loblolly pine at room temperature and ambient pressure for 1 hour. DES pretreatment shows swelling of the biomass, increasing the surface fiber-to-fiber gap length by 52 % and 185 % for ChCl:Urea and MPTB:EG pretreatments, respectively. The total pore volume remained intact (2.6×10^{-3} cm^3/g), although new small pores were evolved, and existing pores were abated with DES pretreatment. Hydrochars prepared from DES pretreated loblolly pine showed a high O/C and H/C ratio resulting in significant increase of energy content (up to 42 %) and decrease of mass yield (up to 50 wt. %), indicating an enhancement of HTC severity due to the alteration of surface morphology by DES. A preliminary process economics revealed that integrated DES pretreatment-HTC would increase fixed capital investment but decrease the cost of operation and manufacturing than standalone HTC process.

Keywords: Biomass; deep eutectic solvent; swelling; hydrothermal carbonization; process economics.

1 Introduction

Over the past decades, lignocellulosic biomass conversion for the development of biorefineries have been an epicenter of biofuel research.[1] Among various conversion techniques, HTC emerges as one the most promising techniques as residual moisture of the wet biomass can act as reaction medium.[2] During HTC, the subcritical water enters the biomass pores, where it reacts with the biopolymers (hemicellulose, cellulose, and lignin) and the liquid and gaseous products leave the solid hydrochar's structure.[3] It is therefore understood that mass transfer limitation plays a significant role on the HTC reactions along with other reaction parameters (e.g., temperature, time).[4,5] In fact, literature supports that the lower particle size results in higher hydrothermal conversion of biomass due to the enhancement of accessibility of subcritical water in the biomass pores during HTC.[4,5] However, reducing the particle size can be an energy-and cost-intensive process, especially for lignocellulosic feedstocks.[5–7] Therefore, a pretreatment of lignocellulosic biomass is imperative, if it could overcome the mass transfer barrier and enhance HTC reaction.

To date, several chemical pretreatment methods are developed for biomass such as acid leaching, dilute alkali extraction, and solvent extraction by ionic liquid or deep eutectic solvents (DES).[8,9] Previous studies suggest that acidic medium significantly modifies the biomass structure,[9,10] but with the sacrifice of mass and energy yield of the pretreated biomass. Also, the cost of handling and disposal of acidic wastewater makes acid leaching less favorable for biomass pretreatment.[9,11] On the other hand, alkali causes swelling of biomass which ultimately makes the biomass surface more accessible for the reaction.[9] Despite that, the main drawback of using alkali as pretreatment precursor is alkali consumption and it is often less effective for high lignin-containing biomass like pine.[12] The ionic liquids (mostly imidazolium salts) dissolute and regenerate the amorphous cellulose and disrupts the inter and intra-molecular hydrogen bonds among cellulose, hemicellulose and lignin.[9] However, studies found that two nitrogen atoms in imidazolium cation undergoes deuterium exchange in deuterated solvent due to its acidic nature and henceforth this deprotonation of imidazolium cation leads to highly reactive carbene and shows non-innocent nature of this costly salt (e.g. unexpected side reaction).[8,13]

Recently, the use of DES has attained more interests in solubilizing lignin and leaving cellulose more accessible for hydrolysis.[14–16] DES is typically made of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) at their eutectic ratio. The tunable physicochemical properties provide a pathway to treat biomass substrates, convert carbohydrates, extract/separate value added components, and show biocompatibility with biomolecules such as nucleic acids, proteins, enzymes and microbes.[8,17,18] Among the five different types of DESs, type-III DESs (organic salt + organic acid or alcohol) are the most studied because of their fast and easy preparation, non-reactivity with solvent water, biodegradable nature, and cost-competitiveness.[8,17,19]

Lignocellulosic biomass typically consists of lignin-carbohydrate complexes (LCC) that are liable for the recalcitrance nature arising from the cross-linking of lignin with carbohydrates (cellulose and hemicellulose) via strong covalent and hydrogen bonding network with benzyl ester, benzyl ether, and phenyl glycoside functional groups.[8,20] During pretreatment, the DES tends to develop new and competing hydrogen bonds with hydroxyl groups present in the carbohydrates and lignin. The DES disintegrates and hydrolyzes the LCC linkages by disturbing the existing bonding interactions between carbohydrates and lignin.[8,20] However, for such disintegration, there are several independent variables that influence the DES-biomass interaction, such as; feedstock type, DES type, pretreatment temperature, pretreatment time, and HBD to HBA molar ratio.[8] The observed trends were lignin dissociation from LCC enhances with the increase of pretreatment temperature and time. For instance, lignin dissociation from LCC for corn cob were increased from 24.8 - 87.6

wt. % for choline chloride-based DES treated at 90-115 °C for 15-24 h.[8,21,22] When betaine and lactic acid mixture (1:2.5 mole/mole) was used for pretreatment of poplar at 130 °C and 12 h, the lignin removal was found 52.4 wt. %.[8,23] For grassy biomass, a low temperature pretreatment (60 °C) resulted in 14.6 wt. % and 87.9 wt. % lignin dislocation from LCC for wheat straw by choline chloride:lactic acid at 1:9 mole/mole and 1:10 mole/mole for 24 h, respectively.[8,24] From above discussion, it could be identified that lignin dissociation occurs during DES pretreatment at high temperature and longer residence time. Unfortunately, among other biopolymers (cellulose, hemicellulose, and starch), lignin has the highest energy content, and it could enhance the fuel properties of pretreated biomass. In this viewpoint, a mild DES pretreatment would be preferable at low temperature-shorter residence time to swell the biomass fibers without affecting the lignin and other biopolymers content significantly.

Therefore, the objectives of this study are (1) to observe the effect of type-III DES pretreatment on loblolly pine's chemical, structure, and morphology at mild pretreatment condition (room temperature and ambient pressure for 1 hour), (2) to investigate hydrochar's chemical and fuel properties with and without DES pretreatment, and (3) to evaluate preliminary process economics of DES pretreatment of loblolly pine and subsequent HTC treatment. To the best of authors´ knowledge, no study has reported surface morphological change at mild DES pretreatment condition let alone the subsequent effect on HTC. Herein, the hypothesis of this study was altering biomass surface morphology at room temperature for 1 hour without significantly affecting the biopolymer compositions could enhance HTC. To prove the hypothesis, loblolly pine was pretreated with two different DESs and morphological properties were evaluated. HTC was performed at three different temperatures using pretreated loblolly pine and fuel properties were measured. A preliminary process economics was performed to evaluate the feasibility of DES pretreatment process prior to HTC compared to standalone HTC process.

2 Materials and Method

2.1 Materials

Loblolly pine residues were obtained from a plantation in southern Georgia. These residues consisted of the tops and limbs of the tree after the main bole is taken for lumber or pulpwood and are considered an underutilized waste from the process. These residues were chipped field side to a 50 mm nominal size, and then passed through an air classification process to further separate the material into what would be considered waste or residuals (high proportion of bark, needles, fines, and exogenous ash) and a higher value, lower ash wood stream. The low-value wood stream was the focus of this study, and readers are directed to Emerson *et. al.*[25], for further details on the mechanism of air classification. The air classified pine (here after raw pine) was further size reduced and then screened through a sieve shaker (Gilson Company Inc., model# SS-15) and particles ranging from 149-595 µm were collected for DES pretreatment.

ChCl was purchased from Acros Organics (Fair Lawn, NJ), urea was purchased from Fisher Scientific (Hampton, NH), MPTB was purchased from TCI America (Portland, OR), and ethylene glycol (EG) was purchased from Sigma-Aldrich (St. Louis, MO).

2.2 DES preparation and pretreatment

First, the ChCl:Urea (1:2 mole/mole) and MPTB:EG (1:4 mole/mole) DESs were prepared at constant temperature (~50 °C) on a magnetic stirrer hot plate. The mixtures were constantly stirred until no trace of solid was visually observed.[26,27] About 20 g raw pine was mixed with 10 parts DES in a 300 mL beaker and sealed with plastic wrap to seal the access of moisture. The mixture was then shaken in an orbital shaker at 300 rpm for 1 h at room temperature (~25 °C). After mixing, the mixture was washed and filtered with approx. 1000 mL DI water to remove >97 % DES from biomass. The washed solid was then kept in a drying oven for 24 h at 105 °C.

2.3 Hydrothermal Carbonization

HTC was carried out in a 300 mL Parr reactor (Moline, IL) for 30 minutes at 180, 220, and 260 °C for raw pine and DES pretreated pine. The experimental procedure was followed from previously published literature.[28] In short, 20 g of dry biomass was mixed with 200 ml of deionized (DI) water and the slurry was poured into the reactor. The reactor was sealed, and content was heated to the desired HTC temperature with constant stirring (~150 rpm) and autogenous pressure. The temperature was kept isothermal for 30 mins and the reactor was cooled down rapidly by a cold-water bath. Finally, the gas was vented in a fume hood and the solid product (hydrochar) was washed thoroughly with ~200 mL of DI water to remove the process liquid adhered to the hydrochar. The washed hydrochar was then dried for 24 h at 105 °C and the dried hydrochar was stored in a sealed container for further analysis. The hydrochars were labelled as untreated H-180, untreated H-220, and untreated H-260, ChCl:Urea-H-180, ChCl:Urea-H-220, ChCl:Urea-H-260, MPTB:EG-H-180, MPTB:EG-H-220, and MPTB:EG-H-260.

2.4 Characterization of solid products

2.4.1 Scanning electron microscopy (SEM)

A Scanning Electron Microscope (SEM: JEOL JSM-6380LV, Tokyo, Japan) was used to investigate the swelling behavior of raw pine after DES pretreatments as well as after HTC. First, a small quantity of dry hydrochar was attached to a carbon tape and coated in gold sputter coater (Denton Vacuum Desk III, Moorestown, NJ) to prevent charging the sample and lower the signal to noise ratio in SEM. The coated sample was analyzed in SEM using the following operating conditions: spot size: 50, voltage: 5 KV, and magnification:

x500. The fiber-to-fiber gap lengths of raw pine and pretreated biomass were measured using the built-in length measuring software (Scandium) to observe the swelling nature after DES pretreatments.

