1 **Steam Gasification of a Thermally Pretreated High Lignin Corn**

2 **Stover Simultaneous Saccharification and Fermentation Digester**

3 **Residue**

4 Daniel T. Howe^{a*}, Danny Taasevigen^a, Manuel Garcia-Perez^b, Armando G. McDonald^c, Guosheng Li^a,
5 and Michael Wolcott^b

6 *^aPacific Northwest National Laboratory, 902 Battelle Blvd., Richland, WA 99352, USA*
7 Daniel.howe@pnnl.gov, Danny.taasevigen@pnnl.gov, guosheng.li@pnnl.gov

8
9 *^bWashington State University, 1935 E. Grimes Way, Pullman, WA 99164, USA*
10 Mgarcia-perez@wsu.edu, Wolcott@wsu.edu

11
12 *^cUniversity of Idaho, Department of Forest, Rangeland, and Fire Sciences, 875 Perimeter Drive,*
13 *Moscow, ID 83844*
14 Armandm@uidaho.edu

15
16
17
18
19
20
21
22 **Keywords:** thermochemical conversions; gasification; lignin; integrated biorefinery; biofuels; bioenergy

23 *Corresponding author:

24
25 Daniel Howe
26 Pacific Northwest National Laboratory,
27 902 Battelle Blvd., Richland,
28 WA 99352, USA
29 Phone: 1-509-372-4355
30 Fax: 1-509-372-1861
31 e-mail: Daniel.howe@pnnl.gov
32

Abstract

Efficient conversion of all components in lignocellulosic biomass is essential to realizing economic feasibility of biorefineries. However, lignin cannot be fermented using biochemical routes. Furthermore, high lignin and high ash residues from simultaneous saccharification and fermentation (SSF) is difficult to thermochemically process due to feed line plugging and bed agglomeration. In this study a corn stover SSF digester residue was thermally pretreated at 300°C for 22.5 minutes and gasified in a fluidized bed gasifier to study the effect of thermal pretreatment on its processing behavior. Untreated, pelletized SSF residue was gasified at the same conditions to establish the baseline processing behavior. Results indicate the thermal pretreatment process removes a substantial portion of the polar and non-polar extractives, with a resultant increase in the concentration of lignin, cellulose, and ash. Feed line plugging was not observed, although bed agglomeration occurred at similar rates for both feedstocks, suggesting that overall ash content is the most important factor affecting bed agglomeration. Benzene, phenol, and polyaromatic hydrocarbons in the tar were present at higher concentrations in the treated material, with higher tar loading in the product gas. Total product gas generation is lower for the treated material, although overall gas composition does not change.

1. Introduction

The current utilization trends for petrochemical fuels is considered unsustainable, with numerous environmental [1], political [2], and economic [3] concerns. According to the 2014 Energy Information Administration reports, 76% of all petroleum consumed by the United States was used to produce liquid transportation fuels, with net imports equal to 5.3 million barrels per day [4]. In order to mitigate the impact the transportation industry has on petrochemical consumption, serious attention is being paid to the use of renewable biomass feedstocks capable of generating liquid transportation fuels [5]. An important concept being developed is the biorefinery. A biorefinery is similar to an oil refinery but uses renewable energy resources such as wood, dedicated bioenergy crops (switchgrass), agricultural residues (corn stover), and industrial residues (pulp and paper mill waste) as feedstocks in conversion processes that generate fuels, chemicals, heat, and power [6]. In order to meet the Department of Energy (DOE) Energy Efficiency and Renewable Energy (EERE) Bioenergy Technologies Office's (BETO) performance goal of \$3 (in 2011 dollars) per gallon gasoline equivalent (GGE) [7], efficient utilization of the three principle biomass components; cellulose, hemicellulose, and lignin, is required. Thermochemical conversion processes, such as gasification, present the opportunity to convert a wide range of whole biomass and waste materials into transportation fuels. Inexpensive, accessible feedstocks in the near term likely include waste (or side-stream) materials such as high lignin, high ash residues from conventional lignocellulosic ethanol production, or residues from pulp and paper manufacturing [8]. The feedstock investigated here is a high lignin corn stover residue (HLCSR) resulting from simultaneous saccharification and fermentation (SSF) of corn stover. Corn stover is an important waste stream from cornstarch based ethanol production, and due to its low commercial cost, widespread geographical accessibility, and high volume availability, it is considered an ideal candidate for an integrated biorefinery feedstock [9].

Biomass gasification is a high temperature partial oxidation process to convert lignocellulosic feedstocks to a mixture of carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), and methane

(CH₄) [10]. The mixture of CO and H₂, often referred to as “syngas”, can then be used for synthesis of transportation fuels [11] or for the production of heat [12]. The use of high lignin feedstocks in fluidized bed biomass gasifiers, however, can be problematic, particularly at research/bench scales [13]. One of the issues identified is the tendency of the lignin to soften at elevated temperatures between 90°C and 190°C [14]. In the case of a biomass gasifier, where the bed operates at temperatures around 900°C, the conduction of heat from the reactor into the injection system used to introduce the feedstock to the bed can lead to premature softening, cross-linking, and polymerization reactions [13]. When this happens, the resulting softened material causes agglomeration of the feedstock, and can quickly plug the injection system. Even when plugs are not formed, melting of lignin inside the fluidized bed can cause agglomerations of ash, sand, and charcoal which eventually lead to losses of bed fluidization [15].

The pyrolysis and gasification of lignin rich feedstocks has been the subject of intense research activity [16-21]. For many years, researchers at the University of Western Ontario [22] have studied novel approaches to feed and fluidize lignin rich feedstocks. Their slug injection system has shown promise for feeding lignin and high lignin feedstocks, although an ice water cooling jacket was still necessary on the feed lines. A mechanical stirring device was employed to prevent bed agglomeration [23]. Utilizing the residue from a SSF reactor has shown that pelletization of the feedstock combined with a cooling nitrogen (N₂) co-feed has been successful at overcoming feed line plugging; however the large particle size of the pellets leads to substantial bed agglomeration and a potential loss of bed fluidization [24].

