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Integrating sustainable biofuel and silver nanomaterial production for *in situ* upgrading of cellulosic biomass pyrolysis





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ABSTRACT

Replacing fossil fuels with biomass-based alternatives is a potential carbon neutral, renewable and sustainable option for meeting the world's growing energy demand. However, pyrolytic conversions of biomass-to-biofuels suffer marginal total energy gain, and technical limitations such as bio-oils' high viscosity and oxygen contents that result in unstable, corrosive and low-value fuels. This work demonstrates a new integrated biorefinery process for the co-production of biofuels and silver nanomaterials. By impregnating pure cellulose and corn stalk with silver nitrate, followed by pyrolysis, the gas yield (especially hydrogen) increases substantially. The condensable bio-oil components of the impregnated samples are considerably higher in furfurals (including 5-hydroxymethylfurfural). Though the overall activation energy barrier, as determined via the Distributed Activation Energy Model, does not change significantly with the silver nitrate pre-treatment, the increase in gases devolatilized, and improved 5hydroxymethylfurfural yield, suggest a catalytic effect, potentially increasing decarboxylation reactions. After using this metal impregnation to improve pyrolysis fuel yield, following pyrolysis, the silver-char composite materials are calcined to remove the biomass template to yield silver nanomaterials. While others have demonstrated the ability to biotemplate such nanosilver on cellulosic biomass, they consider only impregnation and oxidation of the template. This is the first work that demonstrates the potential to extract upgraded biorenewable fuels during the biotemplating of nanomaterials, the same nanomaterials often used in catalytic energy applications.

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1. Introduction

As the world's population continues to increase, and more of its citizens demand access to energy, our global reliance on non-renewable fossil fuel resources to provide this energy strains the environment. Replacing fossil fuel resources with biomass is a potential carbon neutral, renewable and sustainable option. However, biomass-to-biofuel conversions have come under scrutiny in terms of a total energy balance, and fiscal and environmental externalities [1,2]. This is partly overcome by the modern concept of the biorefinery, a facility that integrates biomass conversion to both fuels and chemicals, which may occur by a series of thermal and/or chemical routes [3–5]. Despite the roadblocks, there is clear impetus to develop renewable fuels from both an environmental

* Corresponding author at: Department of Mechanical Engineering, Boston University, 110 Cummington Mall, Boston, MA 02215, United States. *E-mail addresses: JillianLGoldfarb@gmail.com, jilliang@bu.edu* (J.L. Goldfarb). and political standpoint. The Energy Independence and Security Act mandates that at least 36 billion gallons of renewable fuels – a portion of which must be from cellulosic feedstocks – be blended into liquid transportation fuels by 2022 [6]. While the U.S. currently has some infrastructure for oxygenated renewable fuel liquids (i.e. ethanol) for gasoline blending, the reliance on isolating sugar monomers to produce these fuels limits their broader implementation [7].

One of the primary issues with using pyrolysis, specifically, as a thermal conversion route for biomass is the high oxygen content and acidity of pyrolysis oils, which render them corrosive to engines and refinery units, as well as unstable for long storage periods due to intense aging [8]. Many have explored the possible upgrading of pyrolysis bio-oils through chemical and thermal means, such as high pressure and catalytic transformations [9]. One of the most difficult issues encountered when it comes to upgrading the liquid product is the viscous, highly oxygenated polar compounds that lead to thermal instability; bio-oil begins to polymerize around

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120 °C [10,11]. The poor quality and low yield, combined with the cost of such upgrading – especially including catalyst degradation and recovery [12] – currently limits the widespread adaptation of biofuels [13].

In a disparate body of literature within Materials Science is an expanding knowledge concerning the use of biomass as a template to form unique nanowires and nanoparticles [14,15]. A plethora of biological materials and processes have been used to produce silver nanoparticles, from tree and plant extracts [16–20], to soluble starch [21], to cellulose as a support for impregnated nanoparticles [22]. We find examples of templating inorganic nanoparticles and various micro-structured materials using biomass as templates, including iron [23-25], titanium [26-30], and zinc [31-33] across the literature. One of the motivating factors for the use of biomass as a template for nanoparticles is the naturally complex, elaborate structures that biomasses possess [34]. Biotemplates can act as structure-directing agents for controlling nucleation of microstructures, and simultaneously as reducing agents [20]. In biotemplating, where the biomass is impregnated with a precursor of the nanomaterial to be templated, the biomass' carbon is often removed by oxidation at elevated temperatures in air.

The combination of biomass conversions and nanomaterials preformed nanomaterials – is not a new concept. For example, first generation biofuel conversions benefitted greatly from nanomaterials, including improving the transesterification of oils using nanoscaled CaO, γ -Al₂O₃, and Fe₃O₄ [35], as well as the conversion of lactic acid to high-value chemicals using Rh/ZnO and Pt/ZnO [36]. Second-generation cellulosic biofuels, such as the agricultural residues considered here, are significantly improved by nanoparticles, such as ruthenium based catalysts to yield hexitol, sorbitol and isosorbide, and nickel-tungsten based catalysts for ethylene glycol production [37-41]. Others have probed the use of supported nano-catalysts for removal of tar and upgrading of pyrolysis gases, including nano-NiO on γ -Al₂O₃ [42]. The use of nano-SnO₂ particles was shown to catalyze the pyrolysis of hazelnut shell biomass, evolving greater amounts of pyrolysis gas [43]. Al and Ti based nanocatalysts have been shown to improve levoglucosan vields on cellulose and anhydrous sugar pyrolysis [42,44] and sulfated metal oxides are used to improve light furan compound yield from cellulose pyrolysis [45]. Naturally sourced nanocatalysts from red mud were demonstrated to upgrade fast pyrolysis oil components, especially enhancing ketone yields [46]. Other groups have explored the potential in situ upgrading of biofuels by incorporating nanocatalysts such as zeolites into the raw biomass [47]. These - and many other examples - show the potential importance of nano-catalysts on the viability of commercial biomass to biofuel ventures [48]. In fact, nanoparticles for energy applications such as these can be synthesized using biomass templates [49]. However, what has yet to be shown – and the novelty of this paper – is the potential to upgrade biofuels *during* the pyrolysis process by simultaneously making nanoparticles that can be used in a variety of applications. In addition, this is the first paper (that the authors could locate in the literature) demonstrating the catalytic activity of silver ions on the in situ pyrolysis of biomass.

