

Final Report

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Project Title: High Pressure Gasification of Biomass

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Introduction

According to the Billion Ton Report, the U.S. has a large supply of biomass available that can supplement fossil fuels for producing chemicals and transportation fuels. Agricultural waste, forest residue, and energy crops offer potential benefits: renewable feedstock, zero to low CO₂ emissions depending on the specific source, and domestic supply availability. Biomass can be converted into chemicals and fuels using one of several approaches: (i) biological platform converts corn into ethanol by using depolymerization of cellulose to form sugars followed by fermentation, (ii) low-temperature pyrolysis to obtain bio-oils which must be treated to reduce oxygen content via HDO (hydrodeoxygenation), and (iii) high temperature pyrolysis to produce syngas (CO + H₂). This last approach consists of producing syngas using the thermal platform which can be used to produce a variety of chemicals and fuels.

The goal of this project was to develop an improved understanding of the gasification of biomass at high pressure conditions and how various gasification parameters might affect the gasification behavior. Since most downstream applications of synags conversion (e.g., alcohol synthesis, Fischer-Tropsch synthesis etc) involve utilizing high pressure catalytic processes, there is an interest in carrying out the biomass gasification at high pressure which can potentially reduce the gasifier size and subsequent downstream cleaning processes. It is traditionally accepted that high pressure should increase the gasification rates (kinetic effect). There is also precedence from coal gasification literature from the 1970s that high pressure gasification would be a beneficial route to consider. Traditional approach of using thermogravimetric analyzer (TGA) or high-pressure themogravimetric analyzer (PTGA) worked well in understanding the gasification kinetics of coal gasification which was useful in designing high pressure coal gasification processes. However, similar approach for biomass gasification was not very useful and was the impetus for this study.

Specifically, we aimed this study at three broad objectives: (i) defining operating conditions at which C₂-C₄ hydrocarbons are formed since these represent loss of carbon efficiency, (ii) understanding the formation of tar species which create downstream processing difficulties in addition of carbon efficiency loss, and (iii) kinetics of biomass gasification where it would be possible to understand the effect of operating conditions and gas phase composition.

Approach for the Proposed Work

As the biomass is heated, it undergoes two processes in series: (i) pyrolysis at temperatures between 300-600 °C, and (ii) char gasification at temperatures above 800 °C. It should thus be possible to study these two steps separately and understand the effect of operating variables in each step. There are limitations associated with use of a single biomass species, and the results can not be easily extended to a different biomass gasification, it was desirable to consider different biomass species and to understand their compositions to see how these might relate to

the overall performance during gasification. We considered three different species: loblolly or southern pine, switchgrass, and corn stover.

The approach undertaken is centered on two basic premises: (1) the gasification for small particles without internal mass transfer limitations can be treated as the sum of two processes in series (pyrolysis and char gasification), and (2) the reactivity of the char generated during pyrolysis not only depends on the pressure and temperature but is also affected by the heating rates. Thus low heating rates (10-50 °C/min) typical of PTGA fail to produce char that would typically be formed at high heating rates ($\sim 10^4$ °C/sec), encountered in entrained flow gasifiers. The char morphology, also a function of the heating rate, would influence the transport rates during the char gasification phase. Thus, heating rate plays a critical role through which both, pyrolysis and char gasification, are interconnected.

We utilized two complementary gasification experiments: PEFR (pressurized entrained flow gasifier) and PTGA (pressurized thermo-gravimetric analyzer). The PEFR allowed us to study gasification at pressures, temperatures, and heating rates relevant for commercial biomass gasifiers. The PTGA will be useful in understanding the basic chemistry of the evolution of various gaseous species during pyrolysis. In addition, solid residues generated at various stages of pyrolysis can be removed and analyzed using various characterization techniques. These results will help build an improved understanding of the chemistry and chemical changes during pyrolysis. Char gasification using steam and/or CO₂ is known to be catalyzed by alkali metals present in the biomass. This study will generate intrinsic kinetic rate data (free of any transport limitations) for char gasification. The catalytic role of various inorganic matters (including alkali) will be examined.

Results and Discussion

1. Selection of Biomass Species

Table I below shows the elemental composition of various biomass species. It is seen that all biomass species have comparable elemental composition as well as similar volatile matter and fixed carbon. The difference lies mainly in the ash content which can affect pyrolysis and gasification behavior.

