September 4, 2014

Laboratory Gasification Memo
Enthalpy Experiments

Summary

In order to obtain an understanding if the main driving force for conversion of biomass to syngas is driven by residence time or heat transfer limitations, an experimental matrix was designed to test different levels of space time and the maximum possible enthalpy change of the reactants. Experimental results shine light on fundamental driving forces for carbon conversion, and tar and methane production in the laboratory gasification system. It was found that the total enthalpy load on the reactor was the primary driving force for carbon conversion, and lower loads led to higher conversions. Differing residence times did not give expected results for carbon conversion if they were found to be statistically significant at all. Finally, both residence time and enthalpy load are found to be significant factors in the production of methane and tars in the laboratory system.

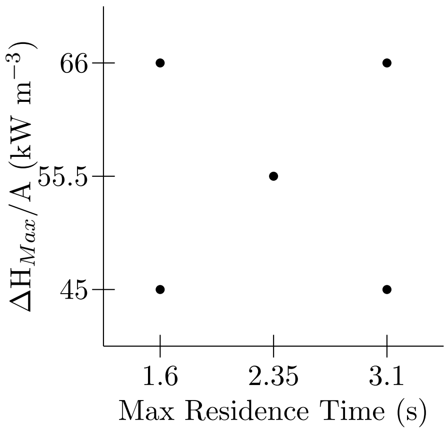

Figure 1: Two factorial experimental matrix used to vary maximum residence time and maximum ΔH between experiments.

Experimental Methods

Design of Experiment

It was desired to create a two factorial matrix with a center point with the two axes representing maximum residence time ($t_{res,max}$) and maximum enthalpy change (ΔH_{max}). The matrix can be seen in Figure 1. Partial pressure of steam and partial pressure of CO_2 was held constant for these experiments at 7 psi and 30 psi, respectively. These values were chosen because a large number of previous gasification experiments had partial pressures of CO_2 and H_2O near these values.

Because of the large number of possible set points in the laboratory gasifier system that would effect both the space time and maximum enthalpy simultaneously, it would have been difficult to manually design this experimental matrix. To aid in the design, a large number of potential gasifier experiments were simulated using Sundrop Fuels' gasifier analysis software suite. First, a flow rate of CO_2 was randomly assigned using a uniform distribution with a minimum possible flow rate of 3 SLPM and a maximum flow rate of 6.6 SLPM. The partial pressure of CO_2 was set at 7 psi, and the appropriate flow rate of steam to lead to a partial pressure of 30 psi was found with Equation 1.

The flow rate of Argon was set at 2 SLPM for all experiments. Biomass flow rate was randomized uniformly between 2 lbs/hr and 4 lbs/hr. The total flow rate of entrainment gas was set to be 6 SLPM for every 1 lb/hr of biomass, which was found to be a good minimum entrainment flow rate in previous experiments using the brush feeder. The remainder of the entrainment gas which isn't CO_2 is nitrogen.

Steam temperature is set at 500 °C, and makeup nitrogen is uniformly randomized between 0 and 20 SLPM. The total pressure is found using the partial pressure of steam and the total flow rate of gas into the system (Equation 2). The maximum residence time and the maximum enthalpy change were calculated for each simulated run using Sundrop Fuel's gasifier analysis software. Experiments which could not be run due to system limitations were removed from the potential runs, and enthalpy and maximum residence time targets were chosen to maximize the change in each measure. Set points for all experiments are outlined in Appendix E.

$$\dot{n}_{H_2O} = \dot{n}_{CO_2} \times \frac{P_{H_2O}}{P_{CO_2}} \tag{1}$$

$$P_{tot} = P_{H_2O} \times \frac{\dot{n}_{tot}}{\dot{n}_{H_2O}} \tag{2}$$

Calculations

Two measures of carbon conversion are discussed in this memo. The first is the fraction of carbon in the biomass which is converted to either CO or CO_2, as these are the two species which are the precursor to synthetic liquid products in the planned commercial process. This measure is refered to as carbon yield, although it has been referred to in the past as good conversion, and is given in Equation 3.

$$Y_{CO+CO_2} = \frac{\dot{n}_{CO,out} + \dot{n}_{CO_2,out} - \dot{n}_{CO_2,in}}{\dot{n}_{C_{biomass},in}} \tag{3}$$

The second measure is carbon release, which has been referred to in the past as total conversion. This was calculated using Equation 4 and is a representation of the fraction of carbon in the biomass which is converted to any gaseous specie detected by the mass spectrometer.

$$X_C = \frac{\dot{n}_{C_{gas},out} - \dot{n}_{CO_2,in}}{\dot{n}_{C_{biomass},in}} \tag{4}$$

Tar loading is a measure of the mass of tars detected by the mass spectrometer (C_6H_6, C_7H_8, and $C_{10}H_8$) in a standard volume of product gas. This value was calculated using Equation 5.

$$C_{tar} = \frac{\dot{m}_{C_6H_6} + \dot{m}_{C_7H_8} + \dot{m}_{C_{10}H_8}}{\dot{V}(\frac{P}{P_{std}})(\frac{T_{std}}{T})} \tag{5}$$

Finally, the last measure discussed in this memo is methane yield. It is a representation of the fraction of carbon in the biomass which is converted to methane, and it was calculated using Equation 6.

$$Y_{CH_4} = \frac{\dot{n}_{CH_4}}{\dot{n}_{C_{biomass},in}} \tag{6}$$

Results and Discussion

Because only inlet conditions of the reactants were needed to calculate the maximum residence time, the experimental matrix was designed based on this calculation. Once experiments were completed and outlet conditions were known, a minimum residence time could be calculated assuming all products reached the wall temperature of the reactor and reacted fully immediately upon entering the reactor. In reality, the actual residence time was somewhere between these boundaries, and the actual residence time would be very difficult to estimate with the data known from the experiments.

Plotted results are shown in Appendices A, B, C, and D for carbon yield, carbon release, tar loading, and methane yield using both the maximum and minimum residence times for visualization purposes. ANOVA results are shown using only minimum residence time. While the magnitude of the effects may be slightly different when using either minimum or maximum residence time, the time chosen for analysis does not change which factors are shown to be statistically significant when using ANOVA.