The successful implementation of integrated biorefineries relies on the understanding that there is not a one-size-fits all process. Rather, the success of such processes depends on a number of factors, including available biomass and valorization of waste [50], potential for upgrading and transforming bio-products, identification of value-added products for a given region, centralization (or lack thereof) of supply chains, transportation costs, and other factors [51]. In this work, we determine the feasibility of simultaneously upgrading bio-oils from pyrolysis and producing silver nanoparticles that can be used across biotechnological, medical and electrochemical applications [52,53] as a new option for incorporation into the integrated biorefinery concept.

2. Experimental

To demonstrate the proposed integrated biorefinery concept, we chose both a homogeneous (cellulose filter paper) and heterogeneous (feed corn stover) biomass. Both samples were subjected to the same metal impregnation and thermal treatment, and the resulting biofuels and nanomaterials characterized in the same manner.

2.1. Materials

Cellulose is a glucose polymer, which represents a carbohydrate building block of many biomasses [54]. Its molecular formula is $[C_6H_{10}O_5]_n$, with neighboring units rotated 180° around the axis of the polymer chain backbone (known as beta linkages). Such a β -linked polymer, exhibiting hydrogen bonding, leads to a strong, fibrous structure. In this study, we used ashless cellulose filter paper (Whatman, 5.5 cm diameter, course; obtained from Fisher Scientific). Cellulose filter papers were used whole for bulk pyrolysis experiments, and "hole-punched" to be 5 mm in diameter as a single piece in thermogravimetric analysis (TGA).

Feed corn stover is a widely available biomass in the United States and beyond; over 97 million acres of corn were planted in the U.S. in 2012. In each acre, there is approximately 1 dry ton of harvestable stover [55]. The feed corn stover was collected in early October 2011 from the Coppal House Farm in Lee, NH, and dried in a laboratory oven overnight. For bulk pyrolysis 10 cm squares were cut of the corn stover, and for TGA experiments pieces 5 mm squares were used. Proximate and ultimate analyses of the biomass are available in Table 1.

2.2. Silver impregnation and thermal treatment

To form silver nanomaterials using the biomasses as a template, the biomass (cellulose or corn stover) was immersed fully in a beaker containing 100 mMol AgNO₃ (ACROS Organics, 99.5%) for 1 min, with a maximum ratio of 5 g of biomass to 100 mL of solution. After which, the Ag⁺ sample was rinsed using absolute ethanol (ACROS Organics 200 proof, 99.5% ACS reagent grade) for 30 s. The impregnated sample was then rinsed using deionized water to remove excess solution. Finally, the impregnated sample was dried under vacuum and stored in a desiccator until treated or for further analysis.

To fabricate biotemplated silver nanomaterials, common practice is to calcine impregnated cellulosic samples between \sim 450 and 500 °C in air to remove the biomass template [56]. However, oxidizing biomass in air will not yield a biofuel because the devolatilizing material (biofuel precursor) is oxidized in the gas phase, followed by char oxidation. The novelty of our proposed process is to first pyrolyze the silver nitrate impregnated sample, which extracts the bio-oil and pyrolysis gas, followed by an oxida-

Proximate and ultimate analysis of cellulose filter paper and feed corn stover.^a

	Cellulose paper	Feed corn		
Ultimate analysis (wt%)				
С	44.45	46.55		
Н	6.22	5.66		
Ν	0	0.95		
S	0	0.13		
0	49.33	39.59		
Proximate analysis (wt%, dry basis)				
Volatile	95.67	75.77		
Fixed	4.33	16.16		
Ash	0	8.07		

^a Elemental Analysis of corn stover performed by Hazen Research, Golden, CO.

tion (calcination) step to remove any remaining biomass template. As such, we placed the raw or impregnated biomass samples (between 0.4 and 0.5 g, each) in a porcelain boat inside a 2" MTI tube furnace. The samples were pyrolyzed in 100 mL/min flowing high purity nitrogen to 600 °C at 10 °C/min and held for 1 h, to minimize char formation and to insure that devolatilization was complete [57,58]. During this time, we monitored evolved gas concentrations using a Quadrupole Mass Spectrometer (Extorr XT Series RGA XT300M) studying AMU signals of 2, 16, 26, 27, 30 and 44 (H₂, CH₄, C₂H₂, C₂H₄, C₂H₆, and CO₂, respectively (for more information on the use of these amu to monitor such pyrolysis gas compounds, we refer the reader to Evans and Milne [59], and Huang et al. [60]). Condensable gases were trapped in 5 mL of dichloromethane in a cold trap for further analysis. After pyrolysis, the solid samples were cooled under N₂ to 500 °C, at which temperature they were held in 100 mL/min flowing dry air for 60 min to remove the organic components. Finally, the samples were naturally cooled to room temperature and removed from the furnace. Samples were made in triplicate to insure reproducibility.

