

SYNTHESIS GAS PRODUCTION BY RAPID SOLAR THERMAL GASIFICATION OF CORN STOVER

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Abstract

Biomass resources hold great promise as renewable fuel sources for the future, and there exists great interest in thermochemical methods of converting these resources into useful fuels. The novel approach taken by the authors uses concentrated solar energy to efficiently achieve temperatures where conversion and selectivity of gasification are high (1000°C – 1200 °C). Use of solar energy removes the need for a combustion fuel and upgrades the heating value of the biomass products. The syngas product of the gasification can be transformed into a variety of fuels useable with today's infrastructure. Gasification in an aerosol reactor allows for rapid kinetics, allowing efficient utilization of the incident solar radiation and high solar efficiency.

Corn stover, a common agricultural byproduct, was gasified in aerosol flow in an electrically heated controlled environment furnace, simulating the conditions seen in a solar furnace. The effects of water concentration, temperature, particle size, and residence time on conversion and selectivity were explored. It was observed that high conversions were achieved in all high temperature cases, with carbon conversions to syngas products of greater than 70% were achieved for temperatures of 1158 °C and residence times of less than 1 s. Longer residence times are likely needed to fully gasify the char. The selectivity of CO over CO₂ was shown to increase with decreasing water concentration. It was demonstrated that the rapid gasification reaction could be achieved under typical solar conditions and that the process could be tuned for the desired end products.

Keywords: solar thermal, biomass, aerosol, gasification, synthesis gas, corn stover

1 Introduction and background

By 2030, world energy demand will climb from a current level of 18 TW to 28 TW.¹ At the same time, concerns over the environmental and national security impacts of fossil fuel use are driving the search for a fuel source that is abundant, clean, and producible within the United States. Fuels produced from biomass (e.g. switchgrass, agricultural residues, forestry waste) could provide a large piece of this energy puzzle, but conventional methods of processing the biomass resource face significant challenges.² This innovation proposes to use solar thermal energy to overcome the problems encountered in conventional conversion. Such an approach lies on the interface between two renewable energy technologies (solar and biofuels) and is uniquely positioned to maximize the positive qualities of both. Solar thermal systems use focusing mirrors to concentrate the sun's rays and efficiently ($\eta > 70\%$ based on energy losses from a receiver operating under high concentration) achieve ultra-high temperatures ($T > 1200$ °C).³⁻⁵ At these temperatures, the biomass can be

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thermally decomposed, possibly in the presence of steam, without the problems encountered in lower temperature systems. The high temperatures allow high conversion with little to no production of unwanted side products, and the use of solar energy negates the need to burn some of the biomass to provide energy for reaction.^{6,7} The process produces a flexible product, synthesis gas, which can be chemically converted to a number of useful fuels (e.g. gasoline, diesel, hydrogen).⁸ Compared to biochemical conversion of biomass, the process is much faster (seconds vs. days), simpler, and has the potential to produce a wider range of chemical products.⁹⁻¹² Although solar radiation is intermittent, the use of a solar driven endothermic chemical process to produce liquid fuels provides a method by which to store solar energy in chemical form. Gasification and downstream reactors can be operated while the sun shines, with systems going to inert gas recycle loops overnight.

There has been much stated in the literature over the past decade with regard to using plant-derived biomass as a source material for fuels or specialty chemicals.² Traditionally, this has entailed fermenting the sugars contained in the reproductive tissues of the plants into alcohols or other usable chemicals.¹³ The foremost of these examples is derivation of ethanol from corn sugars. However, these pathways are limited with regard to the scope of what these plants can supply to the market, the use of the plant sugars as foodstuffs, and the energetics of conversion processes. It currently requires nearly as much fossil energy to ferment and distill ethanol from corn as is available in the fuel itself.¹⁴ Increasing demand and conflicting uses will make it difficult to implement this fuel on a wide scale in the future.