Carbon Yield

Carbon yield results are plotted in Figures 2, 3, 4, and 5 in Appendix A. ANOVA results are given in Table 1, and factors which had a statistically significant effect on carbon yield are highlighted in red. At 1350 °C, minimum residence time was not statistically significant while $\Delta H_{Max}/A$ was. Both minimum residence time and $\Delta H_{Max}/A$ were statistically signficant at 1450 °C. However, as shown in the aforementioned plots, higher residence times led to lower carbon yields, if there was an effect. Since this is the reverse of what would be expected, it's possible that the effect did not exist, or another factor was correlated with the changing residence times that is causing the difference in calculated carbon yields. Fur-

Table 1: ANOVA results on effects of designed experimental campaign for carbon yield.

Effect	Prob <F 1350 °C	Prob <F 1450 °C
$t_{res,min}$	0.1845	0.0059
$\Delta H_{Max}/A$	<0.0001	0.0002
$t_{res,min} \times \Delta H_{Max}/A$	0.5060	0.9646

Table 2: ANOVA results on effects of designed experimental campaign for carbon release.

Effect	Prob <F 1350 °C	Prob <F 1450 °C
$t_{res,min}$	0.1175	0.0017
$\Delta H_{Max}/A$	0.0005	0.0002
$t_{res,min} \times \Delta H_{Max}/A$	0.8289	0.7615

ther tests may be held in the future holding different factors constant to see if the effect seen goes away at 1450 °C.

Carbon Release

Carbon release results are plotted in Figures 6, 7, 8, and 9 in Appendix B. Results from ANOVA, shown in Table 2 reflected what was seen in carbon yield measurements. The total maximum enthalpy load was a significant factor in the carbon release at both 1450 °C and 1350 °C. Again, while minimum residence time was statistically significant at 1450 °C, longer residence times actually gave lower conversions. Since this result is the opposite of what should be expected for longer residence times, further tests may be completed in the future to see if some other factor correlated with the changing residence times was causing the apparent dependency of conversion on residence time.

Tar Loading

Figures 10, 11, 12, and 13 in Appendix C show the results for tar loading values from each experiment in the campaign. Longer residence times and lower enthalpy loads appear to lead to lower tars at 1350 °C. ANOVA results shown

Table 3: ANOVA results on effects of designed experimental campaign for tar loading.

Effect	Prob <F 1350 °C	Prob <F 1450 °C
$t_{res,min}$	<0.0001	0.0654
$\Delta H_{Max}/A$	0.0015	0.8029
$t_{res,min} \times \Delta H_{Max}/A$	0.0002	0.2309

in Table 3 show that both residence time and $\Delta H_{Max}/A$ have statistically significant effects on the amount of tars produced at 1350 °C, but not at 1450 °C. This is similar to past results at 1450 °C where the tar levels are on the order of magnitude of variance between runs, so conclusions about difference in tar levels cannot be made.

It is important to note that residence time had a significant effect on tar loading at 1350 °C, but it did not have a significant effect on conversion measures at this temperature. It is possible that the actual temperature of the gaseous products leaving the reactor is at a temperature where there are still some kinetic limitations on tar cracking reactions, but the temperature is high enough where the primary solids pyrolysis reactions happen extremely quickly. Increasing the heat transfer to the reactants, especially at the bottom of the reactor where fewer solids exist to efficiently transfer radiation energy from the walls of the reactor, may increase the outlet gas temperature to a point where these cracking reactions proceed extremely quickly and the dependence in residence time may vanish.

Methane Yield

Methane yield showed similar results as tar loading. Results are shown in Figures 14, 15, 16, and 17 in Appendix D. ANOVA results, shown in Table 4, show that both residence time and $\Delta H_{Max}/A$ are statistically significant for methane yield at 1350 °C as well as 1450 °C. Longer space times and lower enthalpy loads lead to lower methane yields at both temperatures.

Like with tar loading, it's possible that the temperatures that the product gases are reaching are still at a low enough temperature where

Table 4: ANOVA results on effects of designed experimental campaign for methane yield.

Effect	Prob <F	
	1350 °C	1450 °C
$t_{res,min}$	<0.0001	0.0001
$\Delta H_{Max}/A$	<0.0001	0.0065
$t_{res,min} \times \Delta H_{Max}/A$	0.0009	0.1305

methane reforming is kinetically limited. Increasing heat transfer in the reactor to the gas phase near the exit may raise the temperature of these gases to a point where methane reforming happens very rapidly and the dependency on space time may go away. Further tests will need to be completed in the future to see if this is the case.

Conclusion

Experiments showed that residence time may influence carbon conversions much less than previously thought. While residence time has a statistically significant effect on carbon yield and carbon release at 1450 °C, the effect is opposite of what has been observed in the past and may be due to another factor correlated with residence time in the experimental design. There is no statistically significant effect of residence time on either measure of conversion at 1350 °C. Enthalpy load, on the other hand, has a significant effect on carbon conversion at both temperatures.

Residence time did, however, have an effect on tar loading at 1350 °C and methane yield at both 1350 °C and 1450 °C. Longer times led to lower amount of the undesired products. Effects that enthalpy load had on tar and methane production mirrored those displayed by residence time.

Future experiments should be completed which will hold different factors constant throughout the experimental campaign. Additionally, the conversions seen for given enthalpy loads are lower than previous gasification experiments. The biomass used in these experiments is from a different production run. Experiments will be completed in the near future that repeat previous experimental set points with the new biomass to compare the results with old biomass. If results come back with different conversions, then old biomass will be used under the same conditions to see if there has been a change in the system recently.