2.3. Bio-oil analysis

The condensable bio-oil components collected in dichloromethane were analyzed using a Shimadzu QP2010 Ultra gas chromatograph-mass spectrometer (GC–MS). Analysis was performed in split mode with a split ratio of 0.5 with an injection temperature of 250 °C using helium as a carrier gas. GC conditions started at 50 °C with a hold time of 2 min, followed by heating at 20 °C/min to 100 °C, then 5 °C/min to 300 °C, held for 7.5 min. Interface temperature was set at 325 °C. Mass spectra were recorded under electron ionization within three m/z ranges: (1) m/z 120–250 from 4 to 35 min, (2) m/z 120–400 from 35 to 40 min, (3) m/z 200–400 from 40 to 50 min. By integrating the top (by area) 20 gas chromatogram peaks a semiquantitative analysis was realized. Peaks are only reported if their NIST-library identification similarity was greater than 90%.

2.4. Kinetics analysis

The miniature replicates of the silver-impregnated samples were impregnated as described above, and then placed into a 70 μ L alumina crucible in a Mettler-Toledo TGA-DSC-1 for thermogravimetric analysis. Each sample was heated at 5, 10 and 15 °C/ min in nitrogen up to 600 °C and the Distributed Activation Energy Model (DAEM) was applied to determine the activation energy of pyrolysis [61]. The use of iso-conversional methods such as the DAEM to remove the heating rate and transport dependencies on activation energy is recommended by ICTAC Kinetics Committee [62]. Briefly, the extent of conversion at any time t, X(t), of a solid is assumed to take the form of a distribution function such as:

$$X(t) = 1 - \int_0^\infty \exp\left(-A \int_0^t \exp\left(-\frac{E}{RT}\right) dt\right) f(E) dE$$
(1)

where A is the frequency (pre-exponential) factor, E the activation energy, T the absolute temperature, and R the universal gas constant. X(t) is calculated by the ratio of the mass of volatiles produced at any given time, equal to the initial mass, m_0 , minus the mass at time t, m_t , to the total mass lost at the end of the pyrolysis reaction, m_0 -m_f as:

$$X(t) = \frac{m_0 - m_t}{m_0 - m_f}$$
(2)

f(E) is the distribution of the activation energy, normalized as:

$$\int_0^\infty f(E) \, dE = 1 \tag{3}$$

If the experiment is conducted nonisothermally at a constant temperature ramp rate, $\beta = dT/dt$, Eq. (1) can be rewritten as:

$$X(T) = 1 - \int_0^\infty \exp\left(-\frac{A}{\beta}\int_0^T \exp\left(-\frac{E}{RT}\right)dT\right)f(E)\,dE\tag{4}$$

The frequency factor is often considered a constant for all reactions. However, Miura and Maki [63] allow for a compensation effect between A and E through their Integral method applied to the DAEM, as used here. The integrated form is taken as:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{RT}$$
(5)

The activation energy and frequency factor are calculated from TGA curves from at least three discrete heating rates at selected conversion values. Therefore, the activation energy obtained from the Arrhenius plots of Eq. (5) are across a range of solid decomposition levels. To achieve a 95% confidence in the Arrhenius parameters, if correlation coefficients, R², were below 0.994, additional runs were performed at each ramp rate, and the data added to the plot to insure this statistical limit was achieved.

2.5. Nanomaterial characterization

Scanning Electron Microscopy (SEM) analysis was performed on a Zeiss Supra 55VP field emission scanning electron microscope at 1–3 kV without a metal coating. Large samples were mounted on adhesive copper tape and imaged using the SE2 detector at 1– 1.5 kV. Smaller samples (those in powder form) were immersed in acetone and sonicated for five minutes, then dispersed onto a silicon substrate without adhesives. Samples on the silicon substrate were imaged using the SE2 detector at 3 kV without a metal coating. Energy Dispersive X-ray Spectrometry (EDS) analysis was performed using an Apollo-40 EDAX detector at 7 kV for samples on both silicon and copper substrates. The metallic silver composition of the nanomaterials was confirmed by XRD using a Bruker Disovery D-8 X-ray diffractometer with Cu K α radiation in the 2 θ range of 10–90° at a 0.05° step with a sampling time of 0.5 s using a slit detector.

3. Results and discussion

To demonstrate the potential to *in situ* upgrade pyrolysis biofuels via simultaneous production of silver nanomaterials, we impregnated cellulose (a model biomass) and corn husk (a heterogeneous biomass) with silver nitrate. After impregnation both the biomasses took on a brownish hue, presumably as the silver partially oxidizes (images available in Fig. S1 of online Supplemental Information).

3.1. Thermochemical conversion of raw and silver impregnated biomass

Pyrolysis is a commonly employed thermochemical conversion technique that yields liquid and gaseous biofuels, and a solid carbonaceous char. The motivation behind the pyrolysis of the silver nitrate impregnated biomass in this work was to (1) *in situ* upgrade biofuels (by producing more synthetic gas components and more usable bio-oils) and (2) to yield a silver-impregnated biochar that can be calcined to result in bio-templated silver nanomaterials. The impregnated samples were pyrolyzed in bulk (samples ~0.5 g) and the biofuels analyzed via GC–MS and MS. Immediately following pyrolysis, the samples were calcined to remove the carbonaceous template and form the silver nanomaterials. Milligram quantities of each raw and impregnated biomass were subjected

to thermal analysis on a TGA to assess the impact of silver nitrate impregnation on overall reaction kinetics.