2.4.2 BET surface area and pore size distribution

A High-Pressure Volumetric Analyzer (HPVA II, Norcross, GA) was used to further investigate the effect of pretreatments on Brunauer, Emmett and Teller (BET) surface area, porosity, and the pore volume. The experimental procedure of obtaining surface area, porosity and pore volume was followed from elsewhere.[29] In summary, ultra-high purity nitrogen gas was used as the adsorption gas for the surface area measurement. Liquid nitrogen was used to maintain a constant temperature (-196 °C) throughout the experiment. Prior to gas adsorption, the samples were degassed under vacuum at 20 °C until the pressure stabilized around 0.6–0.7 Pa to eliminate the fraction of water weakly bound inside the samples. Adsorption data were evaluated using the Microactive software from Micromeritics Instrument Corporation (Norcross, GA). The surface area was calculated using BET method which was applied to adsorption isotherm in the relative pressure range (P/P_o) of 0.05-0.35. Total pore volume was determined using nitrogen adsorption data at close to saturation pressure ($P/P_o = 0.99$). Micropore volume were determined by using t-plot analysis. Furthermore, the pore size distribution (PSD) was estimated by applying Non-Local Density Functional Theory (NLDFT) to nitrogen adsorption isotherm.

2.4.3 Higher heating value (HHV)

An IKA C 200 bomb calorimeter (Staufen, BW, Germany) was used to determine the HHV of raw pine and hydrochars following ASTM D240 method. Then energy yield, EY (%) was calculated from equation 1, where MY stands for solid mass yield (calculated from equation 2).

$$EY(\%) = MY(wt.\%) \times \frac{HHV\ of\ dried\ hydrochar}{HHV\ of\ untreated\ dry\ feedstock} \qquad (1)$$

$$MY\ (wt.\%) = \frac{Mass\ of\ dried\ post\text{-}processed\ solid}{Mass\ of\ untreated\ dry\ feedstock} \times 100 \qquad (2)$$

2.4.4 Proximate analysis

Thermogravimetric analysis (TGA) of the raw pine and hydrochars were carried out in a TGA Q5000 (TA instruments, New Castle, DE) to determine the fixed carbon (FC) and volatile matter (VM). The TGA was carried out under inert atmosphere using constant flowrate (40 mL/min) of nitrogen to avoid any possible oxidation and continuously purge the VM. Detailed procedure can be found in our previous article.[28] In short, the sample was first heated to 105 °C and kept isothermal for 5 minutes to determine the moisture content (MC). The sample was then heated to 900 °C at a ramp rate of 20 °C/min and kept isothermal for 5 minutes. The mass loss from 105 °C to 900 °C was labeled as VM. The ash content was found from combustion in a muffle furnace according to ASTM D1102 method.

2.4.5 Ultimate analysis

A FLASH EA 1112 Series (Thermo Scientific) CHNS-O analyzer was used to quantify the elemental carbon, hydrogen, nitrogen, and sulfur content in the sample. The experimental procedure can be found in our earlier publication.[28]

2.4.6 Van Soest fiber analysis

Fiber analysis of the feedstock and pretreated pines were performed in a fiber analyzer (ANKOM fiber analyzer, Model#A200, Macedon, NY) by following Van Soest method.[2] The results were tabulated and shown in supplementary file (Table S1). Neutral detergent fiber (NDF), acidic detergent fiber (ADF), and acidic detergent liquid (ADL) were used to determine the extractives, hemicellulose, and cellulose. The residue after the ADL treatment contains lignin and ash. Lignin was estimated by subtracting ash from ADL residue. Details about the Van Soest fiber analysis can be found elsewhere.[2]

2.4.7 Fourier Transform-Infrared Spectroscopy (FT-IR) analysis

The functional groups for were identified using Thermo Scientific Attenuated total reflector (ATR) FT-IR (Model: Nicolet iS5, Madison, WI). Operating conditions were set at data accumulations: 64, resolution (4), and wavenumber range (500-4000 cm^{-1}). Transmittance was then plotted on Y-axis and wavelength number was on the X-axis. The FT-IR analysis for raw pine, pretreated pines and recycled DESs can be found in supplementary file (Figure S1).

2.5 Preliminary Process Economics

2.5.1 Process overview

From Figure 4, experimentally obtained HHV of untreated-H260 (Case II) was similar to that of ChCl:Urea-H220 (Case I). The aim was to produce hydrochar with similar HHV values, achieved with and without DES pretreatment of the biomass, which could be implemented in industrial scale and hence would require a preliminary economic evaluation of producing hydrochar following both the routes in order to compare the costs associated with both the individual cases of associated processes design. Two different cases were considered in this study where Case I denotes the DES-pretreatment followed by HTC at 220 °C, while Case II represents standalone HTC process at 260 °C, as both hydrochars exhibit similar energy content (more details can be found on section 3.2). Figure 1 shows simplified process flow diagrams (PFD) for both the cases that are used for process economics evaluation.

A basis of 30 tonne/day of raw pine was assumed for both cases to compare the results. In Case I, raw pine and DES (ChCl:Urea) was physically well-mixed and then separated using a screen. The filtrate was reused with an added portion of makeup DES where 1 wt. % of DES fed was assumed to be lost based on the average loss of 0.94 wt. % DES after filtration for 5 cycles in lab-scale experiments (found in Table S3). It was also assumed that the functionality of DES was unchanged over the 5 cycles of reusing DES as found in Figure S3. On the other hand, the pretreated pine in the solid residue was stored in a storage tank prior to mixing with recycled process liquid filtrate from the HTC process. While washing with water was done in lab-scale experiments in order to ensure that no DES is adhered on the biomass, industrial scale of operation would likely not to constitute this step based on the assumption of negligible loss of DES in the biomass residue as well as minimizing wastewater generation. The mixture was then pressurized to 430 psig using a positive displacement pump in order to avoid vaporization of water in the preheater/heat exchanger as well as to account for the major and minor losses of pressure in the system before the stream entered the reactor.[29] The reactor was then operated at 220 °C and 380 psig for a residence time of 30 minutes. It is to be noted that continuous HTC reactor was assumed here, although, the lab-scale reactions were completed using a batch reactor. Heat exchangers and pumps employed in both the cases were assumed to operate at an efficiency of 80 %. After the HTC residence time, the HTC solid product and the process liquid were sent through the preheater for heat recovery. Excess pressure was utilized to drive the cooled product stream to a leaf filter in order to separate the solid hydrochar from the process liquid where the filtered hydrochar was assumed to have a 20 wt. % moisture content.[30] The solid product was stored after drying using a drum dryer such that moisture content was reduced to 11 wt. % which was within typical range of moisture content that is traditionally used in pulverized coal power plants.[31] The gas was vented into the atmosphere and a major portion of the process liquid was recycled to mix with pretreated pine where the remnant was sent to wastewater treatment plant.

In Case II, there was no DES pretreatment and hence untreated raw pine was directly mixed with recycled process liquid filtrate from the HTC process which was then pressurized to 750 psig using a positive displacement pump for the same purpose as in Case I. As the experimentally obtained HHV of untreated-H260 was similar to that of ChCl:Urea-H220, in case II, the HTC was carried out at a higher temperature and hence the reactor was operated at 260 °C and 681 psig for a residence time of 30 minutes. Analogous to Case I, hydrochar and HTC process liquid underwent similar processes of heat recovery, filtration, recycling, and drying to produce dried hydrochar with the same moisture content as in Case I.

2.5.2 Process economics

Mass and energy balance were applied to both Case I and II to determine the feed flowrates and energy demands in order to size the various equipment in the aim of producing solid hydrochar that could be supplied as fuel for any existing powerplant combustion. Cost analysis for the evaluation of process economics generally comprises of estimating capital costs and manufacturing costs. The capital cost estimation was performed similarly for both the cases, Case I and Case II, of with and without pretreatment of the raw pine.

In short, capital cost was evaluated following methodology of Turton *et al.*[32] which was estimated to have an accuracy range of -25%/ +40 %. All dollar values were adjusted for 2020 USD standard using Chemical Engineering Plant Cost Index (CEPCI = 596.2)[33] as the bare module cost of equipment was determined from ‘Matches’ website[34] which provided the cost of equipment for the year 2014. Using the cost of equipment, overall fixed capital investment (FCI) was calculated by applying the following equation where additional costs like general fees, unforeseen costs and supporting site costs were incorporated by using constants of 3 %, 15 % and 50 % from previous literature[35]:

$$\mathrm{FCI} = \sum_{j}^{m} \mathrm{C_{BM\,j}} + 0.03 \sum_{j}^{m} \mathrm{C_{BM\,j}} + 0.15 \sum_{j}^{m} \mathrm{C_{BM\,j}} + 0.5 \sum_{j}^{m} \mathrm{C_{BM\,j}} \tag{3}$$

Working capital investment (WCI) was calculated using:

$$\mathrm{WC} = 0.1(\mathrm{FCI} + \mathrm{C_{OL}} + \mathrm{C_{RM}}) \tag{4}$$

where, C_{OL} and C_{RM} are labor costs and raw material costs, respectively. Total capital investment (TCI) was found by summing FCI and WCI as follows:

$$\mathrm{TCI} = \mathrm{WCI} + \mathrm{FCI} \tag{5}$$

Cost of manufacturing was determined for case I following methodology of Peters *et al.*[36] and for case II following Turton *et al.*[32] as the latter was used by previous literatures [29,37,38] for a similar hydrothermal processing plant. In addition, the various economic parameters used for determining cost associated with manufacturing cost estimation can be found in Table 1. General expenses were then evaluated following estimates of Leon *et al.*[39].

3 Results and Discussion

3.1 Physicochemical and morphological change of biomass by DES pretreatment

Raw pine was pretreated by ChCl: Urea and MTPB:EG at room temperature and atmospheric pressure for 1 hour. Physicochemical and morphological properties were evaluated to study the change in pine due to DES pretreatment and the results are shown in Table 2. For pretreated biomasses, MY can be defined as the percentage of dry mass recovered relative to the raw pine. From the Table 2, it can be observed that very high MYs were resulted in from the DES pretreatment (96.1–96.5 wt. %). This is an indication that biomass biopolymers were not dissociated, unlike what was observed from the literature for DES treatment at higher temperature and longer residence time.[8] To confirm whether the biopolymers were indeed not significantly changed, Van Soest fiber analysis was performed, and the results were presented in Table S1. There was an insignificant change in lignin-carbohydrate composition (Table S1) after DES pretreatment. FTIR was also performed to indicate the change in chemical bonding due to DES pretreatment and results shown in Figure S1 indicates no new bond formation/older bond destruction. Since, the solubilization of hemicellulose, cellulose, and lignin require multiple H-bond (major bond) networks dissociation and reformation to reach a thermodynamically more stable system as discussed in Satlewal *et al.*[8] and Kumar *et al.*[40], it is possible that at such mild DES pretreatment condition (~25 °C, 1 h), the bond dissociation/reformation could not take place due to multiple activation energy (E_a) barriers. This is encouraging as one of the objectives of this study was to pretreat raw pine without losing lignin and other biopolymers content of the pine significantly. It is likely that some portion of pine might have lost during the DES pretreatment and subsequent washing, therefore, the MYs were found a little lower than 100 wt. %.