A Carbon Yield Plots

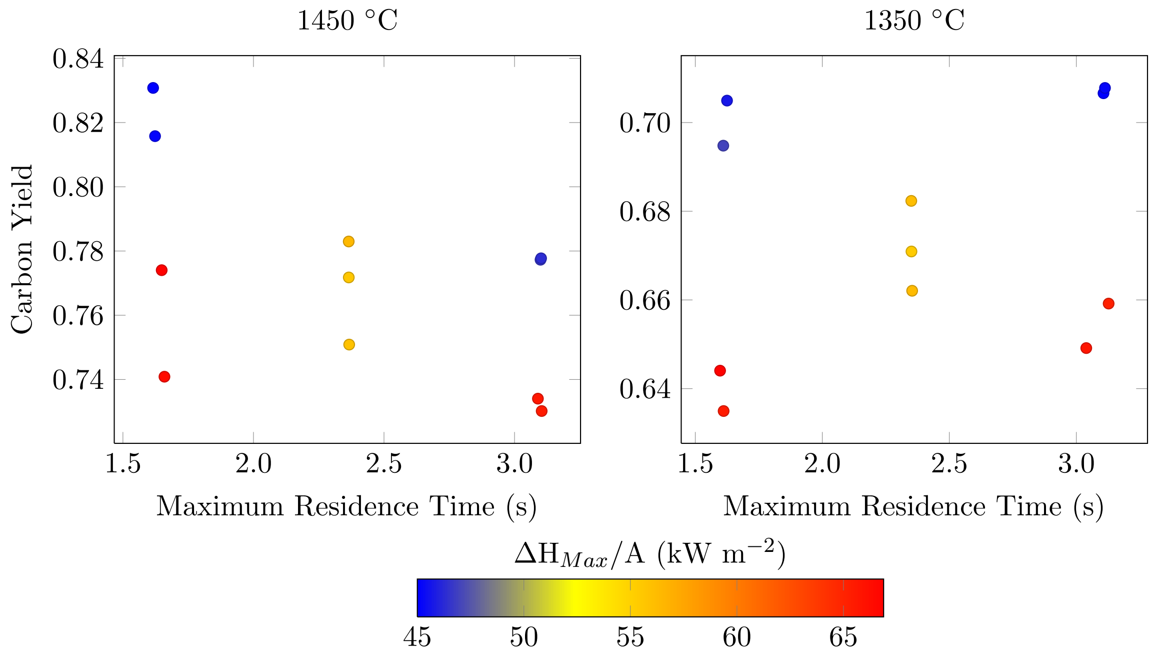

Figure 2: Results for carbon yield plotted against maximum residence time and colored by enthalpy load. At 1450 °C, longer space times actually lead to lower conversions for similar enthalpy loads. At 1350 °C, the difference in conversions at different space times but similar enthalpy loads is close to the variance between replicates, and ANOVA results show that residence time has no effect on carbon yield.

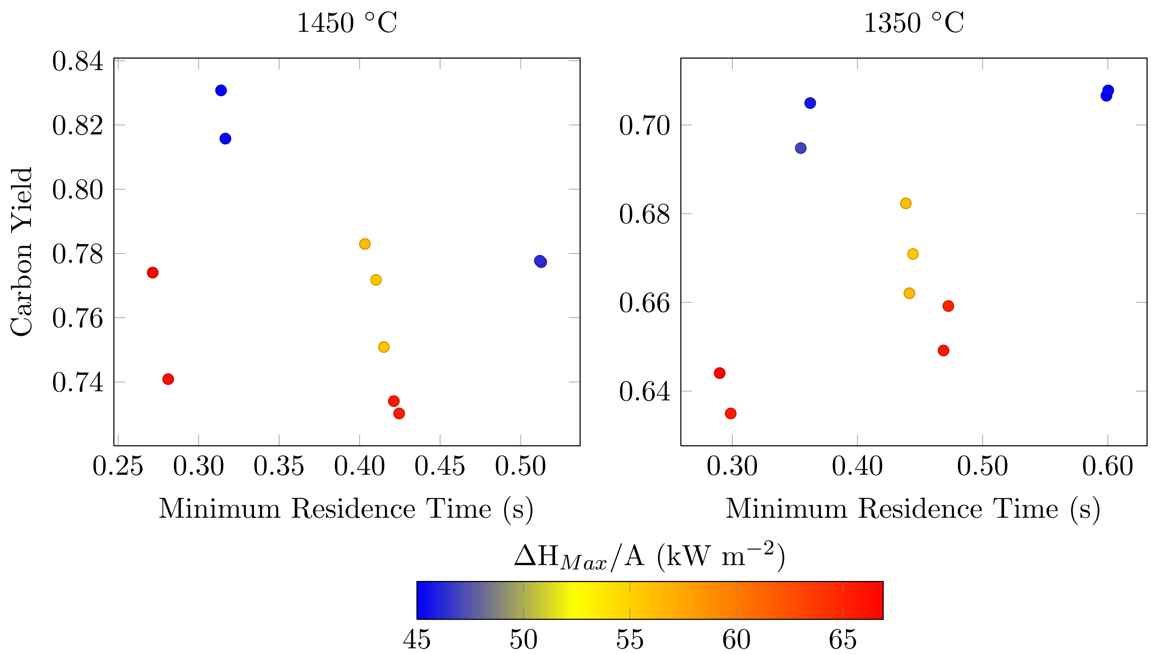

Figure 3: Carbon yield is plotted against minimum residence time rather than maximum residence time. Although data points are shifted across the x-axis relative to each other, the same conclusions are reached when looking at minimum residence time rather than maximum residence time.