One potential method of overcoming the drawbacks to the use of high lignin materials is to employ a thermal pretreatment (TPT) step to render the feedstock less susceptible to premature melting by increasing the softening point of the material [25]. TPT, also known as torrefaction, slow pyrolysis, mild pyrolysis, roasting, and deep drying [26], involves heating the feedstock in an inert atmosphere at temperatures typically ranging from 200°C to 300°C [27]. Studies by Bergman’s group have shown that depolymerization of the hemicellulose and cellulose fractions is followed by volatilization of the intermediates [26, 28]. The resultant volatiles are composed primarily of acetic acid, methanol, CO, CO₂, and furan derivatives [28]. Hemicellulose, the main reactant in torrefaction, is decomposed via a two-step

mechanism starting with depolymerization followed by charring reactions of the remaining solid intermediates. Due to the very low levels of hemicellulose in the SSF digester residue, these reactions are considered minor in relation to the depolymerization and charring of cellulose, a process which takes place at low temperatures ($< 200^{\circ}\text{C}$). At higher temperatures the decomposition of cellulose occurs faster and to a greater degree [29]. Although mass loss due to the partial devolatilization of the material is unavoidable, the energy content of the starting material is predominantly conserved.

The main goal of this study was to determine the effect of thermal pretreatment on the gasification behavior of a high lignin/ash corn stover SSF residue. It is hypothesized that the removal of a portion of the reactive volatiles during the pretreatment will overcome the tendency of the feedstock to plug within the feed lines, and eliminate the need to pelletize the feedstock and therefore overcome the propensity of the residue to agglomerate in the bed.

2. Materials and Methods

2.1. Material Characterization

The residue from an SSF [30] process using corn stover as the feedstock was obtained from the National Renewable Energy Laboratory (NREL) in Golden, CO, USA. Approximately half of the material received was then pelletized at the Idaho National Laboratory (INL) to a nominal particle size of -10 +40 mesh. Pelletization of the SSF residues was necessary due to the fact that the residue as received is a fine powder (-60 mesh). Initial feed system studies showed that the auger feed system employed was unable to consistently meter the unpelletized residue. The feedstock was sent to Microbac Laboratories in Boulder, CO, for compositional analysis including ash, structural protein, polar and non-polar extractives, acid soluble and insoluble lignin, carbohydrates consisting of glucan, xylan, galactan, arabinan, and mannan, and acetyl content using the NREL Laboratory Analytical Procedures (LAP) NREL/TP-510-(42622, 42625, 42619, 42618). Ultimate analysis was performed by Columbia Analytical Services in Tucson, AZ, for C, H, N, O, and S content following the ASTM D5373 and D5291 methods [31, 32].

Inorganic species were determined after digestion in a mixture of nitric and hydrofluoric acid, complexed with boric acid, and analyzed by ICP-AES [33].

Proximate analysis (20 mg) was performed via thermogravimetric analysis (TGA) using a Netzsch STA 409 C using a Pt/Rh sample pan from 30 to 600°C at 10°C/min under He (100 mL/min). The TGA was calibrated using 8 metals (Au, Ag, Al, Bi, In, Sn, Ni, and Zn). The data generated was used to calculate the proximate analysis for each sample consisting of moisture, volatiles, fixed carbon, and ash. Moisture content was defined as the mass loss up to 160°C [34]. Volatiles were measured as the dry basis mass loss at 600°C. Ash content of the starting material was measured separately in a furnace according to the NREL Laboratory Analytical Procedure NREL/TP-510-42622. This value was subtracted from the mass remaining at 600°C to give the fixed carbon value.

Surface area was determined by the N₂ [35] Brunauer–Emmett–Teller (BET) method on degassed samples (under vacuum at 100°C for 7 h) in triplicate using an AUTOSORB-6 Surface Area & Pore Size Analyzer (Quantachrome Instruments). Pore size and pore volume were estimated with the Horvath-Kawazoe (HK) method. The specific surface area was also determined by CO₂ adsorption, in triplicate, using a TriStar II plus automatic physisorption analyzer (Micromeritics Instrument Corporation, Norcross, GA) using 0.20 g of degassed sample (vacuum degassed for 4 hr at 100°C). Each isotherm was collected at 0°C using 75 points between partial pressures of 0.00001 and 0.03. Total surface area and micropore volume (V_{mi}) were determined by the Dubinin-Radushkevick (DR) equation fit to data points between $2 < \log (P_0/P)^2 < 6$, where P is the equilibrium pressure at temperature T and P_0 is the saturated vapor pressure. Average pore width has been calculated from the characteristic energy given by the DR equation [36].

2.2. Thermal Pretreatment

The unpelletized SSF residue was thermally pretreated in a continuous feed auger reactor. A processing temperature of 300°C and residence time of 22.5 min was chosen based on previous work

[25]. Calibration of the residence time was accomplished by filling the void fraction of the reactor with the same unpelletized SSF residue as that to be treated, injecting a spike of material, and recording the time until the material was seen exiting the reactor heating zone. A feed rate of 1.1 kg/hr and N₂ flow rate of 5 L/min were used. Weight loss during the process was calculated by subtracting the total amount of treated material collected from the weight of the starting material and dividing by the weight of the starting material. The pretreated material then underwent compositional, ultimate, and proximate analysis as described above.