Table I. Elemental Composition of Biomass Species

Element	Loblolly Pine	Switchgrass	Cornstover
C	52.4	48.3	43.7
H	6.3	6.1	5.9
N	0.07	0.36	0.59
O	40.9	44.7	45.3
Ash	0.3	2.2	6.1
Volatile Matter	79.1	77.6	74.4
Fixed Carbon	12.8	12.4	12.6

Table II. Ash Composition- main components

Element	Loblolly Pine	Switchgrass	Cornstover
Ca	490	1790	1900
Fe	38	20	437
K	358	4980	8675
Mg	203	1540	1325

Not only the ash content, but also the ash composition differs among the biomass species. As Table II shows, ash composition differs greatly in the composition. Specifically, alkali (K), Ca, Mg, and Fe constitute major ash constituents which can affect the biomass characteristics during pyrolysis and gasification. It has been suggested that Alkali catalyzes char gasification while the catalytic role of other species (e.g., Ca, Mg, and Fe) is not clearly understood. In order to address this issue, we also undertook pyrolysis of avicel-derived char under similar conditions. Avicel does not contain any inorganics and would therefore be unreactive towards CO₂ and/or steam gasification. We can use avicel char to understand the role of different inorganic species by physical mixtures or wet impregnation of chars with the inorganics. The results will be presented briefly.

2. Evolution of Char Morphology

During the pyrolysis stage (300-600 °C), the biomass species lose 60-80% of initial mass which involves loss of free moisture and decomposition of hemi-cellulose, cellulose, and lignin. Various gases and tars species are evolved during this stage, leaving behind a char consisting primarily of carbon and ash. Figure 1 shows the evolution of pine char morphology in an entrained flow reactor at 5 bars and at a residence time of 4 sec.

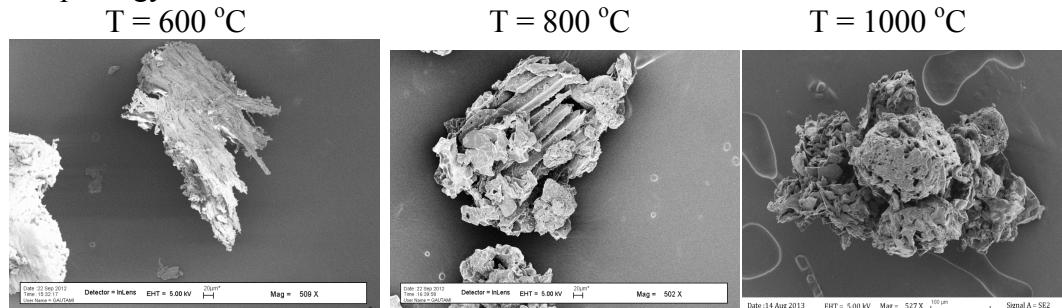


Figure 1. Effect of temperature on the morphology of pine during pyrolysis of pine at constant pressure (5 bars), and a residence time of 4 sec

It is clear that the char generated at 600 °C, 5 bar, and short residence time (4 sec) has morphology very similar to the starting biomass feed (pine). However, at higher temperature (800 °C), some melting of the biomass is observed. At higher temperature still (1000 °C), almost the entire biomass particles appears to have fused molten biomass features. Figure 2 shows the effect of pressure during pyrolysis at 600 °C and a residence time of 28 sec.



Figure 2. Effect of pressure on the char morphology during the pyrolysis of pine at a constant temperature of 600 °C and a residence time of 28 sec.

The effect is far more dramatic than ever seen in a low heating rate pyrolysis as seen in a TGA or a transient heating process. When a small particle (~200 µm) is injected into a heated chamber, the three biopolymers (cellulose, hemi-cellulose, and lignin) become liquid-like around 600 °C, while the decomposition of these biopolymers produces gases. This gives rise to balloon-like effect which makes the char particles hollow spheres. This can be seen most vividly in Figure 3. It should be noted that lower heating rates would start decomposition well before the biopolymers reach melting temperature. Thus a low heating rate char would have morphology similar to that of the starting biomass, albeit a hollow structure.