Proximate and ultimate analyses were performed on the DES pretreated pine to evaluate the change in fixed carbon/volatile contents, and elemental compositions, respectively. The results of proximate and ultimate analysis are reported in Table 2. The FC was increased slightly (~1-2.5 wt. %) with the DES pretreatment for both DESs, while VM decreased from 79.9 wt. % to 77.6 wt. % for only MTPB:EG pretreatment. The ultimate analysis of DES pretreated pine revealed that the elemental carbon content increased from 49.7 wt. % to 52.2 wt. % for DES pretreatments, which were complemented by ~2.4-2.9 wt. % reduction in elemental oxygen content for both DES. The change in such chemical properties could attribute to the relative removal of loosely adhered dirt, entrapped inorganics (~0.2 wt. %) and elemental oxygen content through DES leaching and filtration (Table 2). Physicochemical characterization of DES pretreated pine revealed that biopolymers were mostly conserved, VMs and FCs were slightly changed, and elemental carbon was increased slightly with the DES pretreatment. However, the surface morphology showed a significant modification of pine after DES pretreatment. A close observation of SEM images (Figure 2) uncovers that that the raw pine had a fiber-to-fiber gap length of around ~20 μm, whereas, upon the DES pretreatment, the fiber-to-fiber gap length was increased up to ~32 μm and ~60 μm for ChC:Urea and MPTB:EG pretreatment, respectively. Although Figure 2 is shown for one particle surface, a similar phenomenon is also observed on other particle surface for both DES pretreated pines (Figure S2). The increase in intra-fiber gap length can also be justified by the skeletal density of the fibers. The skeletal density of DES pretreated pine was reduced to 1.0-1.3 g/cc for both pretreatments from 1.4 g/cc for raw pine, which is an indication of a higher volume accessible by the probe gas through the pore network or swollen fibers (Table 3). A detailed investigation reported by Liu *et al.*[41] suggests that pretreatment under the effect of swelling-agent (NaOH/Urea) facilitates the formation of a hierarchical porous carbon structure and improves surface chemical characteristics through swelling the cellulose in biomorphic cotton fibers. It was also observed that when the swelling agent transports through a system of pores and channels, swelling occurs and the intra- and intermolecular H-bonds of cellulose are destroyed.[41,42] As a result, when raw cotton fibers are immersed in the swelling agents, the primary wall bursts and it leads to radial expansion of swollen cellulose to the secondary wall through tears.[41,43–45] Previous studies also suggest that biomass (such as wheat straw) contains relatively high amount of β-O-4 ether linkages (accounts for 50 % of all the linkages), ester linkages, syringyl units, substantial amount of p-coumaric acid and ferulic acid in the lignin, which forms cross-links with hemicellulose.[20,46] These traits make biomass fibers more susceptible to chemical extraction, depolymerization, and/or softening through swelling,[41,46–48] especially by DESs which have high affinity to lignin fraction and its corresponding bonds with cellulose and hemicellulose.[46] Therefore, during the immersion of biomass in the solvents, the fibers could swell (Figure 2) and decrease the skeletal density (Table 3) which ultimately softened the rigid LCC structure.

The BET surface areas of the DES pretreated biomasses, reported in Table 3, reported little changes (up to 0.2 m^2/g of increment relative to the raw pine). The total pore volumes also remained similar (2.6×10^{-3} cm^3/g) after DES pretreatment (Table 3). On the contrary, the incremental pore volume showed intensification for specific pore sizes after each pretreatment (Figure 3, Table S2). The incremental pore volume intensification was calculated by the ratio of incremental pore volume difference (between pretreated sample and raw pine) of any specific pore size to incremental pore volume of the raw pine of the same size. At 55 Å pore width, the incremental pore volume intensification for MPTB:EG lessened by 7.1 %, but a significant change can be observed for 160 Å pore width (40 % abatement). The intensification for 99-160 Å (70-90 %) pore size was found more significant than 50-99 Å range (6.7-26.7 %). One possible explanation is that the accessibility of the DES molecule was completely hindered or reduced due to its size compared to the pore size 20-99 Å. The abatement in pore intensity (55-65 Å and 160 Å) could attribute to the formation of new pores (130 Å) or intensifying existing pores (50-130 Å). Since a significant surface morphological change was observed in the aspect of present study, the effect of this pretreatment on HTC was indeed warranted.

3.2 Effect of DES pretreatment on fuel properties of hydrochars

The physicochemical properties of hydrochars prepared from DES pretreated pine are shown in Table 2. It can be observed that the MYs for DES pretreated hydrochars decreased compared to control hydrochars at any HTC temperature. It is already known that the degree of carbonization is directly correlated to the ease of mass transfer during HTC since water needs to enter the biomass pores, reacts with the organics, and simultaneously, the aqueous products need to leave the pores.[3] Therefore, intensifying the incremental pore volume, swelling the fibers and/or decreasing the skeletal density by DES pretreatment could have broader impacts on less interrupted HTC reactions.

The impacts of DES pretreatments by ChCl:Urea and MPTB:EG showed greater significance in the heating value of the materials (Figure 4). It is evident that the heating value increased from 20.4 to 27.1 MJ/kg for DES pretreated hydrochars, whereas, the control hydrochars showed a change from 19.5 to23.9 MJ/kg. The DES pretreated-H220s showed an energy content close to the untreated-H260 (~23.9 MJ/kg) which signifies high energy content at low temperature HTC, improving the EY as well. EY showed an overall descending order for all the pretreated HTCs (64.4%-71.5 %) and untreated HTCs (64.4%-81.4 %). Since the heating value is positively correlated to the degree of carbonization,[49] the higher HHVs support higher degree of dehydration reactions, resulting in higher loss of oxygen rich carbohydrates from the char during HTC treatment. Henceforth, this supports high degree of carbonization at relatively lower temperature HTC for pretreated pines (HHVs in Table 2). Proximate and ultimate analyses also reveal that the DES pretreatment facilitated carbonization during HTC. The pretreated HTCs showed 20.0-48.6 wt. % FC, 50.8-79.5 wt. % VM and 0.3-0.6 wt. % ash (Table 2). When compared to the untreated HTCs, they showed 19.8-39.4 wt. % FC, 60.3-79.8 wt. % VM, and 0.3-0.5 wt. % ash (Table 2). The ash wt. % remained the same for ChCl:Urea pretreatment and untreated HTCs, except for MPTB:EG pretreatment. This could happen when some inorganics in the crosslinked matrix were leached out to the process liquid during HTC but were re-adsorbed to the pores during condensation.[2,50,51] The pretreated hydrochars showed 53.8-72.6 wt. % elemental carbon and 21.7-39.8 wt. % elemental oxygen, whereas the untreated hydrochars showed only 52.5-63.3 wt. % elemental carbon and 31.1-40.9 wt. % elemental oxygen (Table 2). Moreover, the pretreated H-220s showed ~5-5.6 wt. % higher elemental carbon than untreated H-220 but very close to untreated H-260 (since ~3.7-4.4 wt. % less elemental carbon) (Table 2). This certainly supports that the carbonization was highly facilitated after the pretreatments, in fact, the similar carbonization could be attainable for low temperature pretreated-HTCs than high temperature untreated-HTCs (e.g. pretreated-H220s vs untreated H260s). As expected, the high degree of carbonization (for pretreated biomass) complimented the increasing trend of the heating value.

The enhancement of fuel properties can also be observed from the Van Krevelen diagram (Figure 5). This diagram shows that the closer to the origin of the data points are, the better fuel it is. The following fuel rank can be assigned in terms of the diagram: MPTB:EG-H260>ChCl:Urea-H260>Untreated-H260>MPTB:EG-H220>ChCl:Urea-H220> MPTB:EG-H180>Untreated-H220>Untreated-H180>raw pine. In summary, for the pretreated HTCs, as per discussion (section 3.1), it is possible that the DES could act as a swelling agent which enhanced the radial expansion of LCC fibers (Figure 2). The effect of swelling could augment the carbonization process through softening the LCC bonds (as per the previous discussion in section 3.2) and intensify incremental pore volume (Table S2, Figure 3). Thence, more dehydration and decarboxylation reactions[52] could be favorable for pretreated HTCs than untreated HTCs, supporting the effect of better accessibility of solvent water to the swollen fibers and HTC reaction severity of biomass. Thus, pretreating the biomass prior to HTC could significantly upgrade the hydrochar fuel quality.

3.3 Preliminary process economics

3.3.1 Plant processing conditions of Case I and Case II

The basis of processing plants for both the cases was assumed to be 30 tonne per day of raw pine, assuming the raw pine was dry with minimum water content of 5 wt. %.[53] The processing stream flowrates were calculated by applying experimental data employed to operate batch reactor and tabulated in Table 4. While the solid biomass loading to reactor was 1,188 kg/hr for both the cases, MY of Case I was 63.6 wt. % which was 12.1 wt. % higher than that of Case II and resulted in hydrochar production (on wet basis of 11 wt. % moisture content) of 811 kg/hr and 657 kg/hr, respectively. However, there was approximately 1 wt. %

loss of DES downstream in the post-treatment processing for Case I which resulted in 16 kg/hr of more process liquid that was transferred to the wastewater treatment plant in comparison to Case II. The various equipment required for both cases' process plants along with the approximate sizing parameters are summarized in Table 5. Capital cost was then estimated based on the loading, sizing and quantity of each equipment used.