Instead, it has been widely proposed to convert the non-edible portions of plants, so-called "cellulosic biomass", into fuels or chemicals. This biomass is primarily composed of three biopolymers, cellulose, hemi-cellulose, and lignin. Cellulose is a glucose-based polymer consisting of $C_6H_{10}O_5$ monomer units tied together by β -glycosidic linkages. There is significant hydrogen bonding, making the molecule very stable.¹⁵ In contrast, hemi-cellulose is made up of short, branched chains of sugars, primarily those with five carbons. It is relatively easy to break down compared with cellulose.¹⁵ Lignin is a non-carbohydrate component of plants, a highly polymeric aromatic chemical that gives woody plants their rigidity. It is much more difficult to break down than cellulose or hemi-cellulose, and most biochemical conversion methods cannot decompose it.¹⁵ Cellulose represents between 30% and 50% by weight of typical biomass, depending on the source, with lignin representing 15%-35%, and hemi-cellulose making up 20%-30%.¹⁶ These biopolymers make up the rigid walls of plant cells. The supply of cellulosic biomass is large. In 2001 the United States produced 492 million tons of it.¹⁶ Unlike sugar-based biomass, there is no existing market for this resource, which consists of such varying materials as corn-stalks, sawdust, and tall grasses.¹⁶⁻¹⁸ Varieties of plants that require little water, grow quickly, and consist mainly of cellulosic biomass (e.g. switchgrass, algae) are being developed, and could rapidly expand the existing supply.^{17,18}

Conversion of cellulosic biomass to fuels and chemicals is conventionally achieved in one of two ways. The first is biochemical and involves engineering enzymes and microorganisms that feed on and chemically convert the biomass into more usable chemicals. This method will not be treated here, but currently requires expensive enzymes, a large amount of feed preconditioning, and produces a single product (e.g. ethanol).^{10,11} The second conventional method for converting cellulosic biomass is thermochemical in nature. The biomass is heated, sometimes in the presence of steam or oxygen, to temperatures between 500 °C and 850 °C. Thermochemical conversion in the presence of an oxidant is referred to as "gasification," and this conversion in the absence of an oxidant is referred to as "pyrolysis." The high temperature allows for thermal breakdown of the cellulose, lignin, and hemicellulose of the biomass into a mixture of hydrogen and carbon monoxide known as synthesis gas ("syngas"). Steam aids in the completion and kinetics of this reaction by providing additional oxidant for lignin, which is relatively oxygen poor. This breakdown proceeds through several intermediates, and incomplete gasification results in a variety of higher hydrocarbons and aromatics known collectively as "tar."⁶ These tars are difficult to process further, foul and clog processing equipment, and reduce the overall yield of the thermochemical process to the desired hydrogen and carbon monoxide products. The production of tar has been shown to decrease with increasing temperature, and selectivity of reaction products to syngas has been shown to improve.⁶

The heat required for operating a conventional thermochemical gasifier is provided by combustion, either of a fossil fuel (e.g. natural gas) or of the biomass material itself. Obviously, processing with natural gas is neither renewable nor carbon-neutral, and the price of the biofuel products will be strongly linked to the price and availability of natural gas. By combusting the biomass, the fuel source becomes renewable, but at the cost of some of the feedstock. To maintain gasification temperatures between 500 °C and 800 °C, up to 30% of the biomass resource must be combusted.⁷ Reaching temperatures where conversion efficiency and selectivity are extremely high (1200 °C) require 35%-45% biomass combustion, based on adiabatic flame temperature

calculations. Much of the cost of a gasification plant is in transportation of the feedstock, and use of that feedstock for combustion detrimentally affects the profitability of the process. If natural gas is used, and equivalent amount of energy must be consumed to drive the gasification – it would make more sense to reform that fuel to syngas directly. High temperatures, at which conversion and selectivity have been shown to be improved, are expensive to attain, as too much of the feedstock must be used as fuel to maintain reaction temperatures. The use of the biomass resource as process fuel decreases the scope of replacement the biofuel could have with respect to fossil fuels, as transformation capacity of carbon in the biomass to liquid fuels (e.g. diesel) is directly related to process efficiency.

Solar thermal energy provides a means to efficiently and sustainably provide high temperature (>1000 °C) process heat while utilizing an abundant but underused renewable resource. A solar thermal system consists of concentrating optical surfaces that focus the energy to a target. At this focal point, the original incident energy is concentrated to thousands of times its original intensity, allowing for very high temperatures to be achieved (> 1000 °C).^{3-5, 19} By implementation of a cavity receiver, these high temperatures can be maintained very efficiently (receiver losses <30%).³⁻⁵ Central receiver solar thermal systems are currently operating to produce electricity commercially in Spain, but the technology remains underdeveloped for application to chemical process systems. Gregg, et al. explored this concept with directly irradiated coal mixed with biomass (walnut shells) over 25 years ago.²⁰ These researchers found that solar energy could be stored in the products with an efficiency (energy chemically stored divided by energy delivered) nearing 50%, but did not operate above 1200 K; at these temperatures, some higher hydrocarbons were formed. In this work, we are focusing on increasing kinetic rates by using an aerosol flow geometry, with the intention of increasing efficiencies and decreasing char production.