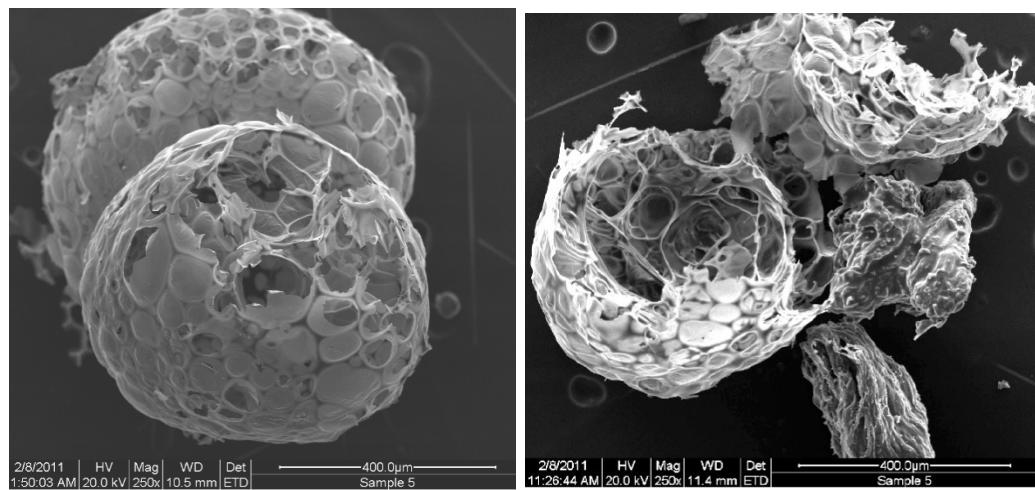


Figure 3. Morphology of pine char formed in a pressurized entrained flow reactor at 15 bars, 1000 °C, and a residence time of 28 sec. The broken particle shows the formation of gas-filled pockets inside the char particle.

3. Pyrolysis Gas Composition

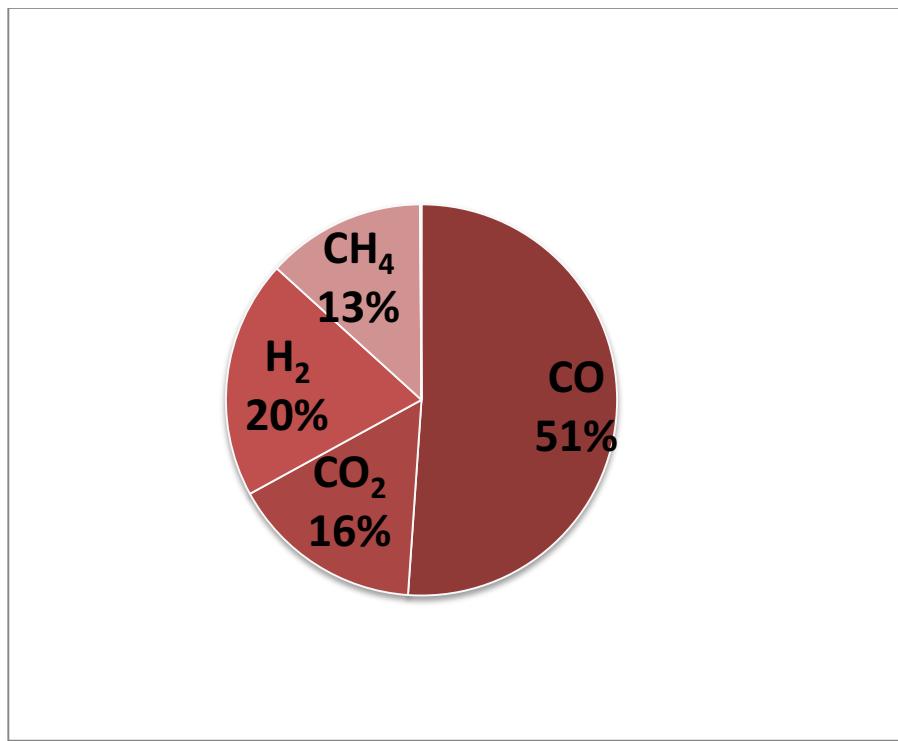


Figure 4. Major gases produced during the pine pyrolysis at high heating rates

Figure 4 shows the dominant gases formed during high heating rate pyrolysis of pine. Excluding water, there are four major constituents: CO, CO₂, H₂, and CH₄. These differ depending on the pyrolysis temperature, pressure and residence time. Complimentary PTGA studies were carried out which showed via FTIR and MS the evolution of various gas species during the heating step. Table III shows the gas composition as a function of pyrolysis conditions. Increasing temperature leads to the reduced formation of methane. It appears that methane might be the initial (primary) pyrolysis products but that it is transformed into CO and H₂ via water-gas shift reaction. We also notice the formation of C₂-C₄ hydrocarbons. The olefins appear to be the primary pyrolysis products which likely oligomerize at larger residence times to yield aromatic species. Also, at low temperatures, greater quantities of C₂-C₄ hydrocarbons are formed. At higher temperatures and residence times, the olefins participate in secondary pyrolysis reactions, leading to a variety of gaseous and possibly tar-like species.