3.1.1. Analysis of pyrolysis gas

Pyrolysis of silver nitrate impregnated biomasses resulted in higher quantities of pyrolysis gas components evolved over the same reaction time and temperatures than the raw biomasses. As shown in Fig. 1 (figures for all gases monitored available in the Supplemental Information), the silver impregnated samples evolved considerably more gas, and at a faster rate, suggesting that the silver impregnation step may catalyze the devolatilization of the biomass samples. By integrating the area under the spectrum for each species devolatilized over the 4950-s reaction time, these observations were semi-quantitatively described (Table 2). The inclusion of silver nitrate into the biomass had a significant impact on the hydrogen gas devolatilized, increasing it by almost 200% in the case of pure cellulose paper, and over 136% for the corn stover. Though less dramatic in nature, the yields of C₂H₆ increased by approximately 45% for both biomasses. Interestingly, the methane produced from the cellulose paper only increased by 2.7% upon silver impregnation, yet increased by over 22% for the corn stover. Conversely, the C₂H₂ evolved increased by 15.6% for the cellulose, but only 2.4% for the corn stover. The ethylene evolved decreased slightly (1.2%) for the cellulose, and more significantly (15.3%) for the corn husk. Collard et al. [64] found a similar increase in CO₂ and H₂ in the pyrolysis gas evolved from iron and nickel nitrate impregnated crystalline cellulose, though they note a higher water and char with lower CO yield. Richardson et al. [65] noted higher H₂ and CO yield for nickel nitrate impregnated wood, with a corresponding decrease in CO₂ and C₁-C₂ hydrocarbons. We note (and our future work will explore) that washing biomass to remove mineral matter is known to change the thermal devolatilization profiles and compounds released as especially alkali and alkaline metals present in the raw biomass can act as catalysts [66,67]. Alkali and alkaline earth metals are known to increase peak gasification value [68], and as such "washed" biomass often shows different thermal profiles and gas yields, However, prior work has shown that such mineral matter often has a catalytic effect in promoting devolatilization, and it would presumably remain in the raw corn but potentially be removed in the impregnation step due to some level of washing. This, coupled with there being no mineral matter present at all in the cellulose, makes it likely that the effects observed here are not due to differences in mineral matter content, but rather the silver impregnation.

The changing yields of these pyrolysis gas components agree with prior literature in terms of metal-catalyzed reactions, and also in terms of peak reactivities. For example, the peak reactivity (via DTG mass loss rates) and peak CO₂ evolution for raw cellulose occurred within 2 °C of each other (Fig. S2 of supplemental information), whereas peak evolution of methane was delayed beyond the peak reactivity temperature; such behavior is often noted for both terrestrial and aquatic biomasses [69–71]. The impact of the metal nitrate catalyst on the evolution of these pyrolysis gas components as a function of temperature (as referenced to peak reactivity) depends on the pyrolysis gas and sample: the evolution of methane for silver impregnated cellulose peaked at 371 °C, but for raw paper occurred at 399 °C, and for raw corn occurred at 360 °C, but for Ag-corn occurred at 370 °C, though overall the concentration of methane evolved at 360 °C for the Ag-corn was still considerably higher than the raw corn, only the peak occurred later.

From an energy production standpoint, the evolution of larger quantities of gaseous fuels at the same temperatures from the same starting biomass is beneficial. As more of the solid matrix devolatilized and formed gas, the carbon dioxide in the pyrolysis gas also increased by 43.9% and 45.6% for the impregnated cellulose and corn stover, respectively. This is not unexpected; if pyrolysis gases are overall increasing due to the inclusion of the silver nitrate, presumably the oxygen present in the samples will devolatilize and form CO₂ with the carbon present. To remove the oxygen from fuels, the oxygen will form H₂O, CO and CO₂; analysis of pyrolysis gas can therefore shed light on whether the silver is acting as a heat transport medium to devolatilize sample (i.e. as a heat "sink" given its higher heat capacity), or if it has a catalytic effect on the types of products released. Interestingly, cellulose has higher initial oxygen content (49 wt%) versus the corn (40 wt%), a



biomasses



Fig. 1. Mass spectra of H₂ and C₂ H₆ evolved in pyrolysis gases from raw and silver impregnated biomasses (•) Raw Cellulose; (•) Raw Cellulose; (•) Raw Corn; (□) Ag Corn (spectra of all monitored gases as both functions of time (including isothermal hold) and temperature available in Supplemental Information).

curre (iter) change in quantity of pyroisis gases evolved due to silver infrequencies and corn biomasses.						
Integrated MS area	$H_2 \\ m/z = 2$	$\begin{array}{l} \text{CH}_4\\ m/z = 16 \end{array}$	C_2H_2 $m/z = 26$	C_2H_4 $m/z = 27$	C_2H_6 m/z = 30	CO_2 m/z = 44
Raw cellulose	4.509E-03	2.180E-03	2.017E-04	6.477E-04	1.519E-04	4.235E–03
Ag cellulose	1.324E-02	2.238E-03	2.332E-04	6.402E-04	2.186E-04	5.274E–03
Rel change	193.7%	2.7%	15.6%	-1.2%	43.9%	24.5%
Raw corn	5.366E-03	1.817E–03	1.423E-04	6.087E-04	1.747E–04	3.445E–03
Ag corn	1.271E-02	2.228E–03	1.457E-04	5.157E-04	2.544E–04	5.741E–03
Rel change	136.9%	22.6%	2.4%	-15.3%	45.6%	66.6%