This research explores the gasification of a biomass waste resource, corn stover. Of greatest interest is developing an understanding of the gasification reaction so that operating conditions where conversion and selectivity are highest can be identified. This would allow optimization of a commercial solar thermal gasification facility.

2 Experimental apparatus

The experiments were conducted in an electrically heated aerosol tube furnace. The furnace simulates the high temperature environment experienced in a solar-thermal furnace, but without the intermittency and control difficulties inherent in using solar radiation. The electrical furnace provided a controlled environment in which to study the gasification chemistry before proving the experiments in a solar furnace.

The experimental setup consisted of a quartz tube 106.68 cm (42”) in length and 5.08 cm (2”) in internal diameter placed vertically inside a ceramic element tube furnace. (Figure 1) This furnace was capable of achieving temperatures as high as 1800 °C, but with a quartz tube the internal wall temperature was limited to 1200 °C, which gave a maximum gas temperature of 1158 °C. Corn stover (43 wt% C, 40.5 wt% O, 5.7 wt% H, HHV=18514 kJ/mol) was milled in a ball mill into three size ranges: <150 µm, 150 µm – 300 µm, and 300 µm – 600 µm. These particles were fed into the quartz tube using a vibratory tray feeder with an Ar purge flow controlled between 2 SLPM and 4 SLPM. The rate of particle feed into the system was controlled at 2 mg/s by adjusting the amplitude of feeder vibration. Before entering the quartz tube, the particles were joined by steam and additional argon. To generate the steam, a capillary tube containing liquid water was placed inside a stainless steel tube in which the additional argon was flowing. The tubes were heated to 140 °C by external heat tape, and water flowrate to the capillary was controlled by a 10 mL syringe pump. The hot argon rushing across the capillary tube carried water vapor into the junction with the particle flow. The flowrate of additional argon was chosen to control the residence time in the reactor.



Figure 1

The gas/particle mixture passed into the heated zone of the furnace, where the gasification reaction took place. The products were cooled in the lower section of the quartz tube before entering a gravity settling vessel. Heavy solids collected on the floor of this vessel, while fine, entrained particles were collected downstream on a 200 nm pore diameter HEPA filter. Condensable tars and product vapors were also collected on this filter. After passing through the filter, the composition of the outlet gas was quantified using a residual gas analyzer (RGA) (Stanford Research Instruments quadrupole mass spectrometer) and an NDIR CO/CO₂ analyzer (California Analytical Instruments Model 602). Product particles were collected for compositional and morphological analysis from the collection vessel, the quartz tube walls, and the filter.

The experiments were planned using a 2_{IV}^{4-1} fractional factorial design, which allows for efficient coverage of an experimental parameter space. (Table 1) Stoichiometric water rates were calculated on theoretical gasification requirements for the content of cellulose, hemicellulose, and lignin in the feed powder. The objective of this design was to determine which physical conditions had the most significant effect on the conversion of the biomass and the selectivity between products. The most significant factors could be studied later in a response surface design focused on finding the optimal operating point where

high conversion and selectivity converge with maximum solar efficiency. Two replicates of the design with four total center points were to be performed. The temperatures selected are representative of those efficiently accessible to solar thermal technology, while the water flowrates, gas flowrates, and particle sizes represented the limits of what might be obtained economically in a commercial implementation.

Experiment #	Temperature (°C)	Total Gas Flow (SLPM)	Ratio of Water Fed to Stoichiometric Req.	Particle Size (µm)
1	962	2	2:1	<150
2	1158	2	2:1	300-600
3	962	4	2:1	300-600
4	1158	4	2:1	<150
5	962	2	4:1	300-600
6	1158	2	4:1	<150
7	962	4	4:1	<150
8	1158	4	4:1	300-600
9	1057	3	3:1	150-300
10	1057	3	3:1	150-300

Table 1: Experimental Plan

3 Results and discussion

A general profile of reaction products as measured by the RGA is seen in Figure 2. For general experiments, between 1.5 g and 2.0 g total corn stover were fed into the gasification reactor. Reactions were observed to start rapidly, with product evolution evidenced on the RGA immediately after feeding. Total mass of solids collected ranged between 12% and 17% of the total fed, and fixed carbon/inductively coupled plasma analysis showed these solids to be nearly pure carbon, allowing the carbon balance to be closed within 95%. Ash slag was deposited on the tube walls. RGA samples of the hot product gas showed that, at the highest temperatures, gas