Table III. Pyrolysis Gas composition at different pyrolysis conditions

Temperature °C	600			800			1000					
RT	40s			40s			1.7s	5s	5	10s	15	
Pressure bar	5	10	15	5	10	15	5	5	5	10	15	
Carbon Monoxide	44.79	39.52	39.44	41.21	41.41	37.43	46.10	45.49	61.03	70.76	65.29	
Carbon dioxide	16.58	17.17	17.68	16.93	15.26	17.7	12.69	13.03	12.07	5.29	5.89	
Hydrogen	9.73	17.23	17.4	24.52	31.32	29.07	19.65	18.71	21.9	22.42	25.98	
Methane	20.94	21.69	21.72	16.6	11.71	15.63	14.27	17.65	4.75	1.52	2.84	
Ethane	1.4	0.38	0.1				0.57	0.49				
Ethylene	5.65	3.78	3.43	0.52	0.26	0.16	5.17	3.98	0.1	0.03		
Acetylene	0.09	0.13	0.2	0.22	0.04	0	0.67	0.36	0.15			
Propane	0.03						0.01	0.00				
Propylene	0.65	0.06					0.61	0.21				
Butane							0.03					
1-Butene							0.23	0.08				
1,3- 1,3- 1,3-	0.14	0.04	0.03									

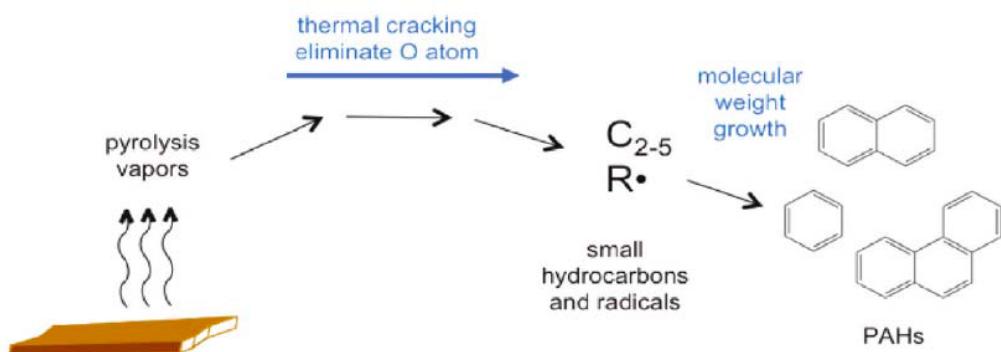


Figure 5. Formation of polyaromatic tars as secondary and tertiary pyrolysis products

Tars formation is also significantly affected by the pyrolysis conditions. Our work indicates the formation of primary, secondary, and tertiary tar species which have a significant role in char reactivity. The chars generated at different pyrolysis conditions differed greatly in their physical characteristics (morphology, BET surface area), but more importantly these chars also had greatly varying gasification reactivity as shown in Figure 6.

4. Gasification Reactivity

Figure 6 below shows the char gasification reactivity in pure CO₂ at 800 °C at 1 atm in a TGA. The conditions were chosen such that external mass and heat transfer effects were negligible.