3.3.2 Estimation of capital, manufacturing, and operating cost

Capital and manufacturing cost estimated for solid hydrochar production plant with (Case I) and without (Case II) DES pretreatment of raw pine prior to HTC is summarized in Table 6. From capital cost analysis, the total estimated C_{BM} was \$736,355 and \$619, 884 for case I and II, respectively, where the discrepancy was expected as there were additional units in Case I associated with DES pretreatment of the biomass. This accounted for a higher proportion of cost invested in storage (18.5 %) and mixer (17.8 %) in the pretreatment unit of Case I in comparison to 14.5 % and 11.0 %, respectively for Case II. Moreover, MY of Case I was higher which lead to the size of filter and dryer to be greater in size than in case II. On the contrary, Case II required higher proportion of capital investment in pump (13.5 %) and heat exchanger (10.0 %) as reactor was operated at higher temperature and pressure to produce hydrochar of similar calorific value as that in Case I. Using the total estimated C_{BM}, FCI and then WCI was calculated for both the cases which added to TCI of \$1.5 M and \$1.3 M for Case I and II, respectively.

Various components of manufacturing cost as listed in Table 6 totaled to be \$1.7 million and \$2.4 million for Case I and II, respectively, where almost 55 % and 32 % of manufacturing cost were accounted for raw materials. Similar observation was made by Saba *et al.*[29] and Wirth *et al.*[54], where raw material cost made up a significant portion, 37- 59 %, of the total manufacturing cost. In addition, where wastewater treatment generally contributes 3-4 % of total manufacturing cost of such plants,[29] it was calculated as 2.2 % and 1.5 % for

Case I and II, respectively. Other components of manufacturing costs like fixed charges, plant overhead cost as well as direct production cost for Case I and Case II were evaluated, as found in Table 6. Moreover, annual general expenses were evaluated for both the cases which incorporated administrative, distribution and marketing in addition to research and development cost for Case I and Case II that summed up to be \$359,596 and \$466,186, respectively. Eventually, total operating and manufacturing cost for Case I and Case II were calculated as \$2.09 M and \$2.84 M. Primarily, the significantly higher throughput of solid hydrochar produced at lower HTC reaction temperature for Case I might have contributed to an overall reduction of operating cost compared to Case II. However, further process improvement with heat integration, increase in MY as well as plant production capacity of Case I might further reduce the total operating and manufacturing cost.

4 Conclusions

This study investigated the surface morphological change after DES pretreatment and the pretreatment effect on HTC. It was found that the DES swelled the biopolymers, reducing the skeletal density by 0.1-0.4 g/cm^3 relative to raw pine. Although the total pore volume remained same (2.6×10^{-3} cm^3/g) for both raw and pretreated pine, some new pores evolved (130 Å pore size) and some others intensified by 10-90 % after pretreatment relative to raw pine. The surface fiber-to-fiber gap of the biomass increased 52-185 % (relative to raw pine) after pretreatment which supported the biomass swelling effect by DES. The profound effect of the pretreatment on HTC was further observed in ultimate analysis, proximate analysis and energy content. The O/C and H/C for pretreated H-220s (0.6 O/C and 0.08 H/C) and H-260s (0.3-0.4 O/C and 0.06 H/C) showed significant difference than untreated H-220 (0.7 O/C and 0.11 H/C) and H-260 (0.5 O/C and 0.08 H/C). Consequently, the high energy content (up to 42 % increase) and low mass yield (up to 50 %) supported the pretreatment effect well on HTC reaction severity. Finally, preliminary process economics revealed that DES pretreatment would add cost to the fixed capital investment compared to standalone HTC process. However, the total operating and manufacturing cost of the DES pretreatment followed by HTC was lower than standalone HTC, as a reduced HTC process temperature was required to generate hydrochar with high energy content.

5 Supporting Information

Elaboration of experimental data about biopolymer composition, surface morphology of pretreated biomass, DES recovery, and change in functionalities of pretreated biomass and recycled DES. This information is available free of charge via the Internet at http://pubs.acs.org/.

6 Acknowledgements

This invited contribution is part of the I&EC Research special issue for the 2021 Class of Influential Researchers. The material is based upon work supported by the National Science Foundation under Grant No. 1856058 and by United States Department of Agriculture, grant number 2019-67019-31594. This work was authored in part by the Idaho National Laboratory under USA Department of Energy (DOE) Idaho Operations Office with Contract no. DE-AC07-05ID14517. The authors are grateful for the air classification technology of the Biomass Feedstock National User Facility (BFNUF) at Idaho National Laboratory. The authors also acknowledge the laboratory assistance from Cadianne Chambers, Aaron Portell, and Thomas Quaid from Biofuels Lab and Tatiana Karpova from microscopy lab at Florida Institute of Technology.

References

(1) Song, Y.; Chandra, R. P.; Zhang, X.; Tan, T.; Saddler, J. N. Comparing Deep Eutectic Solvent (DES) to Hydrotropes for Their Ability to Enhance the Fractionation and Enzymatic Hydrolysis of Willow and Corn Stover. *Sustainable Energy*,**2019**;3(5):1329-37.

(2) Reza, M. T.; Lynam, J. G.; Uddin, M. H.; Coronella, C. J. Hydrothermal Carbonization: Fate of Inorganics. *Biomass and Bioenergy* **2013**, *49*, 86–94. https://doi.org/10.1016/j.biombioe.2012.12.004.

(3) Reza, M. T.; Yan, W.; Uddin, M. H.; Lynam, J. G.; Hoekman, S. K.; Coronella, C. J.; Vásquez, V. R. Reaction Kinetics of Hydrothermal Carbonization of Loblolly Pine. *Bioresource Technology* **2013**, *139*, 161–169. https://doi.org/10.1016/j.biortech.2013.04.028.

(4) Heidari, M.; Salaudeen, S.; Dutta, A.; Acharya, B. Effects of Process Water Recycling and Particle Sizes on Hydrothermal Carbonization of Biomass. *Energy Fuels* **2018**, *32* (11), 11576–11586. https://doi.org/10.1021/acs.energyfuels.8b02684.

(5) Wüst, D.; Correa, C. R.; Jung, D.; Zimmermann, M.; Kruse, A.; Fiori, L. Understanding the Influence of Biomass Particle Size and Reaction Medium on the Formation Pathways of Hydrochar. *Biomass Conv. Bioref.* **2020**, *10* (4), 1357–1380. https://doi.org/10.1007/s13399-019-00488-0.

(6) Luo, S.; Zhou, Y.; Yi, C.; Luo, Y.; Fu, J. Influence of the Feed Moisture, Rotor Speed, and Blades Gap on the Performances of a Biomass Pulverization Technology. *The Scientific World Journal* **2014**, *2014*, e435816. https://doi.org/10.1155/2014/435816.

(7) Cocero Alonso, M. J.; Abad Fernández, N.; Adamovic, T.; Vaquerizo Martín, L.; Martínez Fajardo, C.; Pazo Cepeda, M. V. Understanding Biomass Fractionation in Subcritical & Supercritical Water. **2017**. https://doi.org/10.1016/j.supflu.2017.08.012.

(8) Satlewal, A.; Agrawal, R.; Bhagia, S.; Sangoro, J.; Ragauskas, A. J. Natural Deep Eutectic Solvents for Lignocellulosic Biomass Pretreatment: Recent Developments, Challenges and Novel Opportunities. *Biotechnology Advances* **2018**, *36* (8), 2032–2050. https://doi.org/10.1016/j.biotechadv.2018.08.009.

(9) Agbor, V. B.; Cicek, N.; Sparling, R.; Berlin, A.; Levin, D. B. Biomass Pretreatment: Fundamentals toward Application. *Biotechnology Advances* **2011**, *29* (6), 675–685. https://doi.org/10.1016/j.biotechadv.2011.05.005.

(10) Reza, M. T.; Rottler, E.; Herklotz, L.; Wirth, B. Hydrothermal Carbonization (HTC) of Wheat Straw: Influence of Feedwater PH Prepared by Acetic Acid and Potassium Hydroxide. *Bioresour Technol* **2015**, *182*, 336–344. https://doi.org/10.1016/j.biortech.2015.02.024.

(11) Lynam, J. G., sPretreatment of Lignocellulosic Biomass Using Acetic Acid, Salt, and Ionic Liquids, University of Nevada, Reno, **2011**.

(12) Das, P. K.; Das, B. P.; Dash, P. 13 - Potentials of Postharvest Rice Crop Residues as a Source of Biofuel. In *Refining Biomass Residues for Sustainable Energy and Bioproducts*; Kumar, R. P., Gnansounou, E., Raman, J. K., Baskar, G., Eds.; Academic Press, **2020**; pp 275–301. https://doi.org/10.1016/B978-0-12-818996-2.00013-2.

(13) George, A.; Brandt, A.; Tran, K.; Zahari, S. M. S. N. S.; Klein-Marcuschamer, D.; Sun, N.; Sathitsuksanoh, N.; Shi, J.; Stavila, V.; Parthasarathi, R.; Singh, S.; Holmes, B. M.; Welton, T.; Simmons, B. A.; Hallett, J. P. Design of Low-Cost Ionic Liquids for Lignocellulosic Biomass Pretreatment. *Green Chem.* **2015**, *17* (3), 1728–1734. https://doi.org/10.1039/C4GC01208A.

(14) Xu, G.C.; Ding, J.C.; Han, R.Z.;Dong, J.J. and Ni, Y., Enhancing Cellulose Accessibility of Corn Stover by Deep Eutectic Solvent Pretreatment for Butanol. *Bioresource technology* **2016,** 203, pp. 364-369.

(15) Chen, Z.; Ragauskas, A.; Wan, C. Lignin Extraction and Upgrading Using Deep Eutectic Solvents. *Industrial Crops and Products* **2020**, *147*, 112241. https://doi.org/10.1016/j.indcrop.2020.112241.

(16) Lynam, J. G.; Kumar, N.; Wong, M. J. Deep Eutectic Solvents' Ability to Solubilize Lignin, Cellulose, and Hemicellulose; Thermal Stability; and Density. *Bioresource Technology* **2017**, *238*, 684–689. https://doi.org/10.1016/j.biortech.2017.04.079.

(17) Kohli, K.; Katuwal, S.; Biswas, A.; Sharma, B. K. Effective Delignification of Lignocellulosic Biomass by Microwave Assisted Deep Eutectic Solvents. *Bioresource Technology* **2020**, *303*, 122897. https://doi.org/10.1016/j.biortech.2020.122897.

(18) Zuo, M.; Zeng, X.; Sun, Y.; Tang, X.; Lin, L. Processing of Biomass in Deep Eutectic Solvents. In *Deep Eutectic Solvents*; Ramón, D. J., Guillena, G., Eds.; Wiley, **2019**; pp 235–255. https://doi.org/10.1002/9783527818488.ch12.