 Table 2

 Relative (Rel) change in quantity of pyrolysis gases evolved due to silver impregnation of cellulose and corn biomasses.

ratio of 1.225. The ratio of CO₂ evolved from the raw samples (Raw Cellulose CO₂/Raw Corn CO₂) was equal to 1.229, suggesting that CO₂ could be formed as a function of oxygen content. However, this relative quantity of CO₂ produced from impregnated samples (Ag Cellulose CO₂/Ag Corn CO₂) is 0.919. That is, the "catalyzed" cellulose produced less, and/or the catalyzed corn produced more CO₂ than would be expected if the oxygen present were the only driving factor, suggesting that enhancing heat transfer is not the only function of the silver in the impregnated biomass, but rather has a chemically catalytic effect. Such increases in CO₂ (and overall gas) yield - reducing liquid biofuel yield - were previously noted for waste wood pyrolysis vapors passed over ZSM-5, Y-zeolite and activated alumina catalyst beds [72]. The purpose of such in situ catalyzing of biomass pyrolysis is ostensibly to remove oxygenated components in favor of hydrocarbons. Richarson et al. [65] suggest that CO generated by carbothermal reactions during pyrolysis gas evolution may be immediately oxidized by H₂O into H₂ and CO₂ via water gas shift reactions on the surface of nickel nanoparticles incorporated into the biomass. As CO dismutation to $C + CO_2$ can be catalyzed by nickel nanoparticles, it is possible that the silver transition metal could be catalyzing such reactions, accounting for the variation in CO₂ (and presumable CO, which, given that it shares the same a.m.u. as N₂, we are unable to account for here) for the two different biomasses [73]. The efficacy of incorporating these catalysts into biomass to remove oxygenated compounds can be further probed by analyzing the condensable bio-oil components collected during pyrolysis.

3.1.2. Analysis of condensable bio-oil components

Table 3 compares the bio-oil components identified via GC–MS analysis of the condensable bio-oil components trapped in DCM during pyrolysis (chromatograms available in Fig. S3 of Supplemental Information). Not surprisingly, the primary condensable components identified with a minimum 90% NIST-library match were furfurals, alkanes and phenols with carbonyl and methyl substituent groups. We note that Table 3 represents the top 20 peaks by area, which is approximately one-quarter of the total chromatogram area, and the area given is the percent of the total chromatogram. This analysis is only semi-quantitative in nature, intended to demonstrate the potential for biofuels to be upgraded *in situ* by incorporation of silver into the cellulosic feedstock.

For both pretreated and raw biomasses, the condensable components recovered were considerably more heterogeneous for the corn than the cellulose, as may be anticipated given that the corn comprises cellulose, hemicellulose, lignin and ash, whereas the paper is pure cellulose. Overall, the presence of silver in the cellulose paper generally suppressed the formation of higher molecular weight components in the liquid product recovered, and had a similar, though milder impact on the corn biomass. Under the framework of Garcia-Perez and co-worker's analysis scheme [74], the large peaks at long retention times noted for the pure cellulose paper, not detected for the silver-impregnated paper, suggest that the silver either inhibits the formation and devolatilization of – or

Table 3

Components identified in condensed pyrolysis gases for raw and impregnated biomass pyrolysis at 10 $^\circ$ C/min up to 600 $^\circ$ C.

10 0		
Retention time (min)	Area (% top 20 chromatogram)	Compound
Daw colluloco	, U	
7 082	7 91	Furfuryl alcohol
7.962	11.45	Fullulyi alcollol 5. budrovumotbulfurfural
9.255	0 12	2 othylphonol
11/70	0.15 1 73	Furfural
12 204	4.25	runundi 2 mothulphonol
12.049	16.27	2.6-dimethylphenol
14.026	1/ 38	2.4-dimethylphenol
15 668	8 65	2.methoxy-4.methylphenol
15.008	0.05	2-methoxy-4-methylphenol
Ag cellulose		
7.899	5.72	Furfuryl alcohol
9.231	21.67	5-hydroxymethylfurfural
10.763	7.25	3-ethylphenol
11.472	2.95	Furfural
13.052	7.98	2,6-dimethylphenol
14.88	5.97	2,4-dimethylphenol
15.637	5.35	2-methoxy-4-methylphenol
Raw corn		
8.384	7.71	5-methylfurfural
9.231	8.49	5-hydroxymethylfurfural
9.731	3.02	2,3-Dihydro-benzofuran
10.758	10.29	3-ethylphenol
11.085	6.55	1-tetradecene
12.256	12.32	3-methylphenol
12.792	10.01	2-methoxyphenol
15.216	9.56	2,3-dimethylphenol
18.581	2.78	Isoeugenol
22.982	0.96	Vanillin
Ag corn		
8.079	7.26	3-phenylpropionitrile
8.383	11.92	5-methylfurfural
9.229	5.87	5-hydroxymethylfurfural
9.720	2.01	2,3-Dihydro-benzofuran
10.749	3.84	3-ethylphenol
12.191	6.09	4-carboxy-3-methoxy-2,4,5-
		trimethylcyclopent-2-enone
12.251	4.37	3-methylphenol
13.057	3.54	2,6-dimethylphenol
15.203	7.68	2,3-dimethylphenol
18.582	1.73	Isoeugenol
22.982	3.48	Vanillin