2.3. Gasification

Both the thermally treated and pelletized SSF residues were gasified in a 7.6 cm ID indirectly heated, bubbling fluidized bed (see Figure 1). The feedstock is stored in a hopper that opens into a vibrating metering bin. It is metered into a drop tube and injected into the reactor using screw augers. The gas produced then passes through a filter to remove particulates before being bubbled through a water filled condenser (also called a submerged bed scrubber). After passing through a secondary demister the gas flow rate is measured and analyzed for composition before being vented.

The gasifier was heated to a bed temperature of 910°C before the feed was started, using N₂ as the fluidizing medium, and then switched to a mixture of steam and N₂. Steam was fed at a rate that gave a steam/carbon ratio of 0.9. Nitrogen was co-fed at 10 L/min with the untreated residue, and 5 L/min with the TPT residue. The nitrogen flow rate is controlled using Brooks 5850E mass flow controllers with an accuracy of $\pm 1\%$. The feedstock was fed to the gasifier at a pre-calibrated rate of 1.5 kg/hr. N₂ helped to keep the material at a relatively low temperature in the injection tube before entering the bed. Because of the very fine particle size of the TPT material, pneumatic entrainment of the material was observed during calibration. As such, the nitrogen flow rate was decreased until no further entrainment was seen. The combined steam and nitrogen feeds resulted in a gas velocity equal to 2.5 times the minimum fluidization velocity of 56 mm/s, calculated using the Ergun equation. A copper cooling coil wrapped around the injection tube allows for an indirect measurement of the temperature of the injection tube. The oil used in

the cooling coil enters at 100°C and exits at 525°C. Due to the endothermic nature of the steam gasification reaction the gasification temperature was 895 ± 5 °C. The total time for feeding was 2.75 hours.

[INSERT FIGURE 1 HERE]

Pressure transducers (Swagelok Industrial Pressure Transducer, S model 0-30 psi, error of 0.25% total span) were used to monitor the pressure at different parts of the system; such as the hopper, the drop tube upstream of the injection line, below the reactor bed, above the reactor bed, at the filter inlet, at the condenser inlet, and at the demister inlet. Temperatures in the fluidized bed were monitored using K-type thermocouples (Omega Engineering, 0.75% maximum error) located 2.5, 7.6, 15.2, and 30.5 cm above the bottom of the bed. Aluminum oxide (Al_2O_3 , corundum, α -phase, 99%), screened to -100 mesh ($< 150\mu\text{m}$) was purchased from Sigma-Aldrich and used as the bed material. Temperature and pressure measurements were monitored and recorded using LabVIEW Data Acquisition software (National Instruments, version 6.1).

The product gas exiting the reactor bed was passed through a heated line to the hot gas filter (20 μm steel mesh) maintained at 475°C to avoid tars from plating out on the filter. The filtered product gas was quickly cooled to 100°C using water run through a spray quench nozzle, and it was then bubbled through a jacketed condenser containing water at 50°C. The gas was then passed through a secondary demister to remove any remaining aerosolized liquid products. The demister consisted of a packed bed of stainless steel spheres, the spheres having a diameter of 4.5 mm. The dry product gas was then sampled via an Agilent 3000A micro-GC and analyzed for H_2 , N_2 , CO, CH_4 , CO_2 , ethylene, ethane, acetylene, and propane. Prior to beginning the test the micro-GC undergoes a three-point calibration for each gas listed above. The minimum acceptable R^2 value of the calibration curve for each compound is 0.98. A dry test meter was used to measure the total dry product gas flow rate at the system outlet.

A heated slipstream located between the hot gas filter and the condenser was used to draw a gas sample at 1 L/min through a gas sampling system. This system was used to collect condensable tars according to the European tar sampling protocol CEN BT/TF 143 [37]. Isopropyl alcohol was used as the capture agent.

Following the test, the gasifier system was cooled and the reactor solids (bed) were removed from the reactor, weighed, and run through a series of sieves to determine particle size distributions. The material remaining in the hot gas filter was also removed and weighed. Three samples of each were taken and ashed at 600°C overnight to determine total organic content. The isopropyl alcohol from each sampling impinger was analyzed for tar components using GC-FID on an HP 5890 equipped with an Agilent DB-5 column. Custom standards obtained from Restek Corporation allowed for quantification of 28 different organic species present in the tar.

3. Results and Discussion

3.1 Thermal Pretreatment

As reported in a previous study [25], the thermal pretreatment of the SSF residue results in weight loss attributed primarily to the evolution of volatiles composed primarily of acetic acid, methanol, CO, CO₂, and furan derivatives [28]. When processed in the auger reactor at 300°C and a residence time of 22.5 min, the SSF residue exhibited a weight loss equal to 21.4%. This is in good agreement with the test results from bench scale units, where the same material processed at 30 min and 10 min showed weight losses equal to 32.4% and 14.3%, respectively.

3.2 Material Characterization

As seen in Table 1, compositional analysis of the SSF residue and TPT residue shows that a large decrease in the concentration of hot water (polar) and ethanol (non-polar) extractives is occurring. Although detailed analysis of the extractives present in the SSF residue was not performed, Chen et al [38] reported that the main water soluble extractives in corn stover are composed of monomeric sugars,

alditols, aliphatic acids, oligomeric sugars, and a range of oligomeric derivatives of phenolic glycosides. The non-polar extractives are composed of fatty acids, resins, sterols, steryl esters, and triglycerides [39]. Since most of these species are easily volatilized or cracked at low temperatures, they will comprise a large fraction of the pyrolysis vapors formed and contribute significantly to the weight loss observed during TPT. The amount of the structural components, namely cellulose (glucan) and lignin, increased during pretreatment. This is due to concentration of the compounds caused by the mass loss of the extractives. Ultimate analysis shows that the CHNO/S values of the treated material do not change significantly from the untreated material. Proximate analysis indicates that the pretreatment decreases the amount of volatiles, with a corresponding increase concentration of the ash.