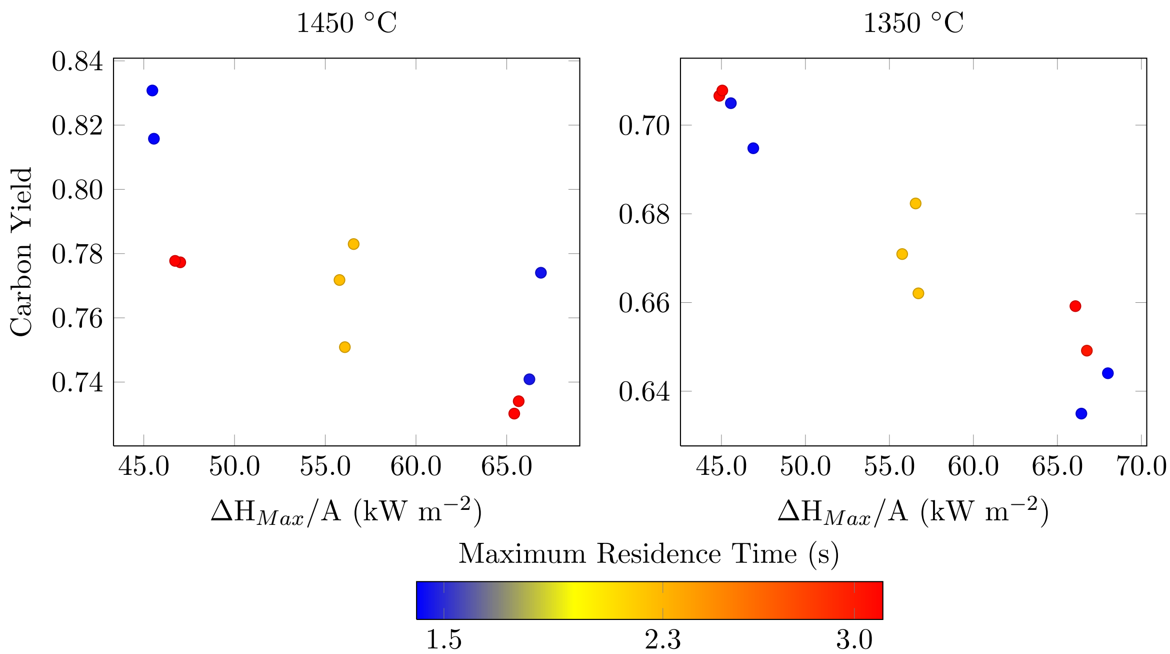

Figure 4: Here, carbon yield is plotted against $\Delta H_{Max}/A$. At 1450 °C, it appears as though lower residence times lead to higher conversions, which is counter-intuitive. At 1350 °C, the conversions at different residence times collapse onto each other, and it is easy to see the lack of effect that residence time has on carbon yield.

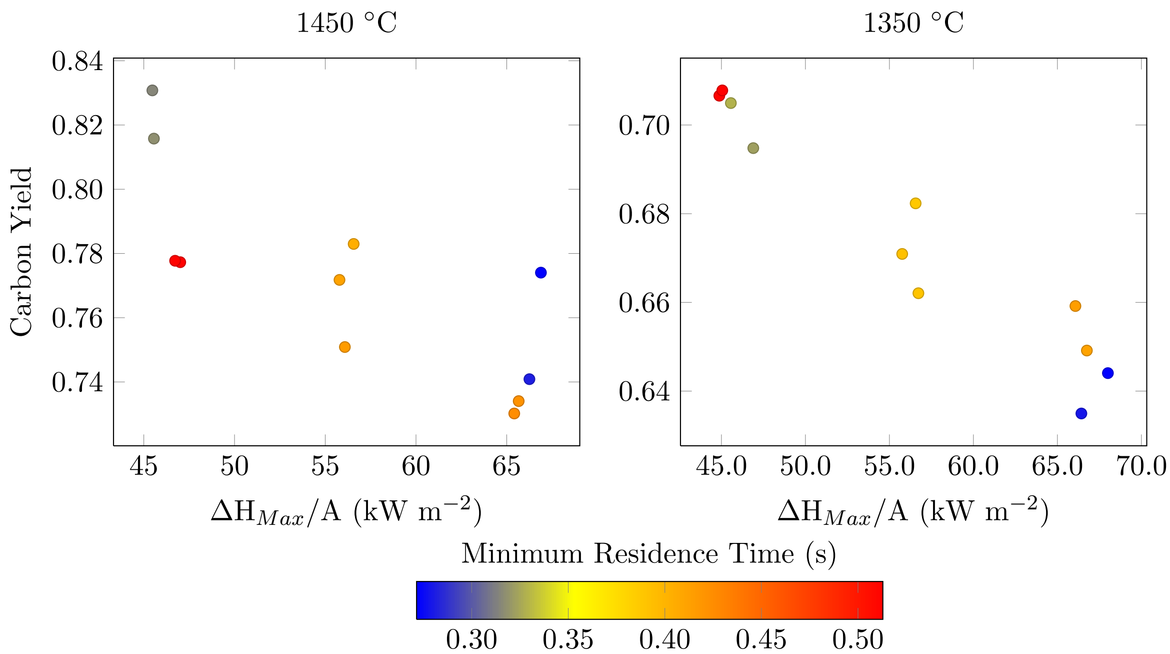

Figure 5: Carbon yield is plotted against $\Delta H_{Max}/A$ and colored according to minimum residence time. Again, the same conclusions are met no matter if minimum or maximum residence time is used for analysis.