thermochemically cracked – the larger compounds with higher boiling points to favor lower molecular weight, moderately volatile compounds. The ability of transition metals such as silver and nickel to chemisorb aromatic compounds on their surface (due to covalency between the π orbitals from the aromatic ring and unoccupied *d*-orbitals from the transition metal) is thought to promote such catalytic activity, reducing tars in biomass pyrolysis [75]. For the corn stover, the silver impregnation reduced some of the less volatile compounds and promoted formation of higher volatile compounds; of note is the significant increase in 5hydroxymethylfurfural produced from cellulose with the incorporation of silver nitrate; the relative concentration of this key biorefinery intermediary - used in plastics, pharmaceuticals, fine chemical production – more than doubled with pretreatment [76]. Similar increases in 5-hydroxymethylfurfural have been observed for the pyrolysis of iron and nickel impregnated crystalline cellulose [64]. The increase of furan components may be attributed to the ability of the metal ions to hemolytically and heterocyclically cleave pyranose rings and glycosidic linkages, resulting in enhanced formation of the intermediary levoglucosan [77]. Likewise, we see for cellulose a reduction in the relative concentration of furfuryl alcohol upon impregnation, demonstrated by Yang et al. to be a key intermediate in the conversion of furfural into cyclopentanone over Ni-Cu bimetallic catalysts by H₂O attack on the 5-position of the furfuryl alcohol [78]. Given the small increase in vanillin and decrease in isoeugenol for the Ag-catalyzed corn stover, it is possible that the *in situ* catalyst was responsible for a modicum of such a conversion, demonstrated previous as a potential hydrogenation reaction over Raney Ni catalysts [79].

The catalytic pyrolysis of biomass often occurs with solid acid catalysts such as zeolites, leading to breaking of C-OH and C-CO (OH) bonds in dehydration and decarbonylation/decarboxylation reactions, respectively [80]. Silver nitrate is known to catalyze decarboxylation of saturated and unsaturated fatty acids, silver (I) for catalytic decarboxylation of aryl carboxylates and benzoic acids, and silver (II) for decarboxylation of amino acids [81]. Metal oxides have been shown to catalyze biomass pyrolysis, albeit not as advantageously as zeolites due to their more mild (predominantly Lewis) acidity [82]. The higher release of CO₂ (and presumably CO) in the pyrolysis gas noted here, coupled with lower yields of phenols and higher furfurals in the bio-oil fraction suggest that the silver may act as a catalyst in dehydration reactions [83]. The increase in evolved hydrogen from both biomasses with silver incorporation, with corresponding increase in CO₂ (and likely decrease in phenols, or at least those observed via GC-MS), suggests that the de-oxygenation observed is a decarboxylation reaction with minimal water formation, in favor of H₂ production. We do not see convincing evidence here for a secondary reaction pathway where the "saved" in situ produced hydrogen participates in hydrogen transfer reactions on silver to form saturated hydrocarbons via a carbenium ion intermediate (as observed by Iliopoulou et al. [82] in their Co- and zeolite catalyzed lignocellulose pyrolysis). However, the relatively high gas flow rates in the fixed bed reactor may mean that the mass transfer of devolatilized hydrogen gas overwhelms the reaction kinetics.

3.1.3. Thermochemical conversion kinetics

If the presence of silver in the biomass had a catalytic effect on pyrolysis, this would be reflected in the conversion kinetics by increasing reaction rates and/or lowering the activation energy of pyrolysis. In fact, both of these catalytic effects were observed, but in opposite ways for each biomass. As shown in Table 4, the peak reactivity for the Ag-treated cellulose paper was actually lower than the raw biomass but occurred at approximately the same temperatures for each heating rate (e.g. the reaction occurs more slowly for impregnated biomass). However, the activation energy of pyrolysis of the impregnated sample, as determined by the distributed activation energy model, was lower than the raw biomass and this difference was statistically significant $(187.5 \pm 6.4 \text{ kJ/mol} \text{ versus } 175.6 \pm 4.3 \text{ kJ/mol})$. As seen in Fig. 2, the activation energy at mass fraction conversions below 0.4 for the raw paper was significantly higher than the Ag-paper; after X = 0.55 the raw paper appears higher though this is not statistically significant (error bars overlap within a 95% confidence interval).

The impact of silver nitrate treatment on the corn biomass was much different. Two DTG peaks were noted for the pyrolytic decomposition of both raw and treated corn biomass; such peaks are often observed for heterogeneous material pyrolysis, while not for "pure" biomasses like the cellulose [70,84] (DTG curves available in Fig. S4 of Supplemental Information). As Table 4 shows, the first peak DTG mass loss rate for the 5 K/min heated samples were approximately equal; for 10 K/min and 15 K/min the first DTG peaks for the raw samples showed considerably higher reaction rates. However, for the 5 K/min and 15 K/min samples, the peak DTG of the impregnated corn was noticeable higher, whereas the 10 K/min impregnated sample reaction rate was somewhat indistinguishable from its raw biomass counterpart. The peak temperatures and reaction rates, and their dependence on heating rate are guite similar to those documented in the literature for corn [85]. Though their rates were variable, the peak reaction temperatures for the raw and impregnated cellulose paper were both within $\sim 1 \,^{\circ}$ C for all three heating rates; the impregnated corn had a peak reaction temperature for peak 1 between 10 and 30 °C less than the raw corn. and between 8 and 17 °C higher for peak 2.