Table 1. Compositional, ultimate, and proximate analysis of HLCSR and TPT-HLCSR on both raw and normalized basis.

	Raw Values		Normalized Values	
	HLCSR	TPT-HLCSR	HLCSR	TPT-HLCSR
Compositional Analysis	(wt%)	(wt%)	(wt%)	(wt%)
Ash	15.93	20.74	15.20	18.91
Structural Protein	7.93	6.93	7.57	6.32
Hot Water Extractives	8.89	1.77	8.48	1.61
Ethanol Extractives	15.99	8.21	15.26	7.49
Acid Soluble Lignin	1.56	2.11	1.49	1.92
Acid Insoluble Lignin	35.58	44.38	33.95	40.46
Glucan	15.81	20.03	15.09	18.26
Xylan	2.29	2.95	2.19	2.69
Galactan	0	0	0	0
Arabinan	0	1.61	0	1.47
Mannan	0	0.70	0	0.64
Acetyl	0.81	0.25	0.77	0.23
Total	104.79	109.68	100	100
Ultimate Analysis				
C	46.95	47.27	50.05	48.00
H	5.08	4.81	5.42	4.88
N	2.09	1.95	2.23	1.98
O	25.17	25.64	26.83	26.04
S	0.26	0.20	0.27	0.20
Ash	15.93	20.74	15.20	18.91
Total	95.48	100.60	100.00	100.00

Proximate Analysis				
Moisture	1.2	1.0	1.2	1.0
Volatiles	55.7	51.9	55.8	51.9
Fixed Carbon	27.1	26.4	27.8	28.2
Ash	15.9	20.7	15.2	18.9
Total	99.9	100.0	100.0	100.0

Table 2 shows the mineral content of the HLCSR and TPT-HLCSR as equivalent oxides or carbonates. All species show an increase during the pretreatment due to the concentration of the ash as mentioned above. Some minerals, such as aluminum, do not volatilize and as such increase by as much as 50%. Others, like sulfur, are more likely to be removed as volatile compounds during the pretreatment process, and therefore are not concentrated to the same degree, and only increase by 2%.

Table 2. Inorganic content of the HLCSR and TPT-HLCSR feedstocks in parts-per-million of the equivalent oxide or carbonate shows a concentration of the mineral content with thermal pretreatment.

Element	Equivalent Oxide/ Carbonate	HLCSR (ppm)	TPT- HLCSR (ppm)
Al	Al ₂ O ₃	6,470	9,720
Ca	CaCO ₃	5,950	7,710
Cr	Cr ₂ O ₃	168	225
Fe	Fe ₂ O ₃	2,060	2,810
K	K ₂ CO ₃	3,580	4,590
Mg	MgCO ₃	1,220	1,380
Mn	MnO ₂	<40	<40
Na	Na ₂ CO ₃	4,970	5,630
P	P ₂ O ₅	1,080	1,430
Si	SiO ₂	113,000	125,000
S	SO ₂	3,570	3,650

The results of the BET analysis of the HLCSR and TPT-HLCSR using both N₂ and CO₂ are provided in Table 3. These results indicate that the TPT process does not substantially alter the morphology of the starting material. The surface area, micropore volume, and pore width of the TPT-HLCSR is slightly higher than the HLCSR when measured with N₂, but slightly lower when measured with CO₂ at 95%,

95%, and 96%, respectively. Since CO₂ BET is regarded as more accurate for materials containing narrow micropores due to the elimination of diffusion effects [40], the CO₂ measurements are considered the most accurate. While values for the surface area of these materials do not exist in the literature, Brewer et al. [41] have reported on the surface area of a slow pyrolysis char using corn stover (20.9 m²/g) and switchgrass (50.2 m²/g). This suggests that the numbers obtained are reasonable for biomass derived materials.

Table 3. BET analysis of the HLCSR and TPT-HLCSR using both N₂ and CO₂.

Sample / analysis gas	Surface Area (m ² /g)	Micropore Volume (cm ³ /g)	Pore Width (nm)	Characteristic Energy (KJ/mol)
HLCSR (N ₂)	4.7	0.0016	1.5	Not Measured
TPT-HLCSR (N ₂)	5.4	0.0018	1.6	Not Measured
HLCSR (CO ₂)	45.9	0.0184	1.25	20.1
TPT-HLCSR (CO ₂)	43.5	0.0174	1.2	20.4

3.3 Gasification

The primary purpose of thermally pretreating the SSF residue is to generate a feedstock that can be fed to the research/bench-scale biomass gasification reactor without the formation of highly reactive liquid intermediates that plug the feed line, and minimization of bed agglomeration that results in loss of fluidization. By monitoring the pressure below the fluidized bed, upstream of the feed, and above the bed, the formation of feed line plugs and bed agglomeration during gasification can be observed. Clogging of the feed lines will result in a pressure increase upstream of the feed lines, but will not affect the pressures above or below the bed. Agglomeration of the bed material will result in pressure increases below the bed and upstream of the feed, but will not affect the pressures above the bed. Any plugs or restrictions formed downstream of the reactor, such as in the particulate filters or tar condensers, will result in a pressure increase for all three. As seen in Figure 2A, a matched rate of increase in the pressures below the bed and upstream of the feed was observed when running the TPT residue, while the pressure above the bed remained constant. This indicates that bed agglomeration was occurring, although

feed line plugging was not. At approximately 130 min into the experiment a matched rate of increase for all three pressures was observed, indicating that clogging of the downstream components was occurring. Figure 2B shows the pressure behavior during the gasification of the untreated material. Linear regression of the pressure data, seen in Table 4, indicates that the pressure increases are approximately equal. While the rate of pressure increase was slightly lower below the bed and upstream of the feed when the TPT residue was processed, this difference is attributed to the experimental error of the system (± 1 kPa).