(19) Kalhor, P.; Ghandi, K. Deep Eutectic Solvents for Pretreatment, Extraction, and Catalysis of Biomass and Food Waste. *Molecules* **2019**, *24* (22), 4012. https://doi.org/10.3390/molecules24224012.

(20) Xia, Q.; Liu, Y.; Meng, J.; Cheng, W.; Chen, W.; Liu, S.; Liu, Y.; Li, J.; Yu, H. 1 Multiple Hydrogen Bond Coordination in Three-Constituent Deep Eutectic 2 Solvent Enhances Lignin Fractionation from Biomass. *Green Chemistry*. **2018**; 20 (12): 2711-21.

(21) Procentese, A.; Johnson, E.; Orr, V.; Garruto Campanile, A.; Wood, J. A.; Marzocchella, A.; Rehmann, L. Deep Eutectic Solvent Pretreatment and Subsequent Saccharification of Corncob. *Bioresource Technology* **2015**, *192*, 31–36. https://doi.org/10.1016/j.biortech.2015.05.053.

(22) Zhang, C.-W.; Xia, S.-Q.; Ma, P.-S. Facile Pretreatment of Lignocellulosic Biomass Using Deep Eutectic Solvents. *Bioresource Technology* **2016**, *219*, 1–5. https://doi.org/10.1016/j.biortech.2016.07.026.

(23) Tian, D.; Chandra, R. P.; Lee, J.-S.; Lu, C.; Saddler, J. N. A Comparison of Various Lignin-Extraction Methods to Enhance the Accessibility and Ease of Enzymatic Hydrolysis of the Cellulosic Component of Steam-Pretreated Poplar. *Biotechnology for Biofuels* **2017**, *10* (1). https://doi.org/10.1186/s13068-017-0846-5.

(24) Jablonský, M.; Škulcová, A.; Kamenská, L.; Vrška, M.; Šíma, J. Deep Eutectic Solvents: Fractionation of Wheat Straw. *BioResources* **2015**, *10* (4), 8039–8047. https://doi.org/10.15376/biores.10.4.8039-8047.

(25) Emerson, R. M.; Hernandez, S.; Williams, C. L.; Lacey, J. A.; Hartley, D. S. Improving Bioenergy Feedstock Quality of High Moisture Short Rotation Woody Crops Using Air Classification. *Biomass and Bioenergy* **2018**, *117*, 56–62. https://doi.org/10.1016/j.biombioe.2018.07.015.

(26) Shahbaz, K.; Baroutian, S.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M. Densities of Ammonium and Phosphonium Based Deep Eutectic Solvents: Prediction Using Artificial Intelligence and Group Contribution Techniques. *Thermochimica Acta* **2012**, *527*, 59–66. https://doi.org/10.1016/j.tca.2011.10.010.

(27) Ibrahim, R. K.; Hayyan, M.; AlSaadi, M. A.; Ibrahim, S.; Hayyan, A.; Hashim, M. A. Physical Properties of Ethylene Glycol-Based Deep Eutectic Solvents. *Journal of Molecular Liquids* **2019**, *276*, 794–800. https://doi.org/10.1016/j.molliq.2018.12.032.

(28) Islam, M. T.; Saha, N.; Hernandez, S.; Klinger, J.; Reza, M. T. Integration of Air Classification and Hydrothermal Carbonization to Enhance Energy Recovery of Corn Stover. *Energies* **2021**, *14* (5), 1397. https://doi.org/10.3390/en14051397.

(29) Saba, A.; McGaughy, K.; Reza, M. T. Techno-Economic Assessment of Co-Hydrothermal Carbonization of a Coal-Miscanthus Blend. *Energies* **2019**, *12* (4), 630. https://doi.org/10.3390/en12040630.

(30) Kambo, H. S.; Dutta, A. Strength, Storage, and Combustion Characteristics of Densified Lignocellulosic Biomass Produced via Torrefaction and Hydrothermal

Carbonization. *Applied Energy* **2014**, *135*, 182–191. https://doi.org/10.1016/j.apenergy.2014.08.094.

(31) Zoelle, A.; Keairns, D.; Pinkerton, L. L.; Turner, M. J.; Woods, M.; Kuehn, N.; Shah, V.; Chou, V. *Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal (PC) and Natural Gas to Electricity Revision 3*; DOE/NETL-2015/1723; National Energy Technology Laboratory (NETL), Pittsburgh, PA, Morgantown, WV (United States), 2015. https://netl.doe.gov/projects/files/CostAndPerformanceBaselineForFossilEnergyPlantsVol1BitumCoalAndNGtoElectBBRRev4-1_092419

(32) Turton, R.; Bailie, R. C.; Whiting, W. B.; Shaeiwitz, J. A. *Analysis, Synthesis and Design of Chemical Processes*;4th edition.; Pearson Education, 2008.

(33) Plant Cost Index Archives. *Chemical Engineering*. https://www.chemengonline.com/pci-home (accessed 2021-07-21)

(34) Matches' engineering to chemical energy manufacturing metallurgical industries. https://www.matche.com/default.html (accessed 2021-07-17).

(35) Mahmood, R.; Parshetti, G. K.; Balasubramanian, R. Energy, Exergy and Techno-Economic Analyses of Hydrothermal Oxidation of Food Waste to Produce Hydro-Char and Bio-Oil. *Energy* **2016**, *102*, 187–198. https://doi.org/10.1016/j.energy.2016.02.042.

(36) Peters, M.; Timmerhaus, K.; West, R.; Peters, M. *Plant Design and Economics for Chemical Engineers*, 5th edition.; McGraw-Hill Education: New York, 2002.

(37) Saha, N.; McGaughy, K.; Davis, S. C.; Reza, M. T. Assessing Hydrothermal Carbonization as Sustainable Home Sewage Management for Rural Counties: A Case Study from Appalachian Ohio. *Science of The Total Environment* **2021**, *781*, 146648. https://doi.org/10.1016/j.scitotenv.2021.146648.

(38) Mazumder, S.; Saha, P.; McGaughy, K.; Saba, A.; Reza, M. T. Technoeconomic Analysis of Co-Hydrothermal Carbonization of Coal Waste and Food Waste. *Biomass Conv. Bioref.* **2020**. https://doi.org/10.1007/s13399-020-00817-8.

(39) León, M.; Silva, J.; Carrasco, S.; Barrientos, N. Design, Cost Estimation and Sensitivity Analysis for a Production Process of Activated Carbon from Waste Nutshells by Physical Activation. *Processes* **2020**, *8* (8), 945. https://doi.org/10.3390/pr8080945.

(40) Kumar, A. K.; Parikh, B. S.; Pravakar, M. Natural Deep Eutectic Solvent Mediated Pretreatment of Rice Straw: Bioanalytical Characterization of Lignin Extract and Enzymatic Hydrolysis of Pretreated Biomass Residue. *Environ Sci Pollut Res* **2016**, *23* (10), 9265–9275. https://doi.org/10.1007/s11356-015-4780-4.

(41) Liu, Y.; Shi, Z.; Gao, Y.; An, W.; Cao, Z.; Liu, J. Biomass-Swelling Assisted Synthesis of Hierarchical Porous Carbon Fibers for Supercapacitor Electrodes. *ACS Appl. Mater. Interfaces* **2016**, *8* (42), 28283–28290. https://doi.org/10.1021/acsami.5b11558.

(42) Cuissinat, C.; Navard, P. Swelling and Dissolution of Cellulose Part 1: Free Floating Cotton and Wood Fibres in N-Methylmorpholine-N-Oxide–Water Mixtures. *Macromolecular Symposia* **2006**, *244* (1), 1–18. https://doi.org/10.1002/masy.200651201.

(43) Cuissinat, C.; Navard, P. Swelling and Dissolution of Cellulose, Part III: Plant Fibres in Aqueous Systems. *Cellulose* **2008**, *15* (1), 67–74. https://doi.org/10.1007/s10570-007-9158-4.

(44) Cuissinat, C.; Navard, P.; Heinze, T. Swelling and Dissolution of Cellulose. Part IV: Free Floating Cotton and Wood Fibres in Ionic Liquids. *Carbohydrate Polymers* **2008**, *72* (4), 590–596. https://doi.org/10.1016/j.carbpol.2007.09.029.

(45) Cuissinat, C.; Navard, P.; Heinze, T. Swelling and Dissolution of Cellulose, Part V: Cellulose Derivatives Fibres in Aqueous Systems and Ionic Liquids. *Cellulose* **2008**, *15* (1), 75–80. https://doi.org/10.1007/s10570-007-9159-3.

(46) Lou, R.; Ma, R.; Lin, K.; Ahamed, A.; Zhang, X. Facile Extraction of Wheat Straw by Deep Eutectic Solvent (DES) to Produce Lignin Nanoparticles. *ACS Sustainable Chem. Eng.* **2019**, *7* (12), 10248–10256. https://doi.org/10.1021/acssuschemeng.8b05816.

(47) Hou, X.-D.; Li, A.-L.; Lin, K.-P.; Wang, Y.-Y.; Kuang, Z.-Y.; Cao, S.-L. Insight into the Structure-Function Relationships of Deep Eutectic Solvents during Rice Straw Pretreatment. *Bioresour Technol* **2018**, *249*, 261–267. https://doi.org/10.1016/j.biortech.2017.10.019.

(48) Loow, Y.-L.; Foo, L. Y. W.; Procentese, A.; Siow, L. F.; Teoh, W. H.; Daud, N. N. N.; Jahim, J.; Mohammad, A. W. Potential Use of Pure and Diluted Choline Chloride-Based Deep Eutectic Solvent in Delignification of Oil Palm Fronds. *Process Safety and Environmental Protection* **2019**, *123*, pp.190-198.

(49) Śliz, M.; Wilk, M. A Comprehensive Investigation of Hydrothermal Carbonization: Energy Potential of Hydrochar Derived from Virginia Mallow. *Renewable Energy* **2020**, *156*, 942–950. https://doi.org/10.1016/j.renene.2020.04.124.

(50) Funke, A.; Ziegler, F. Hydrothermal Carbonization of Biomass: A Summary and Discussion of Chemical Mechanisms for Process Engineering. *Biofuels, Bioprod. Bioref.* **2010**, *4* (2), 160–177. https://doi.org/10.1002/bbb.198.