The activation energies showed vastly different behavior for the raw and impregnated corn stover. At conversions below X = 0.55, the activation energy (E_a) of the raw corn was significantly lower than the Ag-treated corn. At X = 0.65, E_a of the impregnated corn was less than the raw corn, though this was only statistically significant at X = 0.8 (error calculated as 95% confidence interval around each set of data points on the Arrhenius plot; data available in Table S1 of the Supplemental Information). This lower E_a at higher conversion rates may be due to the impregnation step removing some of the soluble fixed carbon (i.e. carbonates) and/ or ash components present in the corn stover (that we do not see in the cellulose filter paper). The average activation energy calculated over all mass fractions for the raw corn was 188.7 ± 28.5 kJ/mol, and for the pretreated corn was 220.9 ± 56.8 kJ/mol. The confidence intervals here and in Fig. 3 are the standard deviation of the average point conversion values; given the large spread in activation energies at each conversion level this leads to a high standard deviation. However, given the statistically significant differences in activation energies at lower conversion levels, it does appear that at lower temperatures, the silver nitrate impregnation increases the energy barrier required to initiate decomposition.

Such catalyst behavior during in situ biomass upgrading, whereby yields and quality of gases increase, but activation energy does not necessarily decrease, is not an uncommon phenomenon in the literature. For example, Nowakowski et al. found higher activation energies (up to two times higher) for potassium impregnated willow biomass with a similar increase in methane evolution from impregnated samples [86]. Nano and micro nickel oxide catalysts have been shown to moderately lower then activation energy of cellulose and xylan, but have little effect on lignin pyrolysis [87,88], confirming the findings here that the impact of the metal impregnation is biomass-specific. Our findings, and others' in the literature, suggest that the "catalyzed" biomass pyrolysis reactions may not decrease the energy required to initiate pyrolysis reactions, but that given increases in gas yields and the production of different compounds, the reactions are indeed "catalyzed" [89]. This lack of change in activation energy may be due to additional heat required to bring the sample to a suitable pyrolysis temperature; as biomass pyrolysis is initially endothermic [90], the higher specific heat of the silver versus the biomass requires more energy to raise the temperature, and this therefore may be reflected in the activation energy of pyrolysis.

3.2. Bio-templated nanomaterials

Using TGA data, the yield of the nanomaterials after calcination as a function of starting total impregnated sample mass was $5.84 \pm 0.77\%$ for the impregnated paper, and $4.91 \pm 0.26\%$ for the

 Table 4

 Thermogravimetric results of pyrolysis of raw and impregnated biomass samples.

	Peak DTG				
	Peak 1 T (K)	Peak 1 Rate (1/s)	Peak 2 T (K)	Peak 2 Rate (1/s)	
5 K/min					
Raw paper	608.2	2.51E-03			
Ag paper	609.9	2.23E-03			
Raw corn	548.7	5.82E-04	591.9	9.08E-04	
Ag corn	537.8	5.48E-04	608.6	1.21E-03	
10 K/min					
Raw paper	619.3	5.05E-03			
Ag paper	617.0	4.43E-03			
Raw corn	565.6	1.54E-03	600.8	2.26E-03	
Ag corn	534.2	1.04E-03	609.5	2.22E-03	
15 K/min					
Raw paper	626.4	7.31E-03			
Ag paper	626.0	6.42E-03			
Raw corn	569.1	2.34E-03	607.8	3.27E-03	
Ag corn	548.1	1.79E-03	618.4	3.54E-03	

300





(a) Activation energy as a function of mass fraction converted calculated by DAEM; (•) Raw Cellulose;
(○) Ag Cellulose; (■) Raw Corn; (□) Ag Corn

(b)Average activation energy and pre-exponential factors calculated by DAEM

Fig. 2. Activation energy of pyrolysis of raw and impregnated biomasses.

corn stover. Just as He et al. [56] found during an investigation into the direct oxidation of silver-impregnated biomasses, the size and morphology of the pyrolyzed-then-oxidized silver nanomaterials depended on the biomass template used. As seen in the SEM images of Fig. 3, calcination of the AgNO₃-impregnated cellulose template produced a "mesh" of semi-spherical silver nanoparticles ranging in size from \sim 20 to 200 nm. The particles formed using the corn stover as a template appear to be, on average, larger and with a larger size distribution. This was confirmed through XRD analysis; both samples show characteristic peaks for crystalline silver (Fig. S5 of the Supplemental Information) at the same 20. However, the peak broadening, as assessed by integrated width (integrated intensity/maximum intensity), was much larger for the cellulosetemplated samples, as detailed in Table 5. The smaller number of parallel diffraction planes for smaller crystalline materials (less than 100 nm) result in the peak broadening observed here [91]. The size distribution of nanoparticles produced via cellulose templating was similar to silver nanomaterials produced using various biomass plant extracts [92]. Others have reported smaller silver nanoparticles (in the range of 5–8 nm) using combinations of biomass as a template and ascorbic acid as a reductant [93]. However, what is often absent from these literature studies is an analysis of the purity of these biomass-templated nanomaterials; though many report XRD results [93], such techniques will miss impurities present in amorphous form. As such, we used EDS to determine the elemental composition of the biotemplated materials.