[INSERT FIGURE 2 HERE]

Table 4. Slopes of the regression lines calculated for the pressure behavior during the gasification experiments in units of kPa/min. Close agreement between the values obtained for each material show that bed agglomeration continues to occur regardless of feed size. For the TPT-HLCSR, only the data prior to 130 min was used for calculation of the regression lines.

	Below Bed	Upstream of Feed	Above Bed
	kPa/min	kPa/min	kPa/min
HLCSR	0.0185	0.0196	0.0019
TPT-HLCSR	0.0132	0.0174	0.0004

Although the pressure transducers indicate that bed agglomeration was occurring, recovery of the reactor solids after the experiment was necessary to determine the extent of bed agglomeration. Particle size distributions of the recovered material are shown in Table 5. Of the starting bed material, 99.9% was -100 mesh. When the HLCSR was processed, this fraction disappears entirely, with all of the recovered material being +100 mesh. The TPT material does not remove this fraction to the same extent, as 8.4% of the material was still -100 mesh. Formation of the largest agglomerates, +10 mesh, is substantially reduced by the use of the TPT material. However, the formation of smaller agglomerates, between -10 and +50 mesh, is more pronounced for the TPT residue, increasing from 32.5% of the recovered HLCSR

solids to 36.9%. Previous studies on the larger HLCSR agglomerates showed that they did not comprise encapsulated bed material, but were rather ungasified feedstock pellets with reactor bed material attached to them [24]. Formation of the smaller agglomerations occurs when the initial pyrolysis reactions form tars, which then proceed to encapsulate the alumina bed material. Given the fine size of the TPT-HLCSR feedstock, the encapsulation mechanism should be the predominant route for bed agglomeration when this material is processed. However, as seen in Table 5, the concentration of char in the agglomerates increases as the size of the agglomerates increases, with a corresponding decrease in the amount of ash. This suggests that a third agglomeration mechanism may be occurring where the unreacted char left in the reactor agglomerates to itself.

Table 5. Particle size distribution, char fraction, and ash fraction of recovered reactor bed material.

Mesh Size	Fresh Bed Material (wt% of solids)	HLCSR Recovered Reactor Solids (wt% of solids)	TPT-HLCSR Recovered Reactor Solids (wt% of solids)	Char in TPT-HLCSR Reactor Solids (wt% of solids)	Ash in TPT-HLCSR Reactor Solids (wt% of solids)
-325	0.1	0	0.2	0	0
-200 +325	39.7	0	0.6	0	0
-100 +200	60.1	0	7.6	0	0
-60 +100	0.1	61.7	50.5	6.8	93.2
-50 +60	0	0.6	3.6	32.7	67.3
-40 +50	0	0.7	7.9	35.1	64.9
-20 +40	0	5.1	18.4	37.9	62.1
-10 +20	0	26.7	10.6	46.2	53.8
+10	0	5.1	0.7	0	0

The generation of tars during the gasification reaction may also help to explain how the agglomerates are forming. As seen in Table 6, the TPT material forms a greater concentration of tar species than the untreated residue, increasing from 50 to 58 g/Nm³. Most of the tar species remain relatively constant, with the largest increases coming from benzene, phenol, and the polyaromatic hydrocarbon (PAH) species. Formation of these PAH groups from lignin proceeds according to a

mechanism proposed by Hosoya's group [42], where the primary products of lignin pyrolysis are guaiacol based compounds with unsaturated side chains. These compounds then undergo coupling and condensation reactions to form a condensed product. The condensed products further undergo cracking reactions to form phenolic compounds with saturated alkyl side chains. In addition to lignin, the pyrolysis of cellulose can result in phenolic and alkyl phenolic products as reported by Sung-Seen Choi [43]. In his proposed mechanism, cleavage of the ether bond between the C1 and C5 carbons in a glucose unit results in the formation of cyclohexane, which is then rearranged to form a tetrahydroxycyclohexane (THCH) unit. This unit is very important, as further rearrangement, dehydration, and hydrogenation reactions can result in phenol, 1,3 and 1,4-dihydroxybenzene, and other alkyl phenolics. As discussed above, the large amounts of tar being formed may be acting as agglomeration agents for both the unreacted carbon (char) remaining in the reactor and potentially even the bed material.

Table 6. Dry gas loading of the various tar species in the filtered gasifier product stream.

Component	Dry Gas Composition (g/Nm ³)	
	HLCSR	TPT-HLCSR
Benzene	25.20	29.91
Pyridine	1.19	1.22
Toluene	2.55	2.17
Ethylbenzene	0.01	0.00
m,p-Xylene	0.08	0.05
Phenylacetylene	0.30	0.30
Styrene	1.13	0.97
o-Xylene	0.00	0.00
Phenol	0.99	5.18
2,3-Benzofuran	0.17	0.17
Indane	0.01	0.00
Indene	2.02	1.01
Naphthalene	7.65	8.55
2-Methylnaphthalene	0.52	0.00
1-Methylnaphthalene	0.19	0.19
Biphenyl	0.53	0.54
1-Ethylnaphthalene	0.06	0.00
Acenaphthylene	1.65	2.01

Acenaphthene	0.17	0.11
Dibenzofuran	0.55	0.40
Fluorene	0.59	0.62
Anthracene	0.82	1.39
Phenanthrene	0.50	0.92
4,5-Methylenephenanthrene	0.17	0.24
Fluoranthene	0.55	0.99
Pyrene	0.49	1.02
D-allose	0.00	0.00
Levoglucosan	0.00	0.00
Unknowns	2.25	0.55
Total	50.34	58.49

The formation of bed agglomerates may be in part due to the increased tar production exhibited by the TPT-HLCSR. The amount of unreacted carbon left in the bed would also be an important factor, both for understanding the mechanism of bed agglomeration as well as evaluation of the overall feedstock performance. As seen in Table 7, the TPT material generated significantly less product gas than the untreated residue, decreasing from 1051 to 675 L/kg dry feed measured at 25°C and 101 kPa. This is due to the removal of a portion of the volatile materials during the pretreatment process. The lower gas production rate is evidenced by the carbon conversion to product gas, which decreases from 59 to 47 mol%. The lower gas production rate results in a much higher percentage of the carbon being recovered in the bed material, increasing from 29 mol% in the untreated residue to 42 mol% in the TPT residue.