B Carbon Release Plots

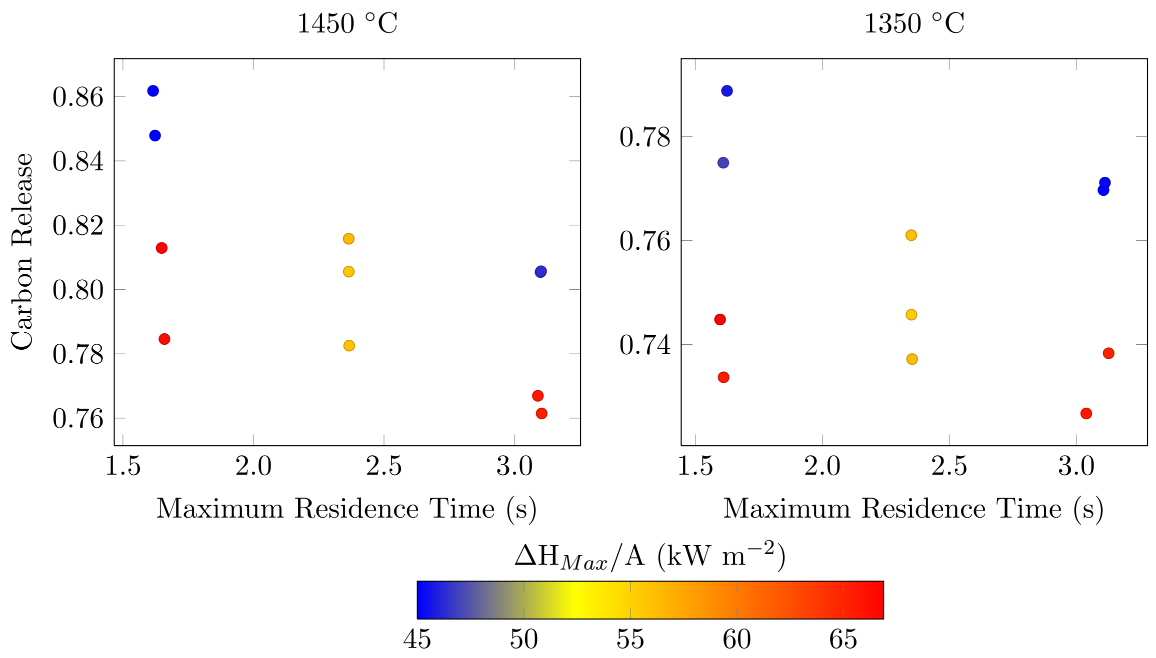

Figure 6: Carbon release results show the same trends as carbon yield, but the difference in carbon release for similar residence times and different enthalpy loads are slightly larger than they were for carbon yield. At 1450 °C, maximum residence time shows a negative effect on conversion and has no effect on conversion at 1350 °C.

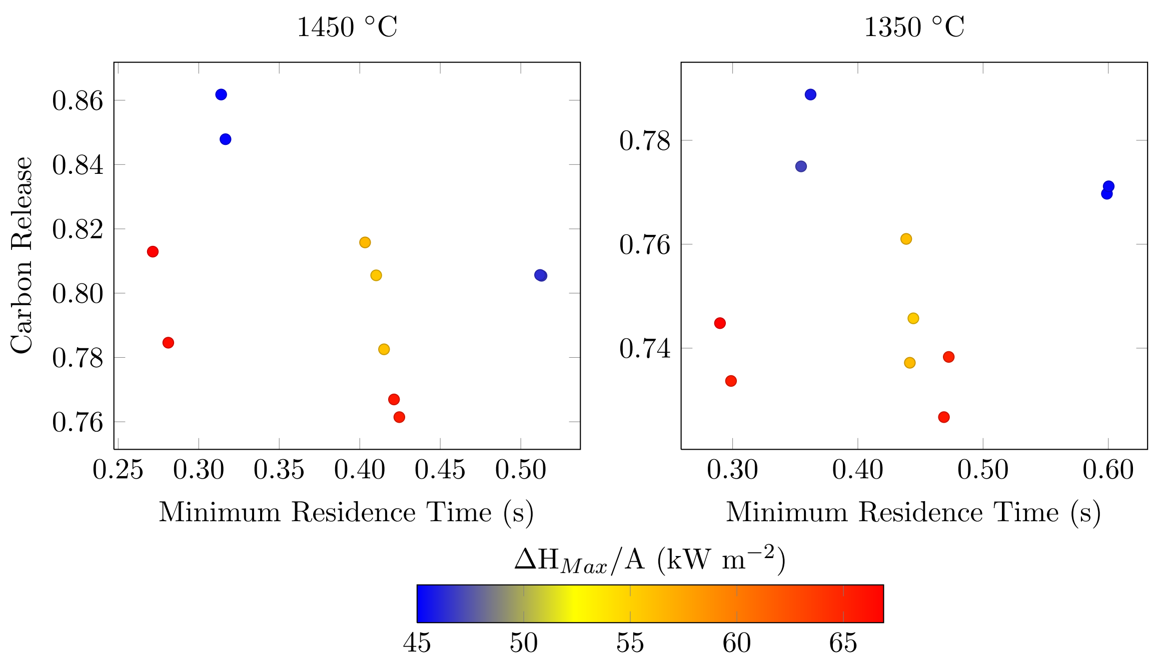

Figure 7: Carbon release versus minimum residence time colored by enthalpy load.

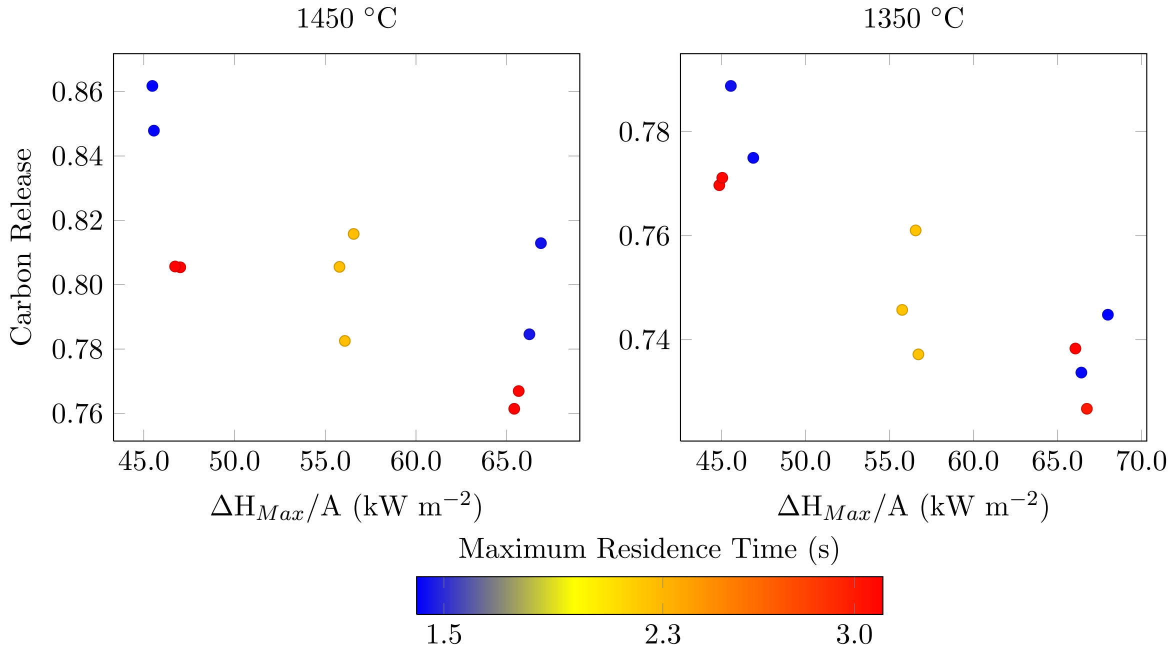

Figure 8: Carbon release plotted against enthalpy load clearly shows dependence that carbon release has on $\Delta H_{Max}/A$ at both temperatures.