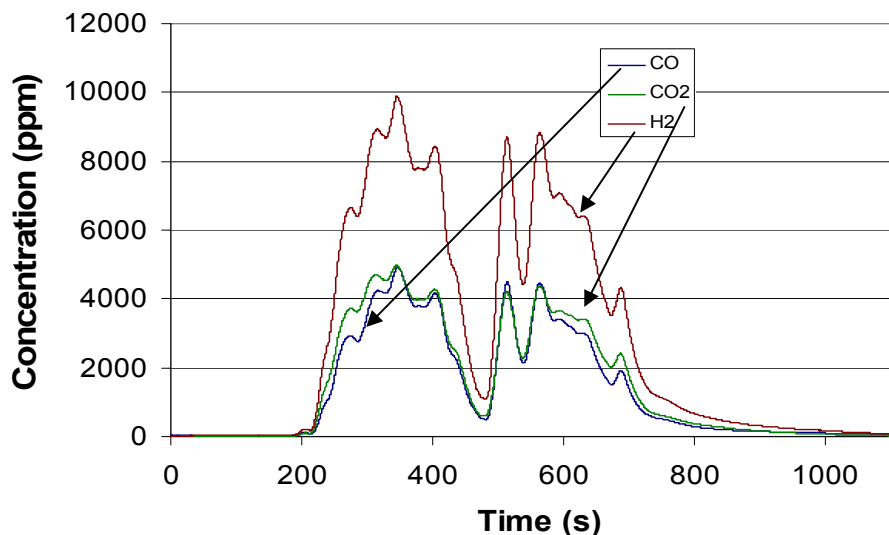


Figure 2

products consisted solely of H₂, CO, and CO₂, and CH₄, with the latter being produced at less than 5% of the total CO and CO₂ levels. Methane, although not convertible in Fischer-Tropsch and other syngas conversion processes, is not harmful to the catalysts in those processes. It could be separated and sold as a secondary product. No higher molecular weight products were observed by the RGA at high temperatures,

indicating that production of these products was negligible. At the lowest temperatures, volatile tars were seen in small proportions on the RGA, but were much more evident in plugging of the HEPA filter. This is discussed below.

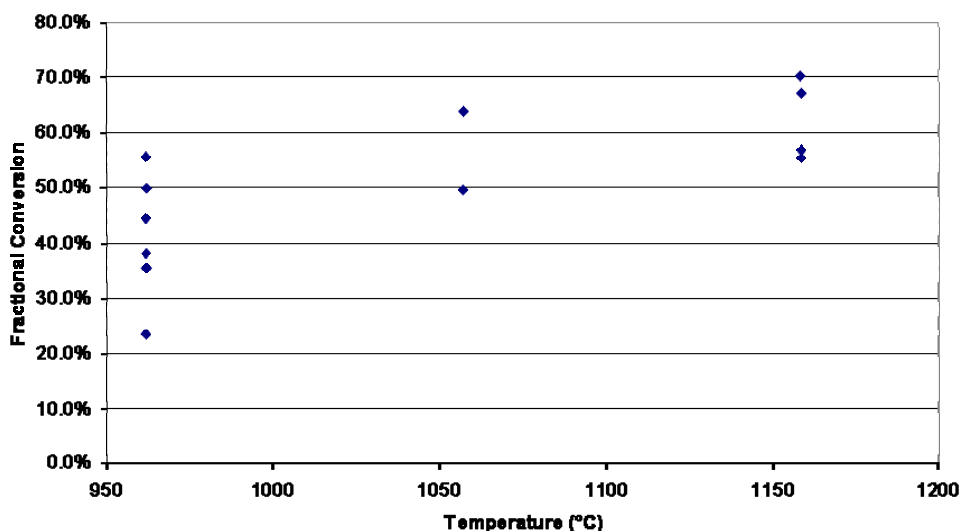


Figure 3

clear from the conversions increased significantly with gas temperature, with maxima around 70%. Carbon not contained in CO or CO₂ was generally found in methane (<5%) and in solid carbon, which accounted for most of

Conversions for the experiments were generally high, given that the residence times for reaction were very short. Here, conversion is measured as the molar fraction of carbon in the fed biomass that exited the reactor as CO and CO₂. Feedstock carbon composition was determined using combustion elemental analysis (LECO TC-200), with an average value of 43% carbon by mass. The effect of temperature on conversion is shown in Figure 3. It is

the balance. The mass of the HEPA filter increased significantly over experiments at the lowest gas temperature, suggesting volatile tar buildup could be a large portion of the carbon balance at these temperatures.