Table 7. Gas production rates (at 25°C and 101 kPa) on a mass fed basis, carbon recovery partitioning, and overall carbon balances for the gasification experiments show that the TPT residue only produces 64% of the product gas generated by the untreated residue. The decrease in the gas production results in a higher percentage of the feedstock carbon being left in the bed. The similar carbon balances between the two runs suggests that roughly equivalent error in the collection and measurement of the outlet carbon is occurring.

	HLCSR	TPT-HLCSR
Gas Production Rate (L/kg dry feed)	1051	675
Product Gas (mol%)	58.6	46.5
Tar (mol%)	11.8	9.2
Filter (mol%)	0.2	2.3

Reactor Bed (mol%)	29.4	42.0
Carbon Balance (mol%)	84.0	82.4

The TPT residue generates less product gas than the untreated residue, however the composition of the final gas is important for downstream processing into synthetic fuels [44]. The H₂/CO ratio will determine the optimal conversion process, or establish the need for further gas-phase catalytic processing to increase or decrease the ratio for targeted fuels [45]. As seen in Table, the untreated residue has an H₂/CO ratio of 1.2 compared to 1.1 for the TPT residue. Although these H₂/CO ratios are well-suited for the production of alcohols [46], the optimal ratio for Fischer-Tropsch processing is about 2.1 [47]. Methane and CO₂ concentrations were approximately equal, with slightly more CO₂ being formed by the pretreated material. Overall, the product gas composition is essentially the same for both materials, meaning that there would be no major differences in the downstream processes to generate liquid fuels.

Table 8. Outlet gas composition generated by HLCSR and TPT-HLCSR. Nitrogen is added to the system rather than created in the reaction, therefore the gas composition is given on both a raw and nitrogen free basis. Approximately twice as much cooling nitrogen was used on the HLCSR experiment compared to the TPT-HLCSR.

Gas	HLCSR	TPT-HLCSR	N ₂ Free HLCSR	N ₂ Free TPT-HLCSR
H ₂	27.7	29.3	39.3	36.3
N ₂	29.6	19.4	0.0	0.0
CH ₄	8.4	10.1	11.9	12.5
CO	23.3	26.2	33.0	32.5
CO ₂	8.5	11.0	12.1	13.6
Ethylene	2.1	3.2	3.0	4.0
Ethane	0.1	0.1	0.1	0.1
Acetylene	0.5	0.8	0.7	1.1
Propane	0.0	0.0	0.0	0.0
Total	100.2	100.0	100.0	100.0
H ₂ /CO Ratio	1.2	1.1	1.2	1.1

One important factor, especially at the bench scale, is the amount of nitrogen co-fed with the feedstock. The nitrogen is added with the feed in order to keep the feedstock cool and minimize

premature pyrolysis in the feed lines. It is neither consumed nor created in the gasification reaction, and serves as a diluent in the final product gas. Separation of the N₂ from the gas stream prior to downstream processing is required to maximize conversion efficiency. Since the TPT residue is more resistant to premature pyrolysis, the amount of cooling nitrogen required to be co-fed is reduced. Table 9 shows the energy balances for this process as cold and hot gas efficiencies, as well as the amount of energy required to heat up the cooling nitrogen for each mole of product gas generated. Cold gas efficiencies assume the product gas is cooled to ambient temperature with tar vapors removed, while the hot gas efficiency assumes that the gas is fed to downstream processes without cooling, allowing for the sensible heat of the gas to be utilized [48]. As seen in the table and discussed previously, the carbon conversion efficiency to product gas (as a wt%) is considerably lower for the pretreated material compared to the untreated. This is due to a large amount of the feedstock carbon remaining in the reactor as char. The cold and hot gas efficiencies are also considerably lower. The difference of the cold gas efficiency between the two materials is 17.8%, while for the hot gas efficiency it is 21.1%. The difference in the efficiencies is due to the energy required to heat up the nitrogen. This energy per mol of product gas is shown, with the lower nitrogen flow rate of the pretreated material causing a lower required energy flow. The pretreated material only requires 64% of the energy required to heat the nitrogen for the untreated material per mole of product gas generated, even though the outlet gas flow rate is substantially reduced. With optimization of the TPT process the need for a nitrogen co-feed could be eliminated entirely.

Table 9. Energy balances for the untreated and thermally pretreated residues as carbon conversion efficiency on a weight basis, hot gas efficiency, cold gas efficiency, and the amount of energy required to heat the diluent nitrogen per mole of product gas generated.