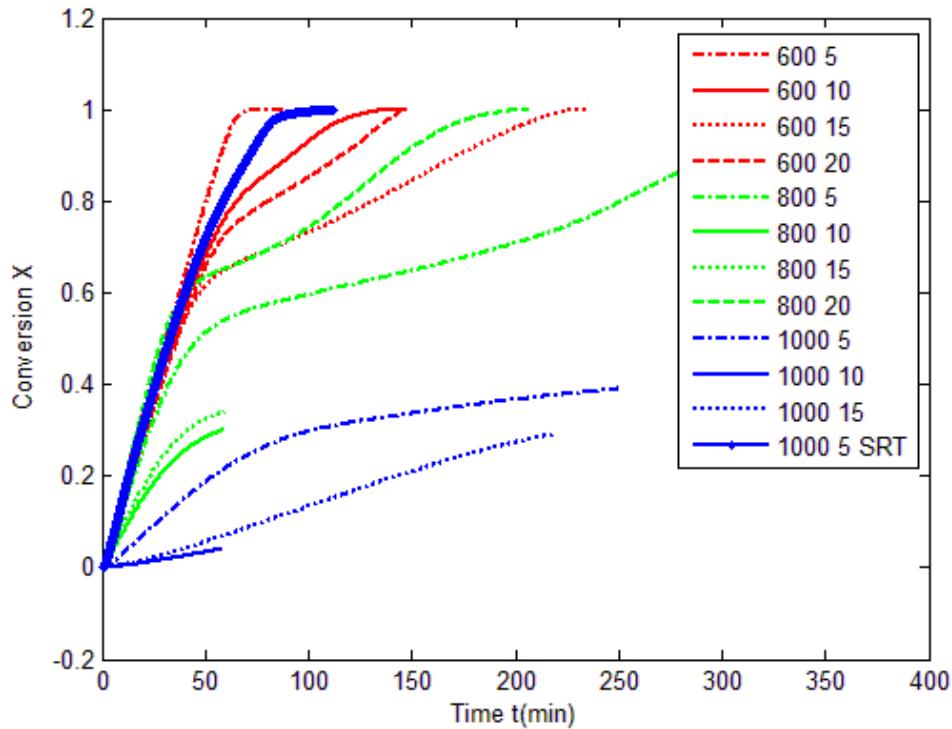


Figure 6. Effect of pyrolysis conditions on char gasification reactivity in pure CO₂ at 1 am and 800 °C.

The initial slope gives the reactivity of the char which has been well characterized. It is seen that the reactivity differs by more than an order of magnitude. The legends in the figure indicate temperature and pressure during the pyrolysis. In general, pyrolysis at higher temperatures and higher pressures lead to a low reactivity char. All chars shown in Figure 6 had been obtained with a residence time of 28 sec. The sole exception is the curve shown in bold blue color which appears to have the highest reactivity, in spite of being formed at 1000 °C. This particular char was produced as a short residence time (4 sec) pyrolysis. This suggests that higher temperature chars can be active but that their activity drops significantly at larger residence times. This is consistent with our model that olefins formed as primary pyrolysis products are trapped inside the bubbles formed at higher pressures and are converted to polyaromatic hydrocarbons (PAHs) which have much lower gasification reactivity. This is also supported by the XRD and Raman

spectroscopy results. Figure 7 shows the effect of pyrolysis conditions on the Raman results of chars formed.

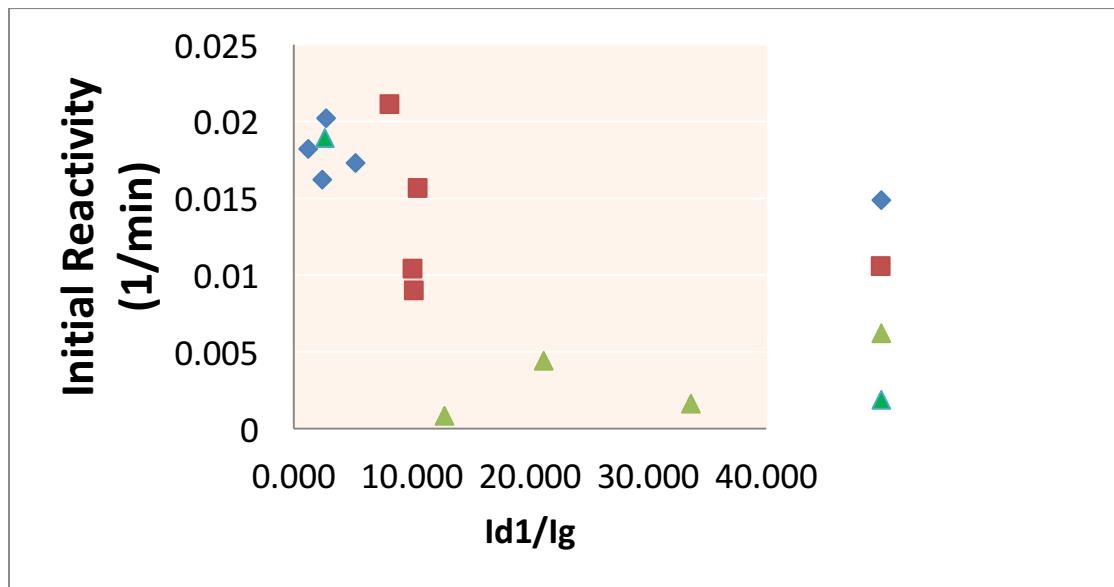


Figure 7. Raman Spectroscopic results of chars formed. The x-axis represents the ratio of graphitic char to amorphous char. Increasing ratio results in reduced reactivity. Blue diamonds - chars formed at 600 °C, green triangles- chars formed at 1000 °C. Red squares- chars formed at 800 °C. Blue triangle- short residence time char at 1000 °C.