Table 5 details results of the SEM-EDS elemental analysis of the biotemplated silver. The cellulose template sample showed a material almost entirely composed of silver – over 96 wt% (99 at. %) – confirming XRD analysis that the cellulose templated nanomaterials were elemental silver, and not silver oxides. The picture is slightly murkier for the corn-templated sample, where only 71 wt% of the sample was silver, with the balance comprised of carbon, oxygen, sodium, phosphorus and magnesium, the latter



(c) Ag corn stover, 10K mag (scale bar indicates 1 µm) (d) Ag corn stover, 35K mag (scale bar indicates 300 nm)

Fig. 3. SEM images of calcined silver-impregnated biomasses.

Table 5 Elemental analysis (weight and atomic percent elements detected via SEM-EDS) and integrated XRD peak width of silver impregnated and calcined biomasses.

Element	Cellulose paper		Feed	Feed corn		
	wt%	at.%	wt%	at.%		
Ag	96.23	99.49	71.48	29.54		
С	1.73	0.2	1.34	4.97		
0	2.04	0.31	16.29	45.39		
Na			7.79	15.1		
Р			1.47	2.21		
Mg			1.01	1.85		
	Inte	grated width at 2	θ			
38.0°	1.453		1.0	1.038		
44.2°	0.663		0.492			
64.4°	0.392		0.2	0.277		

three of which are elements naturally presents in the corn biomass, having been up-taken from the soil during cultivation. They were likely present in the amorphous form, as separate XRD peaks were not noted for crystalline forms of these elements. In sum, the more "pure" biomass (cellulose paper) produced a smaller size distribution of purer silver nanomaterials than the heterogeneous biomass (corn stover). Thus, the ability to use heterogeneous biomasses in this integrated biorefinery concept will depend on (1) the ability of pretreatment to remove inorganic contaminants from the biomass matrix in an efficient manner, and (2) the end-use of the produced nanomaterials. For example, the trace Na, P, and Mg present in the corn template materials may not present a barrier for use of the silver in membranes for gas separation and catalytic upgrading, but are not suitable for biomedical or electronic devices. Future work will explore the ability of biomass pre-treatment and nanomaterial post-treatment steps to remove such contaminants.

3.3. Future directions

In this work we posit a new direction for the integrated biorefinery: by integrating silver nanomaterial and biofuel production we can improve the bio-oil quality (for example seen through increasing 5-hydroxymethylfurfural concentration), and pyrolysis gas (especially H₂) yield, while producing a nanomaterial with widespread applicability. Future work will explore more detailed catalytic mechanisms of the biomass pyrolysis, including elemental fuel analysis and water content. Though this work demonstrates a proof-of-concept, one of the primary barriers that the authors foresee to commercialization of such a technology would be the advent of a continuous process for manufacture. As Dzido and Jarzębski [94] note, the ability to prepare various metal nanoparticles has increased exponentially over the past thirty years, but our ability to prepare them in continuous processes as opposed to time-consuming bench-scale processes hampers widespread use.

Bringing integrated biorefinery conversions of heterogeneous feedstocks such as corn stover online at a commercial scale will require some form of biomass pretreatment. For example, Bond et al. [7] detail an integrated biorefinery that begins with a pretreatment step designed to maximize recovery of pentose sugars from hemicellulose while leaving cellulose relatively unchanged. The degree of pretreatment required to incorporate nanomaterial production will depend on a number of factors, including perceived value of the pretreatment step as compared to the enhancement in product recoveries, and the ability to separate the cellulose materials from inorganic matrices, if necessary. Prior work in the field suggests that pre-washing biomass (thereby removing mineral matter) increases activation energy overall and does little to affect pyrolysis fuel yields at all but the lowest temperatures [95]. Given this, it is unlikely that simply "soaking" the biomass in AgNO₃, especially for the corn sample, is to credit with the observed increase in pyrolysis gases devolved and the modest increase in activation energy. However, the benefit of pre-washing to remove inorganic constituents in this integrated biorefinery scenario may serve a purpose beyond fuel yield, in that it would increase the purity of the resulting nanomaterials. Future work will consider not only the soaking time for the biomass in metal salts, but also the rate of diffusion and loading of these salts onto biomass to determine if there is an optimal balance between processing time, materials use, and fuel/nanomaterial yield.

4. Conclusions

This work demonstrates a new integrated biorefinery process for the co-production of biofuels and silver nanomaterials. By impregnating pure cellulose and corn stalk, a heterogeneous cellulosic biomass, with silver nitrate, followed by pyrolysis, the yield of pyrolysis gases increased substantially, especially of hydrogen gas. The condensable bio-oil components of the impregnated samples were considerably higher in furfurals (including key intermediary compound 5-hydroxymethylfurfural) and lower in other identifiable oxygenated components. The incorporation of silver nitrate into the biomass moderately lowers the activation energy of the cellulose and raises the corn stover barrier, though this is within confidence intervals. Though the overall activation energy barrier to pyrolysis does not change with the silver nitrate pretreatment, the higher amounts of gases devolatilized, and improved quantity of 5-hydroxymethlfurfural, suggests a catalytic effect, potentially increasing decarboxylation reactions. The novelty of the proposed biorefinery concept goes beyond using a metal salt impregnation step to improve pyrolysis fuel gas yield; following pyrolysis, the silver-char composite material was calcined to remove the biomass template to yield silver nanomaterials. While other studies have demonstrated the ability to biotemplate similar silver nanostructures on cellulosic biomass, they consider only impregnation and oxidation of the template, overlooking the potential to extract valuable biorenewable fuels in an integrated process.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.enconman.2017. 03.001.

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