	HLCSR	TPT-HLCSR
Carbon Conversion Efficiency (wt%)	51.3	41.8
Cold Gas Efficiency (%)	64.0	46.2
Hot Gas Efficiency (%)	74.2	53.1
Nitrogen Heating (kJ/mol product gas)	8.3	5.3

4. Conclusions

In this study a SSF digester residue was thermally pretreated at 300°C and 22.5 min and then gasified in a bubbling fluidized bed gasifier to study the effect of thermal pretreatment on its processing behavior. Untreated, pelletized residue was gasified at the same conditions to establish the baseline processing behavior. Results indicate that the TPT process removes a substantial portion of the polar and non-polar extractives, with a resultant increase in the concentration of lignin, cellulose, and ash. The thermally pretreated material is able to be consistently fed into the reactor without the need of pelletization, and with approximately half the amount of cooling nitrogen co-feed required by the untreated feedstock, saving 3 kJ per mole of product gas generated. While feed line plugging was not observed, bed agglomeration is still occurring. Although bed fluidization was not lost, the comparatively equal rates of the pressure increases across the bed for both feedstocks indicates that the overall ash content of the residue is the most important factor affecting bed agglomeration. The agglomeration mechanism appears to be one where the evolution of tars results in unreacted char agglomerating to itself and the bed material. The tar created from the thermally pretreated material shows higher concentrations of benzene, phenol, and poly aromatic hydrocarbons than the untreated residue, and the total tar loading in the product gas is increased. Less product gas is generated by the treated feedstock, due in part to the removal of volatiles during the thermal pretreatment process. The decrease in the conversion to product gas results in a large fraction of highly recalcitrant biogenic carbon remaining within the reactor bed. Although total gas production is decreased, the resultant tar-free product gas shows little difference between the feedstocks. Overall, the ability to reliably feed the thermally pretreated digester residue without a large volume of cooling nitrogen co-feed is a positive improvement, however the higher tar loading, and continued bed agglomeration problems indicate that the TPT process does not solve all concerns relating to the use of high lignin and high ash feedstocks.

5. Acknowledgements

This manuscript has been authored by Battelle Memorial Institute under Contract No. DE-AC05-76RL01830 with the U.S. Department of Energy. The United States Government retains and the

publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

6. References

- [1] IPCC. Climate Change 2007: Synthesis Report section 2.4, Attribution of Climate Change. Intergovernmental Panel on Climate Change (IPCC); 2007.
- [2] Watkins E. Watching the World: Iran Woos Latin America. *Oil & Gas Journal*. 1/16/2012;110(1b).
- [3] Jimenez-Rodriguez R, Sanchez M. Oil Price Shocks and Real GDP Growth: Empirical Evidence for Some OECD Countries. *Applied Economics*. 2005;37(2):201-28.
- [4] EIA. August 2014 Monthly Energy Review. Washington DC: Department of Energy - U.S. Energy Information Administration; 2014.
- [5] Logan BE. Extracting Hydrogen and Electricity from Renewable Resources: a roadmap for establishing sustainable processes. *Environmental Science & Technology*. 2004;38(9):160A-7A.
- [6] Pinatti DG, Conte RA, Soares ÁG, Pereira MLG, Romão ÉL, Ferreira JC, et al. Biomass Refinery as a Renewable Complement to the Petroleum Refinery. The Berkeley Electronic Press; 2010.
- [7] DOE. Bioenergy Technologies Office Multi-Year Program Plan. Washington DC: Department of Energy; 2013.
- [8] Mourant D, Wang Z, He M, Wang XS, Garcia-Perez M, Ling K, et al. Mallee wood fast pyrolysis: Effects of alkali and alkaline earth metallic species on the yield and composition of bio-oil. *Fuel*. 2011;90(9):2915-22.
- [9] Öhgren K, Rudolf A, Galbe M, Zacchi G. Fuel ethanol production from steam-pretreated corn stover using SSF at higher dry matter content. *Biomass and Bioenergy*. 2006;30(10):863-9.
- [10] McKendry P. Energy production from biomass (part 3): gasification technologies. *Bioresource Technology*. 2002;83(1):55-63.
- [11] Dry ME. The Fischer–Tropsch process: 1950–2000. *Catalysis today*. 2002;71(3):227-41.
- [12] Higman C, van der Burgt M. Chapter 1 - Introduction. *Gasification (Second Edition)*. Burlington: Gulf Professional Publishing; 2008. p. 1-9.
- [13] Nowakowski DJ, Bridgwater AV, Elliott DC, Meier D, de Wild P. Lignin fast pyrolysis: Results from an international collaboration. *Journal of Analytical and Applied Pyrolysis*. 2010;88(1):53-72.
- [14] Hatakeyama H, Hatakeyama T. Thermal properties of isolated and in situ lignin. *Lignin and Lignans: Advances in Chemistry* CRC Press, New York. 2010:301-16.
- [15] Palmisano P, Berruti F, Lago V, Berruti F, Briens C. Lignin Pyrolysis in a Fluidized Bed Reactor. Conference Lignin Pyrolysis in a Fluidized Bed Reactor, Chicago, IL.
- [16] de Wild P, Van der Laan R, Klokhorst A, Heeres E. Lignin valorisation for chemicals and (transportation) fuels via (catalytic) pyrolysis and hydrodeoxygenation. *Environmental Progress & Sustainable Energy*. 2009;28(3):461-9.
- [17] Kawamoto H, Horigoshi S, Saka S. Pyrolysis reactions of various lignin model dimers. *Journal of Wood Science*. 2007;53(2):168-74.
- [18] Kinoshita CM, Wang Y, Zhou J. Tar formation under different biomass gasification conditions. *Journal of Analytical and Applied Pyrolysis*. 1994;29(2):169-81.
- [19] Klein MT, Virk PS. Modeling of Lignin Thermolysis. *Energy & Fuels*. 2008;22(4):2175-82.

484 [20] Kumar V. Pyrolysis and Gasification of Lignin and Effect of Alkali Addition: Georgia Institute of
 485 Technology, 2009.

486 [21] Laskar DD, Yang B, Wang H, Lee J. Pathways for biomass-derived lignin to hydrocarbon fuels.
 487 Biofuels, Bioproducts and Biorefining. 2013;7(5):602-26.

488 [22] Berruti FM, Ferrante L, Berruti F, Briens C. Optimization of an intermittent slug injection system for
 489 sawdust biomass pyrolysis. International Journal of Chemical Reactor Engineering. 2009;7(1).