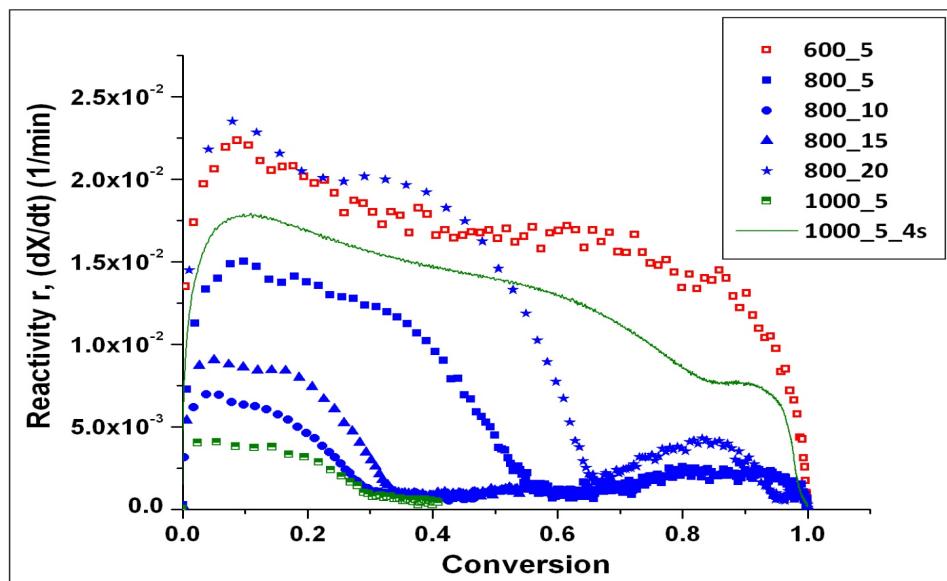


Figure 8. Reactivity of chars generated at different pyrolysis conditions in pure CO₂ at 1 atm and 800 °C.

Figure 8 shows the char reactivity over the entire range of conversions. The results are the same as those shown in Figure 6. These results suggest that even when initial char reactivity is high, the subsequent reactivity may drop off sharply due to a large presence of graphitic char. Therefore, to achieve good carbon conversion efficiency, one must take efforts to minimize the formation of graphitic char. **These are short residence time pyrolysis, low temperatures and low pressures.**

Langmuir-Hinshelwood Gasification Kinetics

The gasification kinetics of one specific char was measured in a PTGA in the presence of steam and CO₂ at transport-free conditions at 800 °C and 20 bars. The following L-H kinetic rate expression was fitted to the data.

$$r_c = \frac{k_1 P_{CO_2} + k'_1 P_{H_2O}}{1 + k_2 P_{CO} + k_3 P_{H_2O} + k_4 P_{CO_2} + k_5 P_{H_2} + k_6 P_{CH_4}}$$

The rate constants for the above expression are listed in the below table:

Constant at 800°C	w/o H ₂ O	all
k ₁ , min ⁻¹	0.017	0.018
k _{1'} , min ⁻¹		0.12
K ₂ , bar ⁻¹	6.29	6.39
K ₃ , bar ⁻¹		0.00
K ₄ , bar ⁻¹	0.15	0.19
K ₅ , bar ⁻¹	60.5	87.9

The quality of the fit can be seen in Figure 9. It validates the quality of the mathematical model. The most noteworthy item from these data is the value of K₅ which represents the

inhibition effect associated with hydrogen. It is generally known that the presence of CO (one of the gasification products) reduces char gasification rate. However, the magnitude of K_2 is an order of magnitude smaller than that for K_5 . Thus hydrogen product inhibition would play a more important role than the CO inhibition. For future study, we would recommend exploring the role of higher temperatures on inhibition. However, the transport effects will then come into play.