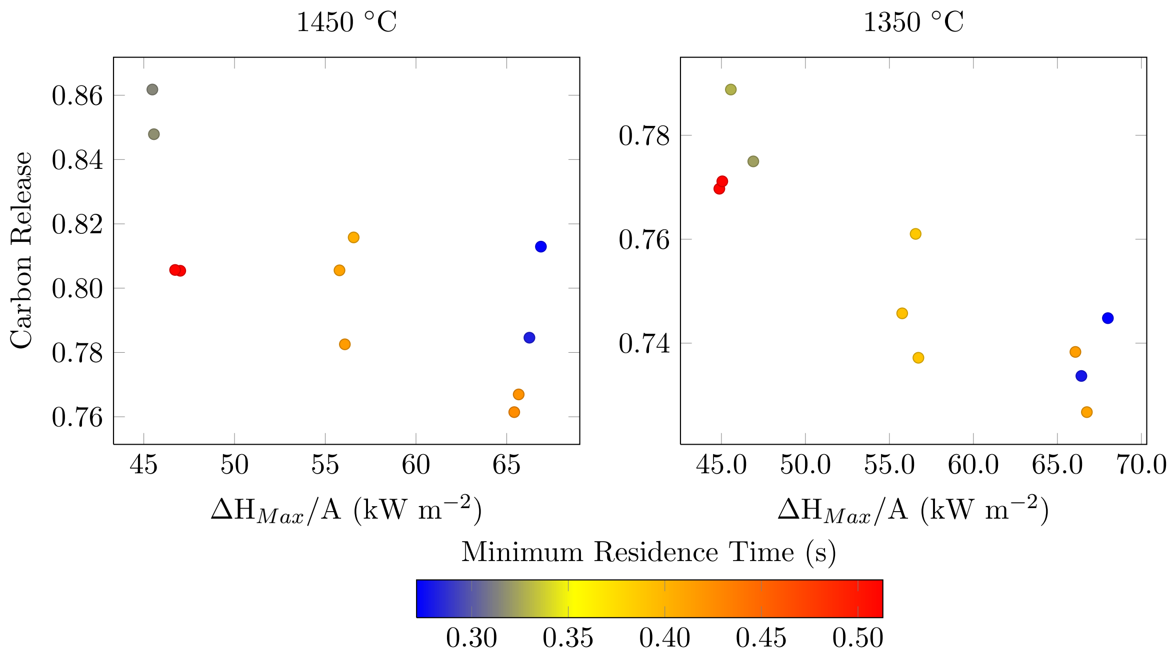

Figure 9: Carbon release versus $\Delta H_{Max}/A$ colored according to minimum residence time.

C Tar Loading Plots

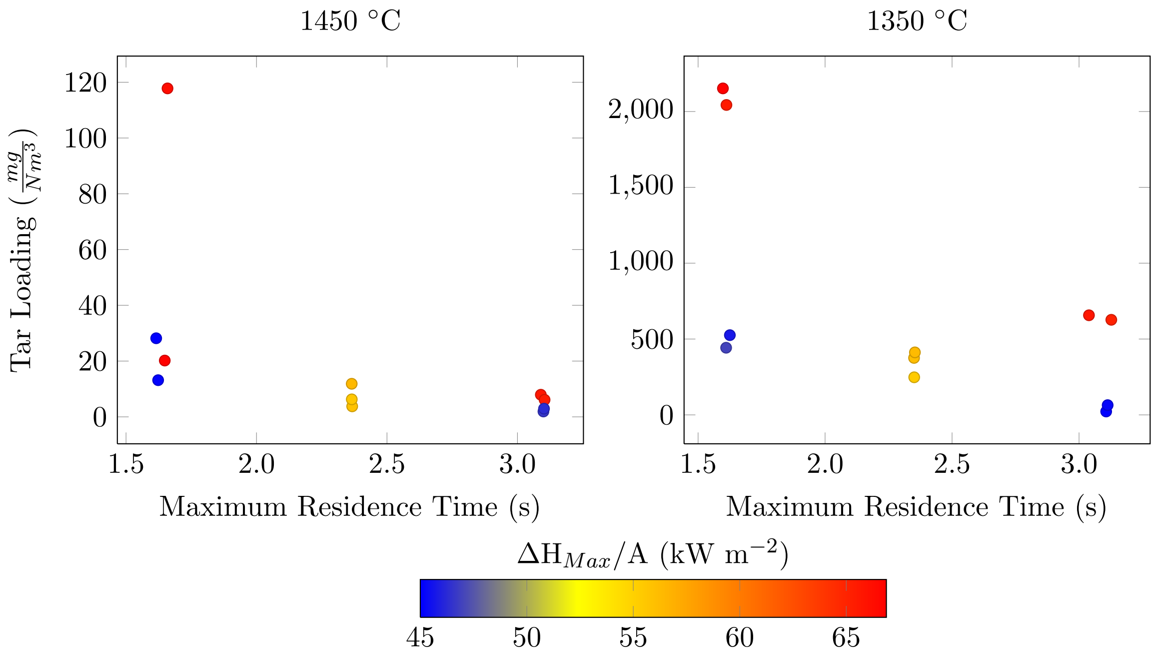

Figure 10: Tar loading results plotted against maximum residence time. Tar levels at 1450 °C are too low to see any effects that residence time or enthalpy load may have on tar make. At 1350 °C, there are effects from both factors. Lower tar loads are a result of longer space times and lower enthalpy loads.