490 [23] Tumbalam Gooty A, Li D, Berruti F, Briens C. Kraft-lignin pyrolysis and fractional condensation of its
 491 bio-oil vapors. Journal of Analytical and Applied Pyrolysis. 2013.

492 [24] Howe D, Taasevigen D, Gerber M, Gray M, Fernandez C, Saraf L, et al. Bed Agglomeration during the
 493 Steam Gasification of a High-Lignin Corn Stover Simultaneous Saccharification and Fermentation (SSF)
 494 Digester Residue. Energy & Fuels. 2015;29(12):8035-46.

495 [25] Howe D, Garcia-Perez M, Taasevigen D, Rainbolt J, Albrecht K, Li H, et al. Thermal pretreatment of a
 496 high lignin SSF digester residue to increase its softening point. Journal of Analytical and Applied
 497 Pyrolysis. 2016.

498 [26] Bergman P, Boersma A, Zwart R, Kiel J. Torrefaction for biomass co-firing in existing coal-fired
 499 power stations. Energy Research Centre of the Netherlands, ECN-C-05-013. 2005.

500 [27] Bergman PC, Kiel JH. Torrefaction for biomass upgrading. Conference Torrefaction for biomass
 501 upgrading. p. 17-21.

502 [28] Bergman PC, Boersma AR, Kiel JH, Prins MJ, Ptasiński KJ, Janssen F. Torrefaction for entrained-flow
 503 gasification of biomass. 2005.

504 [29] Gaur S, Reed T. Thermal data for natural and synthetic materials. Marcel Dekker, New York; 1998.

505 [30] Dowe N, McMillan J. SSF Experimental Protocols — Lignocellulosic Biomass Hydrolysis and
 506 Fermentation. Golden, CO: NREL; 2008.

507 [31] International A. ASTM D5373 - Standard Test Methods for Determination of Carbon, Hydrogen, and
 508 Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke. ASTM
 509 International West Conshohocken, PA; 2014.

510 [32] International A. ASTM D5291 - Standard Test Methods for Instrumental Determination of Carbon,
 511 Hydrogen, and Nitrogen in Petroleum Products and Lubricants. ASTM International West Conshohocken,
 512 PA; 2015.

513 [33] CEM. Application Notes for Acid Digestion. Matthews, NC: CEM; 2014.

514 [34] Gašparovič L, Koreňová Z, Jelemenský Ľ. Kinetic study of wood chips decomposition by TGA. Chem
 515 Pap. 2010;64(2):174-81.

516 [35] Colomba DB. Combustion and gasification rates of lignocellulosic chars. Progress in Energy and
 517 Combustion Science. 2009;35(2):121-40.

518 [36] Stoeckli F, Guillot A, Slasli A, Hugli-Cleary D. The comparison of experimental and calculated pore
 519 size distributions of activated carbons. Carbon. 2002;40(3):383-8.

520 [37] CEN. Biomass Gasification - Tar and Particles in Product Gases - Sampling and Analysis. CEN BT/TF
 521 1432004.

522 [38] Chen S-F, Mowery RA, Scarlata CJ, Chambliss CK. Compositional analysis of water-soluble materials
 523 in corn stover. Journal of agricultural and food chemistry. 2007;55(15):5912-8.

524 [39] Peng P, Bian J, Sun R-C. Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels -
 525 Chemistry, Extractives, Lignins, Hemicelluloses and Cellulose. Oxford, UK: Elsevier, 2010.

526 [40] Lozano-Castello D, Cazorla-Amoros D, Linares-Solano A. Usefulness of CO₂ adsorption at 273 K for
 527 the characterization of porous carbons. Carbon. 2004;42(7):1233-42.

528 [41] Brewer CE, Schmidt-Rohr K, Satrio JA, Brown RC. Characterization of biochar from fast pyrolysis and
 529 gasification systems. Environmental Progress & Sustainable Energy. 2009;28(3):386-96.

530 [42] Hosoya T, Kawamoto H, Saka S. Secondary reactions of lignin-derived primary tar components.
 531 Journal of Analytical and Applied Pyrolysis. 2008;83(1):78-87.

532 [43] Choi S-S, Kim M-C, Kim Y-K. Formation of Methoxybenzenes from Cellulose in the Presence of
533 Tetramethylammonium Hydroxide by Pyrolysis. BULLETIN OF THE KOREAN CHEMICAL SOCIETY.
534 2013;34(2):649-52.

535 [44] Lv P, Yuan Z, Wu C, Ma L, Chen Y, Tsubaki N. Bio-syngas production from biomass catalytic
536 gasification. Energy Conversion and Management. 2007;48(4):1132-9.

537 [45] Tijmensen MJA, Faaij APC, Hamelinck CN, van Hardeveld MRM. Exploration of the possibilities for
538 production of Fischer Tropsch liquids and power via biomass gasification. Biomass and Bioenergy.
539 2002;23(2):129-52.

540 [46] Dutta A, Phillips S. Thermochemical ethanol via direct gasification and mixed alcohol synthesis of
541 lignocellulosic biomass: National Renewable Energy Laboratory Golden, CO, 2009.

542 [47] Kumar A, Jones D, Hanna M. Thermochemical Biomass Gasification: A Review of the Current Status
543 of the Technology. Energies. 2009;2(3):556-81.

544 [48] Basu P. Combustion and Gasification in Fluidized Beds, CRC Press. Boca Raton. 2006.

545

Figure 1. Schematic of major gasifier system components. The submerged bed scrubber is cooled with 60 wt% propylene glycol (PG) in water.

Figure 2. Pressure behavior in the gasifier of A) the TPT residue and B) the untreated residue. Bed agglomeration is still occurring when the TPT residue is gasified, as indicated by the matched pressure increases below the bed and upstream of the feed. The increase in pressure at 130 min of the TPT-HLCSR experiment indicates the formation of plugs downstream of the reactor.