(51) Qadi, N.; Takeno, K.; Mosqueda, A.; Kobayashi, M.; Motoyama, Y.; Yoshikawa, K. Effect of Hydrothermal Carbonization Conditions on the Physicochemical Properties and Gasification Reactivity of Energy Grass. *Energy Fuels* **2019**, *33* (7), 6436–6443. https://doi.org/10.1021/acs.energyfuels.9b00994.

(52) Saba, A.; Saha, P.; Reza, M. T. Co-Hydrothermal Carbonization of Coal-Biomass Blend: Influence of Temperature on Solid Fuel Properties. *Fuel Processing Technology* **2017**, *167*, 711–720. https://doi.org/10.1016/j.fuproc.2017.08.016.

(53) Oginni, O.; Fasina, O.; Adhikari, S.; Fulton, J. Contribution of Particle Size and Moisture Content to Flowability of Fractionated Ground Loblolly Pine, Auburn University, 2014. https://doi.org/10.13140/RG.2.1.4752.6643.

(54) Wirth, B.; Eberhardt, G.; Lotze-Campen, H.; Erlach, B.; Rolinski, S.; Rothe, P. Hydrothermal Carbonization: Influence of Plant Capacity, Feedstock Choice and Location on Product Cost. In *Proceedings of 19th European Biomass Conference & Exhibition, 2011 Jun 6–10, Berlin, Germany*; 2011; pp 2001–2010.

(55) Ulrich, G. D. *A Guide to Chemical Engineering Process Design and Economics*, 1st edition.; Wiley: New York, 1984.

(56) Choline Chloride 70% 75% Liquid Low Price By Manufacturer - Buy Animal Feed Additive Promote Growth And Healthy,Poultry And Livestock Feed Additive,Used For Fish Cow Pig Product on Alibaba.com https://www.alibaba.com/product-detail/Choline-Chloride-70-75-liquid-low_1600117349864.html?spm=a2700.7724857.normal_offer.d_title.6084e1ebKMnlvg (accessed 2021-09-21).

(57) Urea - Buy Urea N46,Urea For Sale Product on Alibaba.com https://www.alibaba.com/product-detail/Urea_60419772906.html?spm=a2700.7724857.normal_offer.d_image.179f327bHLF0HT (accessed 2021-09-21).

(58) Langholtz, M. H.; Stokes, B. J.; Eaton, L. M. *2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy*;

https://www.energy.gov/eere/bioenergy/downloads/2016-billion-ton-report-advancing-domestic-resources-thriving-bioeconomy (accessed 2021-09-21)

(59) Homepage - U.S. Energy Information Administration (EIA) https://www.eia.gov/index.php (accessed 2021-07-17).

(60) United States Natural Gas Industrial Price (Dollars per Thousand Cubic Feet) https://www.eia.gov/dnav/ng/hist/n3035us3m.htm (accessed 2021-07-17).

(61) Statnick, R. Ohio Coal Development Agency Site Visit and Economic Analysis Recommendations. *Funding Agency Program Manager Tax Usage Reccomendation.; State of Ohio Development Services Agency: Athens, OH, USA* **2018**.

(62) Davis, R.; Tao, L.; Tan, E. C. D.; Biddy, M. J.; Beckham, G. T.; Scarlata, C.; Jacobson, J.; Cafferty, K.; Ross, J.; Lukas, J. *Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons: Dilute-Acid and Enzymatic Deconstruction of Biomass to Sugars and Biological Conversion of Sugars to Hydrocarbons*; National Renewable Energy Lab.(NREL), Golden, CO (United States), 2013.

Table and Figure Captions

Table 1. Economic parameters for estimation of manufacturing costs used for process economics

Table 2. Mass yield, proximate and ultimate analysis of raw pine, DES-treated pine, and pine hydrochars prepared at HTC various temperatures. *below detection

Table 3. BET surface area, total pore volume, and skeletal density of pine after DES pretreatment

Table 4. Process flowrates used for material and energy balance to size various equipment

Table 5. Process equipment required with corresponding quantity and required size for Case I and II

Table 6. Cost summary for solid hydrochar production plant with (Case I) and without (Case II) DES pretreatment of raw pine prior to HTC

Figure 1: Process flow diagram of Case I (top figure) and II (bottom figure) used for preliminary process economics (Note: Raw pine is referred to as loblolly pine)

Figure 2. SEM images of one random particle with fiber-to-fiber distance of (a) raw pine, (b) ChCl:Urea-treated pine, and (c) MPTB:EG-treated pine

Figure 3. Pore size distribution of pine after DES pretreatment

Figure 4. Higher heating value (HHV) and energy yield (EY) of raw pine, hydrochars from standalone HTC, and hydrochars from DES pretreated pine followed by HTC.

Figure 5. van-Krevelen diagram of raw pine, hydrochars from standalone HTC, and hydrochars from DES pretreated pine followed by HTC

Table 1. Economic parameters for estimation of manufacturing costs used for process economics

Parameter	**Value**		**Reference**
	Case I	**Case II**	
Number of labors	10	9	55
Choline chloride ($/kg)	0.55	-	56
Urea ($/kg)	0.02	-	57
Loblolly pine ($/tonne)	84		58
Waste water disposal ($/tonne)	13.21		37
Operating labor salary ($/year)	45,000		37
Electricity cost ($/kW/h)	0.066		59
Natural gas cost ($/m^3)	0.132		60
Tax rate (%)	25		61
Annual interest rate (%)	10		62
Plant life (years)	20		29
Depreciation	7-year MACRS		62
2014 CEPCI	576.1		33
2020 CEPCI	596.2		33

Table 2. Mass yield, proximate and ultimate analysis of raw pine, DES-treated pine, and pine hydrochars prepared at HTC various temperatures. Where BD indicates below detection limit.

	Sample type	MY (wt. %)	Proximate analysis			Ultimate analysis				
			VM (wt.%)	FC (wt.%)	Ash (wt.%)	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)
	Raw pine	100±0.0	79.9±0.2	19.2±0.1	0.9±0.1	49.7±0.5	5.9±0.0	0.4±0.1	BD*	43.7±0.0
Pretreatment	ChCl:Urea-treated	96.1±0.6	79.3±0.5	20.1±0.4	0.7±0.2	52.2±1.4	5.8±0.0	0.4±0.0	BD*	40.8±1.4
	MPTB:EG-treated	96.5±0.7	77.6±0.4	21.7±0.3	0.7±0.1	52.1±0.1	5.8±0.2	BD*	BD*	41.3±0.2
Standalone HTC	Untreated H-180	80.0±0.0	78.3±2.3	21.2±2.3	0.5±0.0	52.5±0.8	6.1±0.0	BD*	BD*	40.9±0.8
	Untreated H-220	68.0±0.0	79.8±2.3	19.8±2.4	0.4±0.1	54.0±0.7	5.9±0.1	BD*	BD*	39.7±0.7
	Untreated H-260	51.5±0.0	60.3±1.1	39.4±1.2	0.3±0.1	63.3±0.5	5.1±0.0	BD*	BD*	31.1±0.7
Pretreated HTC	ChCl:Urea H-180	63.8±2.8	79.5±0.0	20.0±0.1	0.5±0.1	53.8±1.2	5.5±0.1	BD*	BD*	39.8±1.4
	ChCl:Urea H-220	54.2±3.8	65.8±0.5	33.9±0.6	0.4±0.1	58.9±0.5	4.8±0.1	BD*	BD*	35.7±0.6
	ChCl:Urea H-260	47.2±1.3	51.8±0.0	47.9±0.1	0.3±0.1	67.7±0.2	4.4±0.0	BD*	BD*	27.6±0.3
	MPTB:EG H-180	65.6±1.2	77.5±0.7	21.9±0.7	0.6±0.0	54.0±0.1	5.8±0.2	BD*	BD*	39.5±0.3
	MPTB:EG H-220	63.5±0.1	67.1±2.8	32.1±2.6	0.6±0.2	59.6±1.1	5.0±0.1	BD*	BD*	34.9±1.2
	MPTB:EG H-260	47.8±0.5	50.8±0.3	48.6±0.3	0.6±0.0	72.6±0.3	4.7±0.0	0.4±0.0	BD*	21.7±0.3

Table 3. BET surface area, total pore volume, and skeletal density of pine after DES pretreatment

Biomass type	BET surface area (m^2/g)	Total pore volume ($\times 10^3$ cm^3/g)	Skeletal density (g/cc)
Raw pine	1.9±0.0	2.6	1.4
ChCl:Urea-treated	2.0±0.0	2.6	1.3
MPTB:EG-treated	2.1±0.0	2.6	1.0

Table 4. Process flowrates used for material and energy balance to size various equipment

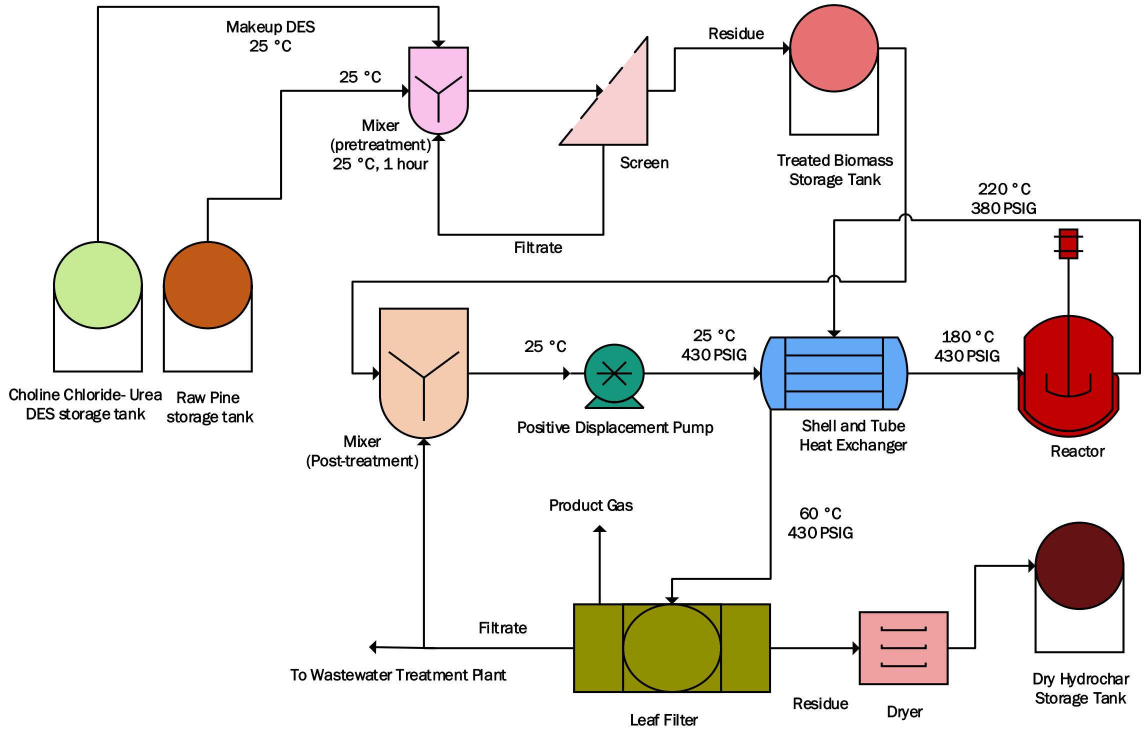
Parameters	**Case I**	**Case II**
Reaction temperature (°C)	220	260
DES: Raw Pine ratio (mass/mass)	10:1	-
ChCl:Urea ratio (mole/mole)	1:2	-
Raw Pine: total liquid feed to reactor (mass/mass)	1:10	1:10
Makeup DES (kg/hr)	119	-
Total process feed to the reactor (kg/hr)	13,063	13,063
Total solid feed to the reactor (kg/hr)	1,188	1,188
Total liquid feed to the reactor (kg/hr)	11,875	11,875
HTC conversion (%)	63.6	51.5
Process liquid recycled (kg/hr)	11,693	11,813
Gas produced from reactor (kg/hr)	59.4	129
Process liquid to wastewater treatmemt (kg/hr)	403	387
Moisture dried in dryer (kg/hr)	97	77
Hydrochar produced with 11% moisture (kg/hr)	811	657