Conversions above 70% were not observed, for a number of possible reasons. First, residence times were fairly limited, especially at the highest temperatures. At the highest temperatures and gas flows, residence times were below 0.3 s, while at lower temperatures they were nearer to 0.8 s. Figure 4 shows the effect of carrier gas flow on conversion for the three examined temperatures. Within each temperature series, conversions are lower for higher gas flows (shorter residence times), although this is less pronounced at high temperatures. The data shows a large amount of variability, mostly due to the small masses of material processed during experiments. The second limiting factor is temperature; due to the use of quartz, temperatures were limited to 1200 °C, leading to much lower effective gas temperatures. At temperatures above 1200 °C, it was shown in previous experiments that char was nearly completely gasified. Finally, water diffusion to the particle surface could be limited by the short residence times, although no statistically significant effect was seen for water concentration or for particle size in these experiments. Both would be expected to be important if diffusion were a driving factor.

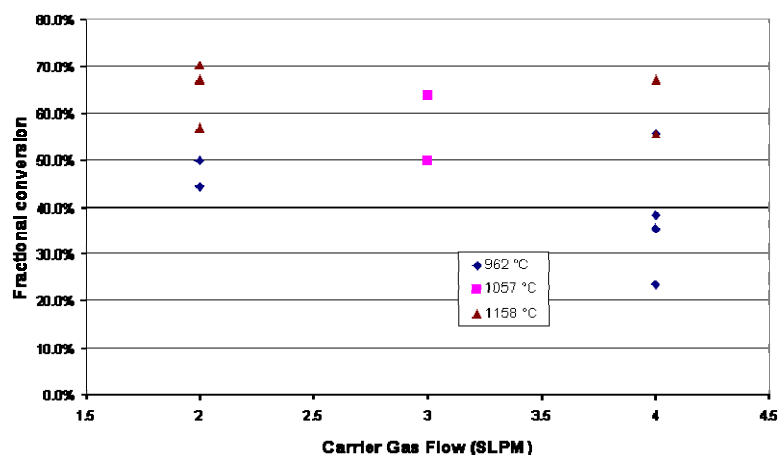


Figure 4

Another response that depended heavily on temperature was the pressure drop across the HEPA filter at the gas exit of the system. Condensable vapor products that did not deposit before arriving at the HEPA filter could deposit in the filter pores, clogging them and increasing the pressure drop over the filter. This pressure drop was an indicator for the selectivity away from heavy tars and toward smaller, highly decomposed gases (CO, CO₂, CH₄). As can be seen in Figure 5, the pressure drop did not increase significantly over a period of 1500 s for the 1200 °C condition. However, the increase was rapid and exponential at 1000 °C, only dropping after a safety pressure relief valve opened. This indicated the presence of tars at this decomposition temperature. As non-solar thermal systems cannot efficiently achieve temperatures in excess of 1000 °C, they will be burdened by some tar production, which decreases yield and can foul downstream catalysts and equipment. This is completely eliminated at 1200 °C, adding more impetus to operate the gasification reaction in the solar thermal temperature regime.

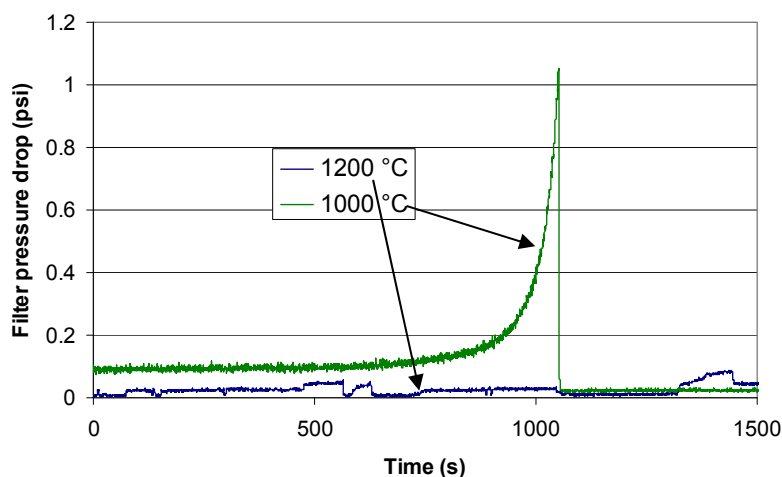
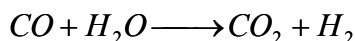