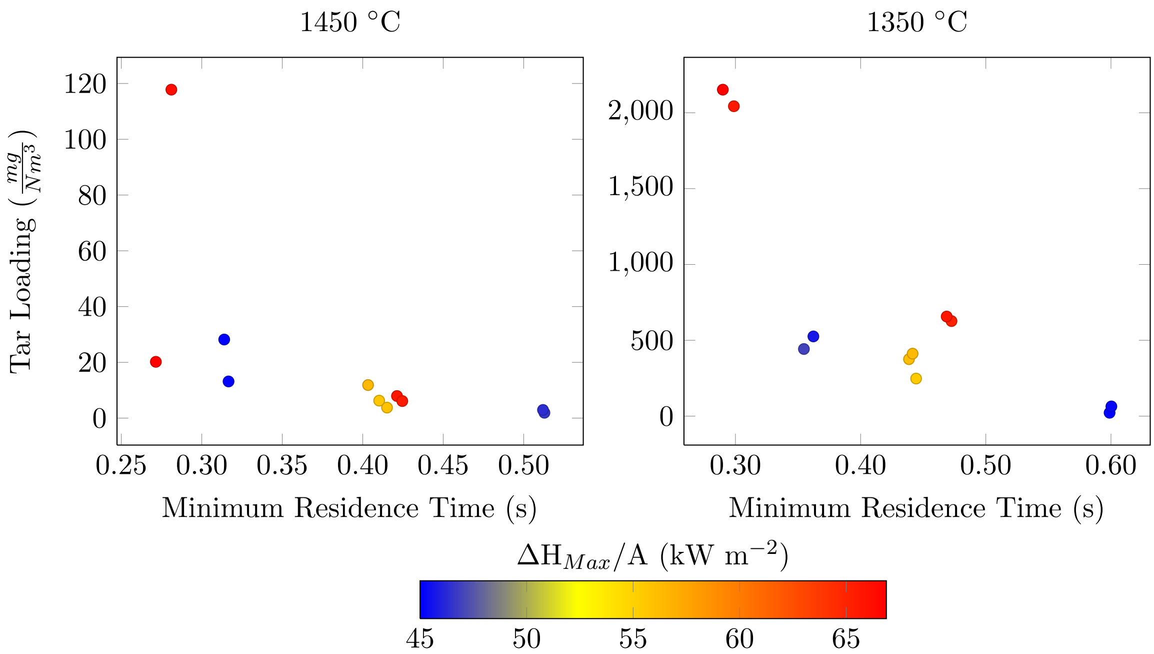

Figure 11: Tar loading versus minimum residence time colored by enthalpy load.

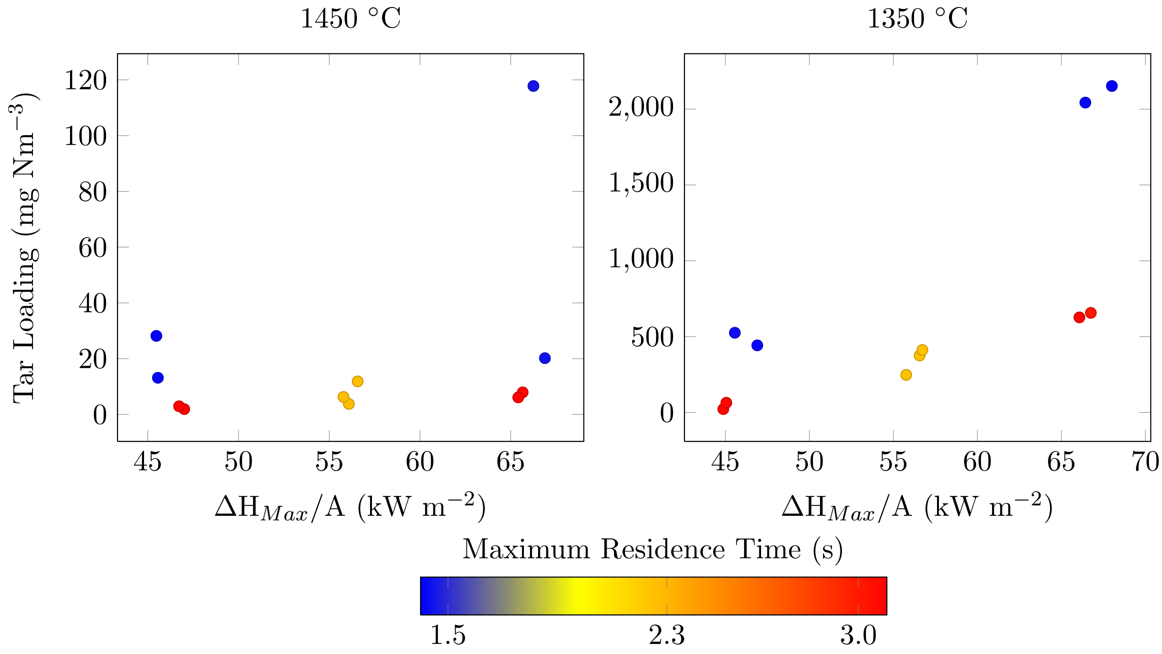

Figure 12: Tar loading versus enthalpy load colored according to maximum residence time.