Table 5. Process equipment required with corresponding quantity and required size for Case I and II

Process Equipment	**Unit**	**Case I**		**Case II**	
		Quantity	**Size**	**Quantity**	**Size**
Raw pine storage tank (API fixed roof)	gallon	3	9,500	3	9,500
DES storage tank (API fixed roof)	gallon	1	2,753	-	-
Mixer (Pre-treatment)	hp	1	17	-	-
Vibratory Screen	ft^2	1	10	-	-
DES-treated loblolly pine Storage Tank	gallon	4	9,500	-	-
Mixer (Post-treatment)	hp	1	18.9	1	19.0
Positive displacement pump	kW	1	11.6	1	20.3
Shell and tube heat exchanger	ft^2	1	613	1	1,220
Jacketed agitated reactor	gallon	1	1,779	1	1,779
Leaf filter	ft^2	1	110	1	89
Drum dryer	ft^2	1	117	1	95
Hydrochar storage tank (API fixed roof)	gallon	1	2,507	1	2,030

Table 6. Cost summary for solid hydrochar production plant with (Case I) and without (Case II) DES pretreatment of raw pine prior to HTC

Cost Component	**Item**	**Case I**	**Cost Distribution (%)**	**Case II**	**Cost Distribution (%)**
Capital Costs ($)	Storage	135,882	18.5	89,829	14.5
	Pump	65,307	8.9	84,011	13.6
	Mixer	131,327	17.8	67,992	11.0
	Heat exchanger	34,358	4.7	62,100	10.0
	Reactor	197,831	26.9	177,380	28.6
	Dryer	112,493	15.3	103,903	16.8
	Separation Process	59,157	8.0	34,669	5.6
	Total C_{BM}	736,355		619,884	
	FCI	1,237,076		1,041,405	
	WC	282,852		221,141	
	TCI	1,519,928		1,262,546	
Manufacturing Costs ($/year)	Raw material	943,308		765,000	
	Labor	432,000		405,000	
	Wastewater treatment	38,333		36,774	
	Fixed charges, plant overhead and other direct production cost	314,542		1,193,562	
General Expenses ($/year)	Administrative	89,219		81,066	
	Distribution and marketing	185,884		264,770	
	Research and development	84,493		120,350	
Total operating and manufacturing cost ($/year)		2,087,779		2,836,411	



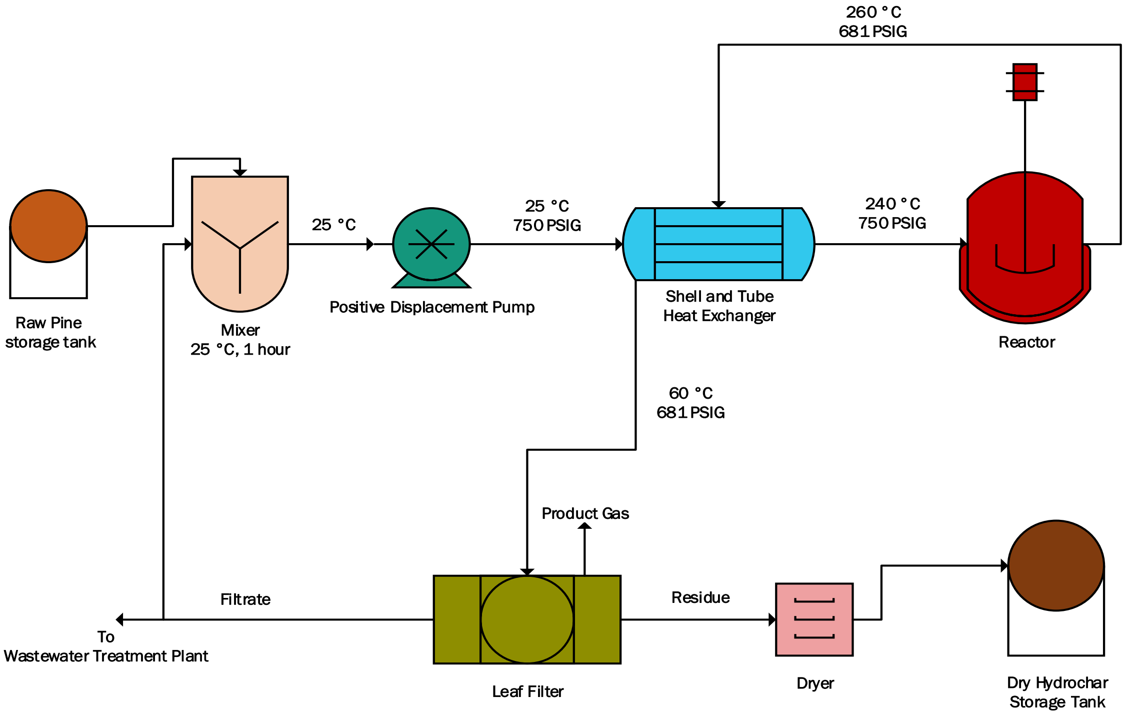
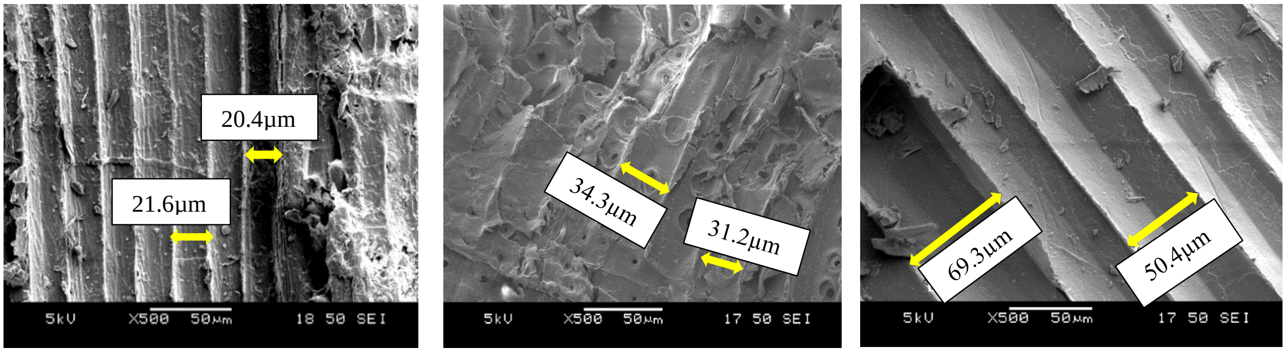


Figure 1: Process flow diagram of Case I (top figure) and II (bottom figure) used for preliminary process economics (Note: Raw pine is referred to as loblolly pine)



(a) Raw pine **(b) ChCl:Urea-treated** **(c) MPTB:EG-treated**

Figure 2. SEM images of one random particle with fiber-to-fiber distance of (a) raw pine, (b) ChCl:Urea-treated pine, and (c) MPTB:EG-treated pine