Figure 5

The last response examined was selectivity of CO over CO₂. The general gasification reaction will produce CO and H₂ in stoichiometric amounts. If extra water is available, CO₂ and additional H₂ can be produced during cooling by the water-gas shift reaction:



When processing synthesis gas, the catalytic process to produce a desired product often requires a specific H₂ to CO ratio. For example, mixed alcohols require a 1:1 ratio, while Fischer-Tropsch fuels and methanol prefer a

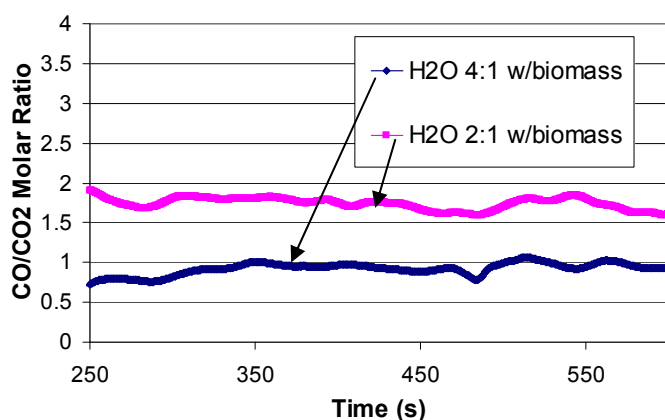


Figure 6

2:1 ratio. As a result, the composition of the exit gas from the solar gasifier is of great importance to a syngas processing plant. The ratio of CO to CO₂ in the exit gas is an indicator of the overall level of water gas shift in the system, and is thus a proxy for H₂ to CO ratio. This concept was confirmed out by measurements of H₂ from the RGA, but as RGA calibrations for H₂ (only) tended to shift daily, it was not as convenient a technique for determining the ratio.

This ratio did not strongly depend on particle size, wall temperature, or residence time, but it was greatly affected by the ratio of water fed relative to the stoichiometric water requirement for

complete gasification of the biomass. As the water concentration was increased, the CO to CO₂ ratio decreased, indicating downstream water-gas shift. (Figure 6) This shift may have been catalyzed by the ash in the biomass or the quartz tube wall; more experimentation is required to determine this. The correlation between water feed ratio and CO to CO₂ ratio was highly repeatable across experiments and steady throughout the period of the experiment. The significance of this observation for the overall process is great. Simply by adjusting the steam-to-biomass feed ratio, the H₂ to CO ratio can be adjusted to the needs of the downstream catalytic reactor. This of course adds CO₂, but it is impossible to get solely CO and H₂ in a Fischer-Tropsch ratio (1:2.1) from biomass without generating this side-product. The advantage is that no additional water-gas shift reactor or processing would be required, greatly reducing the complexity and cost of a commercial plant. The selling price of products would be lower, making the solar gasification process more competitive economically.

4 Conclusions

Corn stover was gasified in falling particle flow at high temperatures in an electrically heated furnace designed to mimic a solar reaction environment. A fractional factorial design was employed to study the effects of reactor wall temperature, steam concentration, particle size, and residence time on the conversion of carbon in the feed to CO and CO₂ and selectivity of CO over CO₂. Initial results showed that conversion was a strong function of temperature, with experiments performed at 1158 °C having much higher conversions at 962 °C. Evidently, the kinetics are rapid enough at the higher temperatures to achieve the thermodynamically predicted decomposition products (CO and H₂), while at lower temperatures residuals of the complex compounds in the biomass remained. This bodes well for the solar thermal approach, as it has strong economic advantages over other techniques at high temperatures (i.e. the biomass or other fuels are not consumed). At lower temperatures, pressure built up across the exit filter much faster, indicating a higher fraction of tars in the product stream than at 1158 °C, where RGA analysis showed negligible tar formation. Finally, it was shown that selectivity of CO over CO₂ was inversely related to steam concentration in the carrier gas. This selectivity was repeatable across experiments and steady throughout the experimental period. This is important, because a downstream process may need a specific CO:H₂ ratio to operate well (e.g. Fischer-Tropsch requires ~1:2.1), although some CO₂ separation may be required, depending on the catalyst type. Future work includes completion of a response surface design on the significant factors to find the optimal operating point and determination of a global model for the reaction kinetics. Verification of this model will be performed in a solar furnace, demonstrating the technology in a future commercial framework. Finally, the gasifier will be integrated with a downstream catalytic processing reactor, demonstrating conversion of solar derived syngas into useful fuels and chemicals.

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