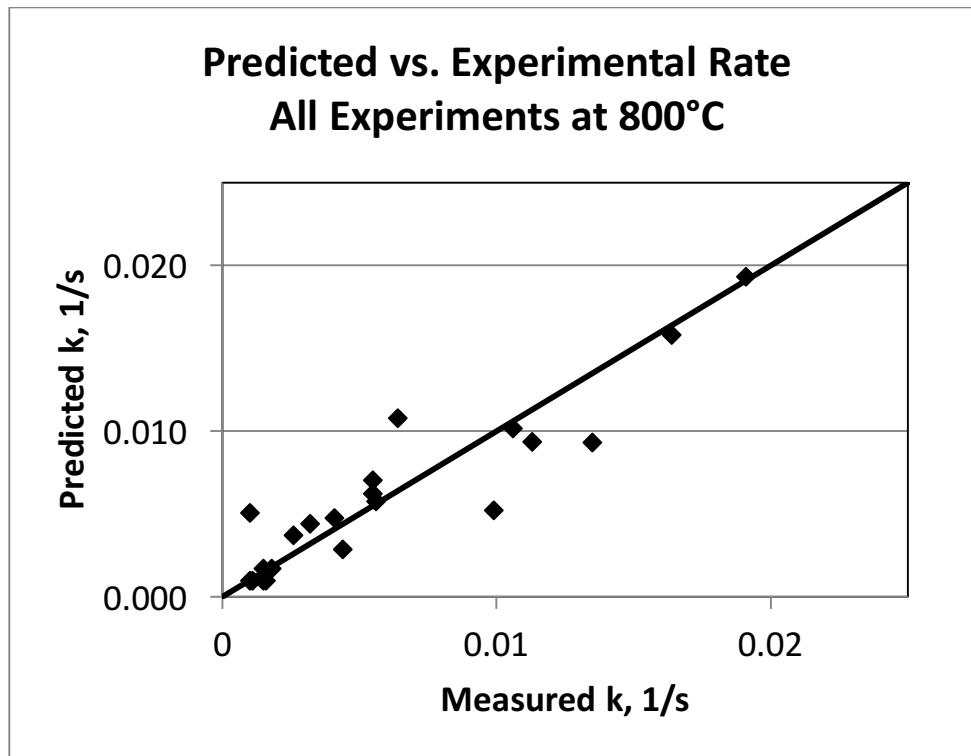


Figure 9. A comparison of observed vs. predicted char gasification rates

5. Catalytic Role of Inorganic Species in Char Gasification

We have done a more detailed quantitative evaluation of different inorganic species. Avicel char was generated in an entrained flow pyrolysis unit by pyrolyzing at 900 °C and 5 bars. Avicel is a form of pure cellulose and is not supposed to contain any inorganics. It is envisaged that the char generated from avicel can serve as a baseline char having zero or very little gasification activity. One can then add different inorganic species to examine the catalytic role these species play in char gasification. Figure 11 below shows the results obtained using different inorganics: MgO, CaO, Al₂O₃, and K₂CO₃. In all data shown below, the mixture contained 10 wt% inorganic – 90 wt% avicel char. Gasification runs were carried out at 900 °C in pure CO₂. The catalytic effect of inorganics decreases in the following order: K₂CO₃> CaO>MgO>Al₂O₃. The effect of Fe₂O₃ was determined to be negligible. Figure 10 below shows the effect of K₂CO₃ and CaO addition to avicel char on its gasification reactivity at 900 °C.

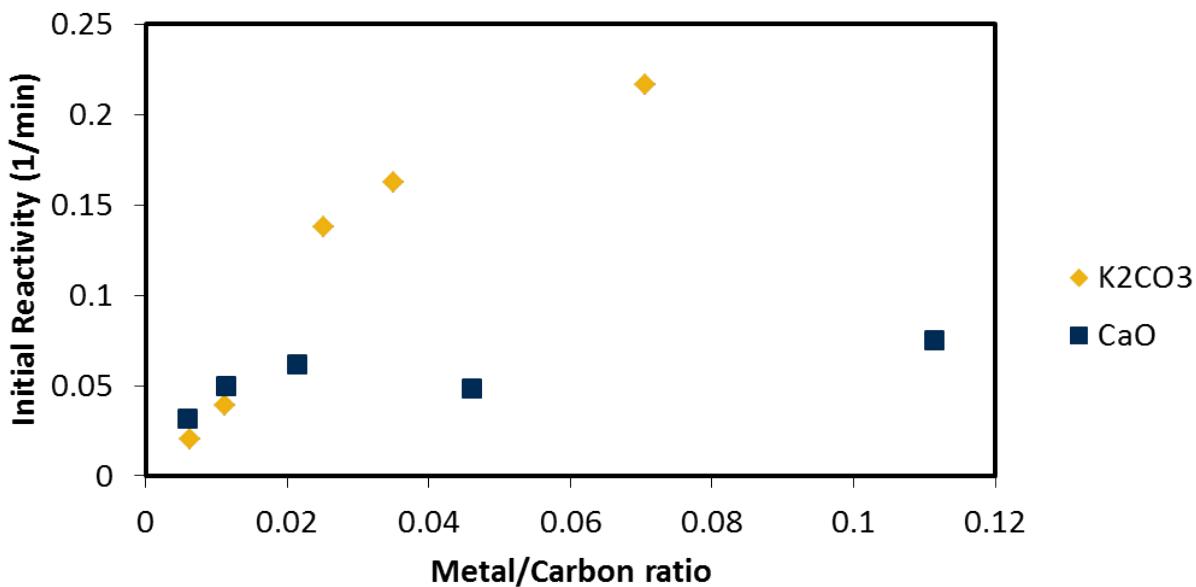


Figure 10. Catalytic effect of inorganic salts on avicel char gasification reactivity at 900 °C