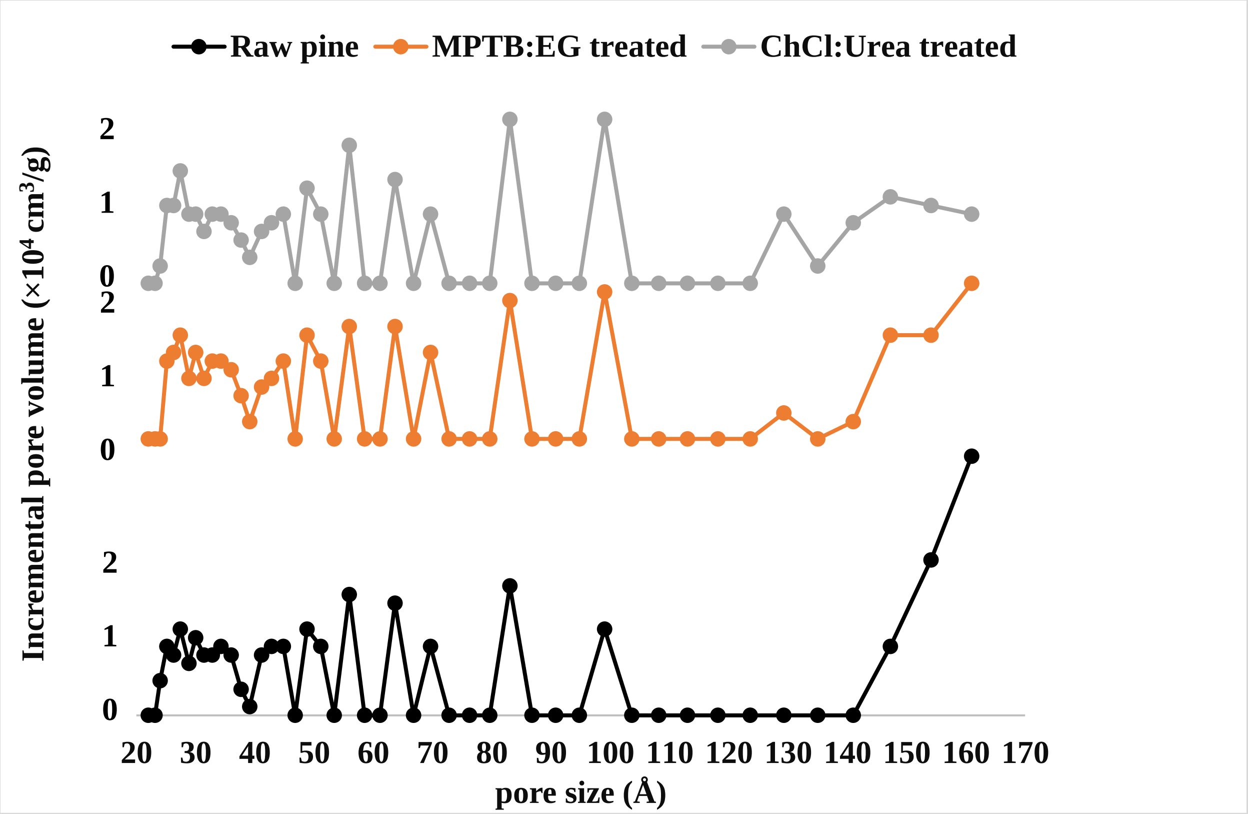


Figure 3. Pore size distribution of pine after DES pretreatment

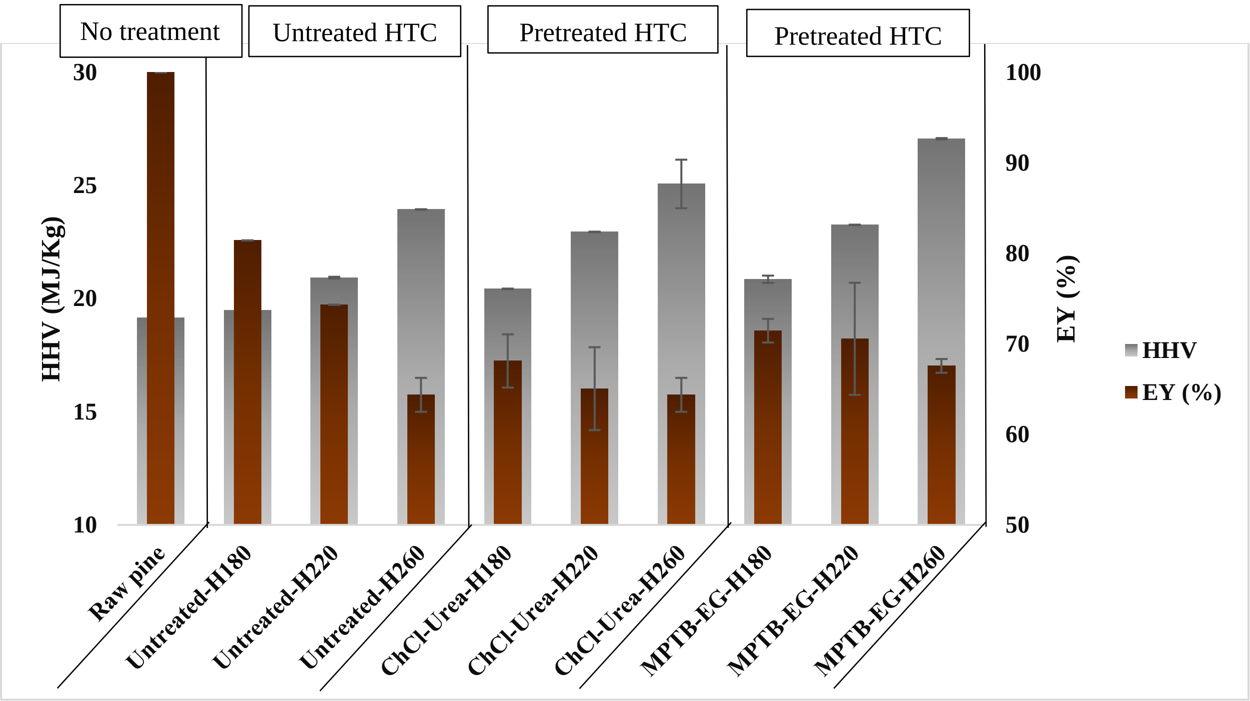


Figure 4. Higher heating value (HHV) and energy yield (EY) of raw pine, hydrochars from standalone HTC, and hydrochars from DES pretreated pine followed by HTC.

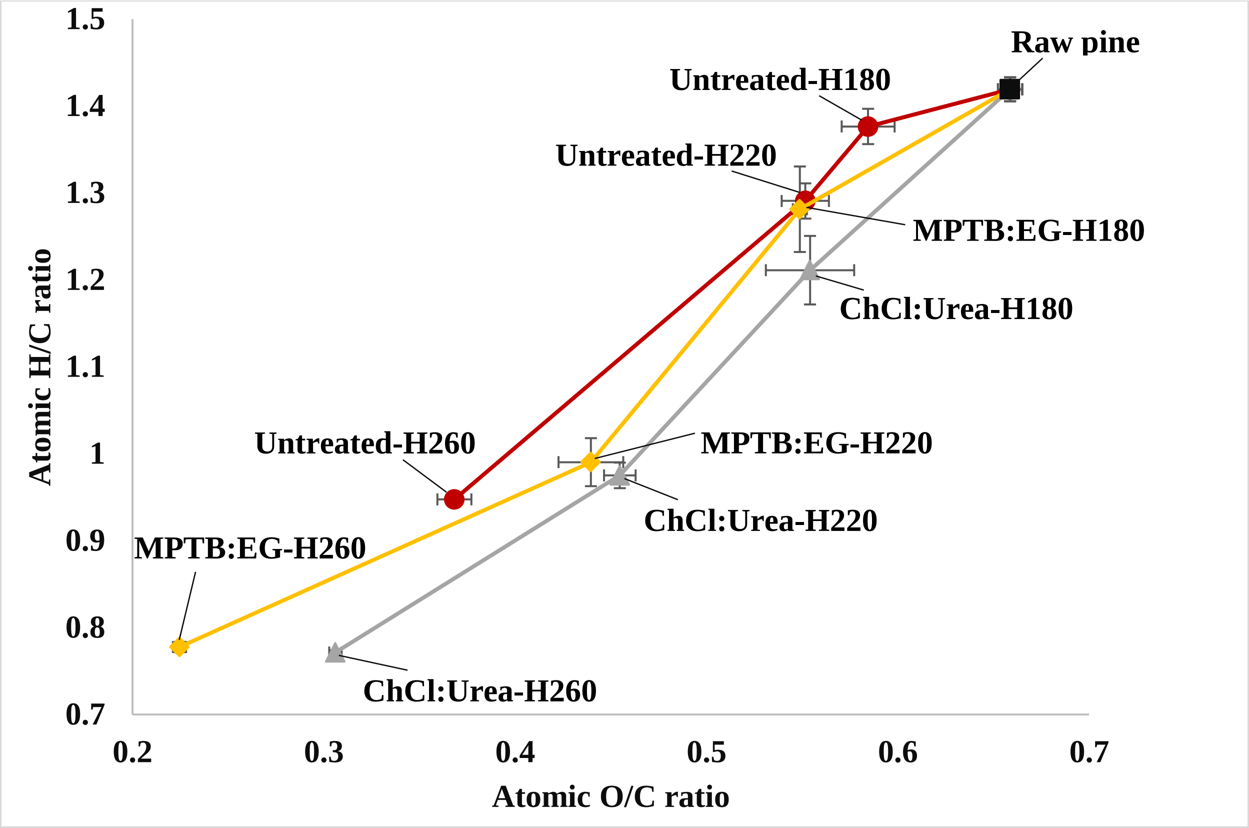


Figure 5. van-Krevelen diagram of raw pine, hydrochars from standalone HTC, and hydrochars from DES pretreated pine followed by HTC

Biography of the Authors

Md Tahmid Islam

Tahmid Islam is a third year PhD student in the Department of Chemical Engineering at Florida Institute of Technology. He received his BS in Chemical Engineering from Bangladesh University of Engineering and Technology in 2019. Currently, he is working on mild hydrothermal preprocessing (MHP) to upgrade high ash lignocellulosic biomass into low ash, energy dense hydrochar. His research interest includes Hydrothermal Carbonization, Deep Eutectic Solvent, Pelletization, and Adsorption. He is the recipient of 2021 outstanding graduate student presenter at Florida Academy of Science.

Al Ibtida Sultana

Al Ibtida Sultana is a graduate research assistant in the Biofuels Lab at Florida Tech. She acquired her BS (class of 2019) in Chemical Engineering from Bangladesh University of Engineering and Technology and joined FIT for Ph.D. in Chemical Engineering. Her research interest revolves around optimizing the development of superactivated hydrochar from various biomass sources for its application in gas and energy storage.

Nepu Saha

Dr. Nepu Saha is a Postdoctoral Research Associate at Idaho National Laboratory, USA. He received his Ph.D., with research focus on biomass processing, in Chemical Engineering from the Florida Institute of Technology in 2021. He received his MSc and BSc in Chemical Engineering from Texas A&M University and Bangladesh University of Engineering & Technology in 2016 and 2011, respectively. His primary research focuses are feedstock preparation and thermochemical conversion of biomass to energy and material.

Jordan Klinger

Dr. Jordan Klinger is a researcher in Idaho National Laboratory's Energy Environment Science & Technology directorate. He studied at Michigan Technological University, where he earned his bachelor's and research thesis master's in chemical engineering and his doctorate in mechanical engineering studying thermochemical conversion of biomass and wastes. Currently he is involved in bioenergy research to determine relationships between key physical and mechanical properties and feeding/handling performance of granular elastic solids, as well as feedstock attributes' impacts on thermochemical conversion.

M. Toufiq Reza

Dr. Toufiq Reza is an Assistant Professor of Chemical Engineering at the Department of Biomedical and Chemical Engineering and Sciences of Florida Institute of Technology. He has received his Ph.D. and M.S. in Chemical Engineering from University of Nevada, Reno in 2013 and 2011, respectively. Dr. Reza leads the Biofuels Research Lab at Florida Tech with primary research interest on thermochemical conversions of biomass and biowastes.

For Table of Contents Use Only