A number of observations can be made from the results shown in Figure 10. K₂CO₃ reduces to K₂O at ~ 900 °C which is then reduced to metallic K during gasification in the presence of carbon. Metallic potassium (K) migrates inside carbon matrix, enhancing its gasification activity. In contrast, CaO does not reduce to metallic Ca at the gasification temperature. In fact, CaO is known to sinter at increasing conversion, which would cause it to lose its effectiveness as catalyst. It also points to the fact that as char is being gasified, its proportional ash content increases, resulting in increasing gasification activity.

The effect of adding 10 wt% inorganics on avicel char gasification reactivity is shown below in Figure 11. Avicel char has very low gasification reactivity, due to its low (or zero) inorganic content. Adding MgO or Al₂O₃ increases its reactivity, but it is still low. CaO and K₂CO₃ addition appears to cause the biggest impact on the gasification reactivity.

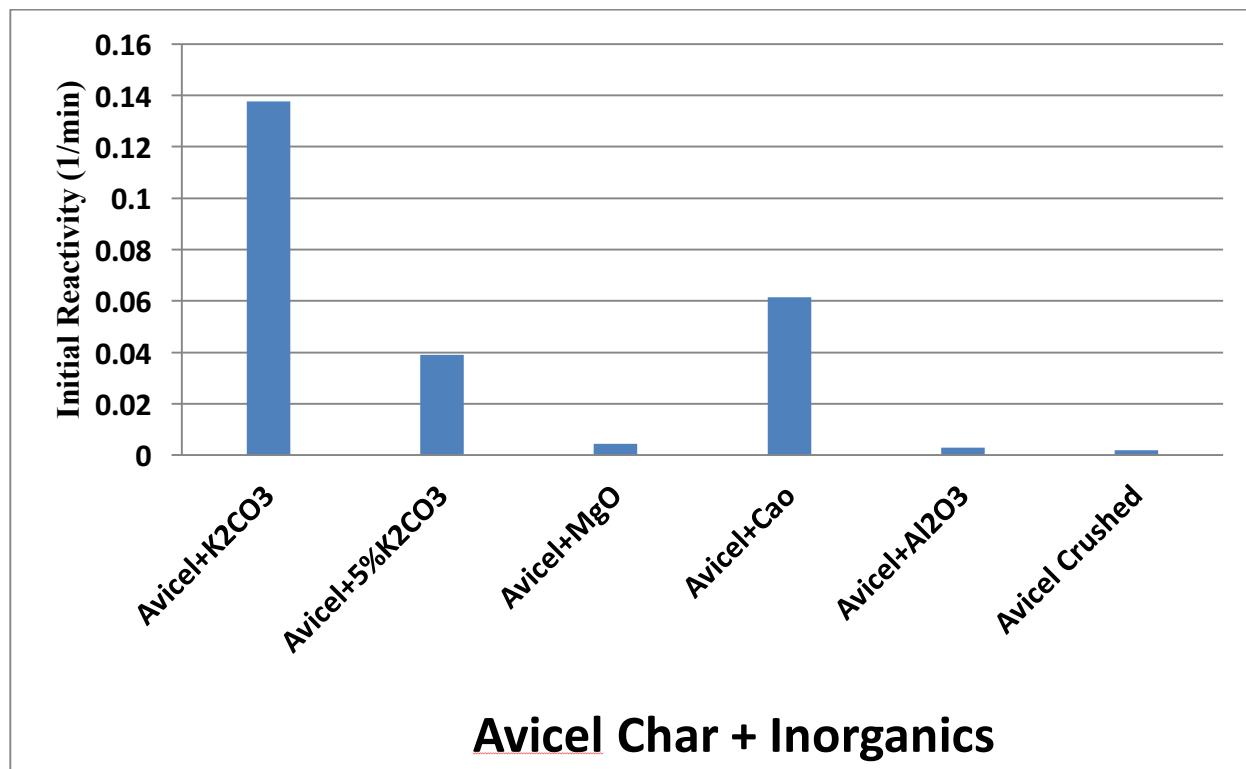


Figure 11. Reactivity of avicel char blended with 10 wt% inorganics (except where noted)