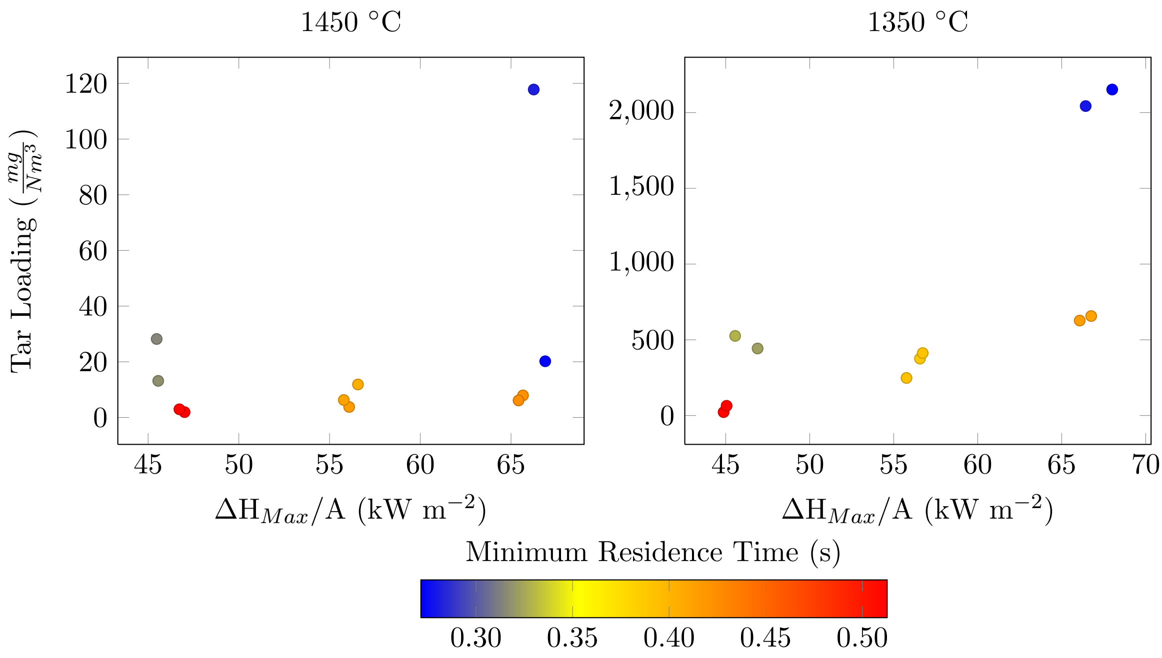

Figure 13: Tar loading plotted against $\Delta H_{Max}/A$ and colored by minimum residence time.

D Methane Yield Plots

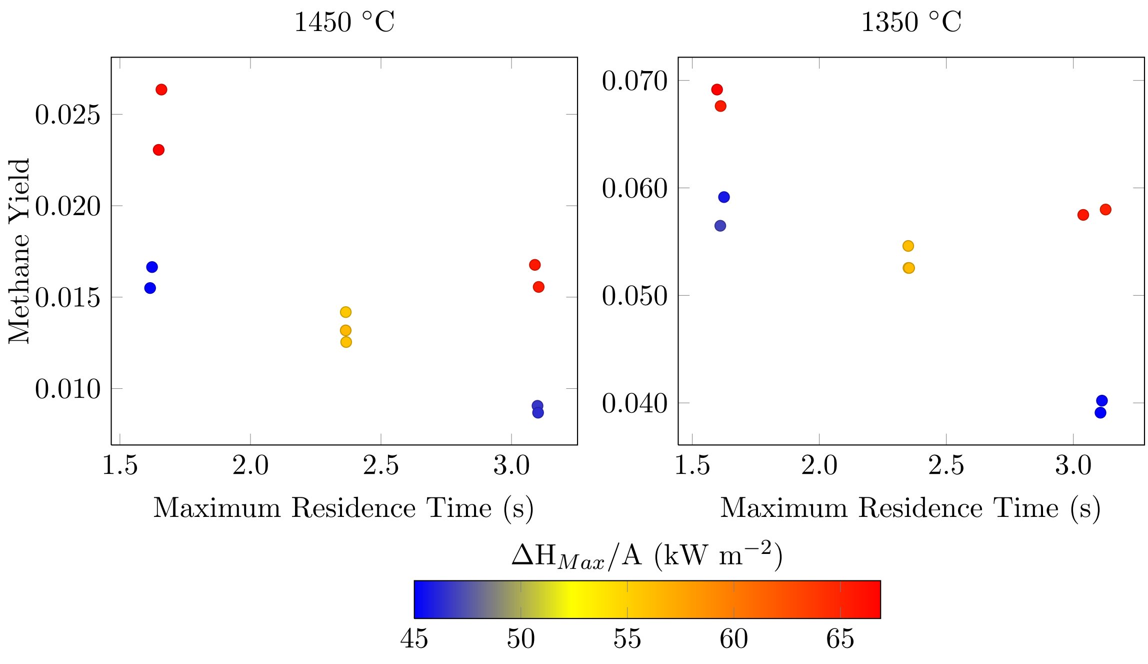

Figure 14: Blah blah blah blah SDPFOICJPFOIJD

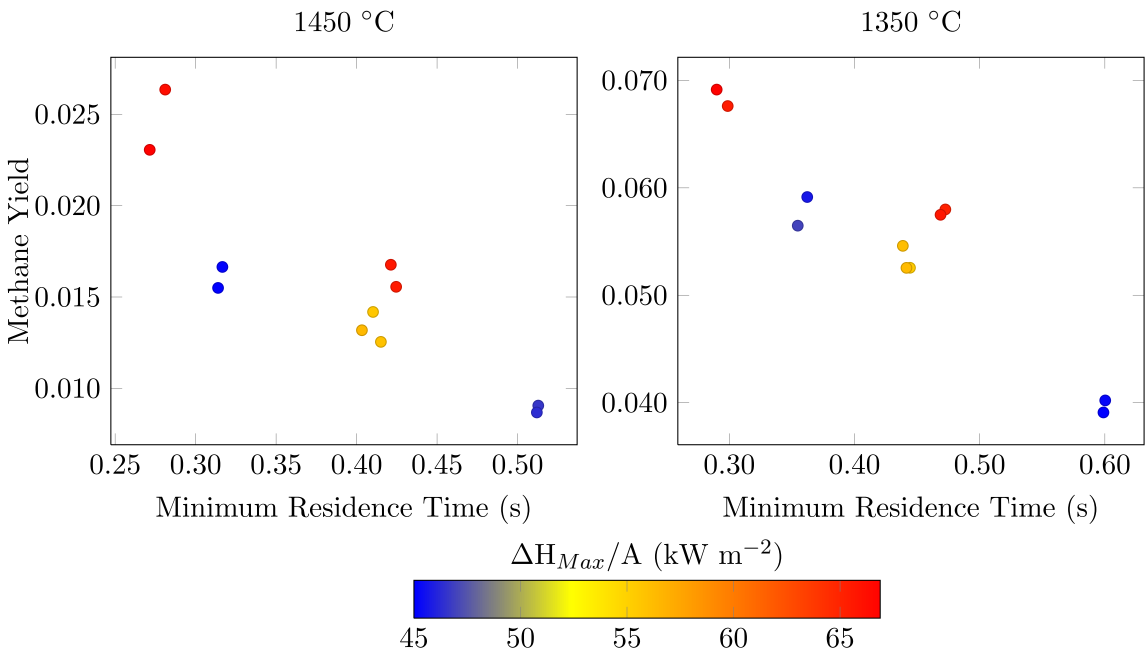

Figure 15: Blah blah blah blah SDPFOICJPFOIJD

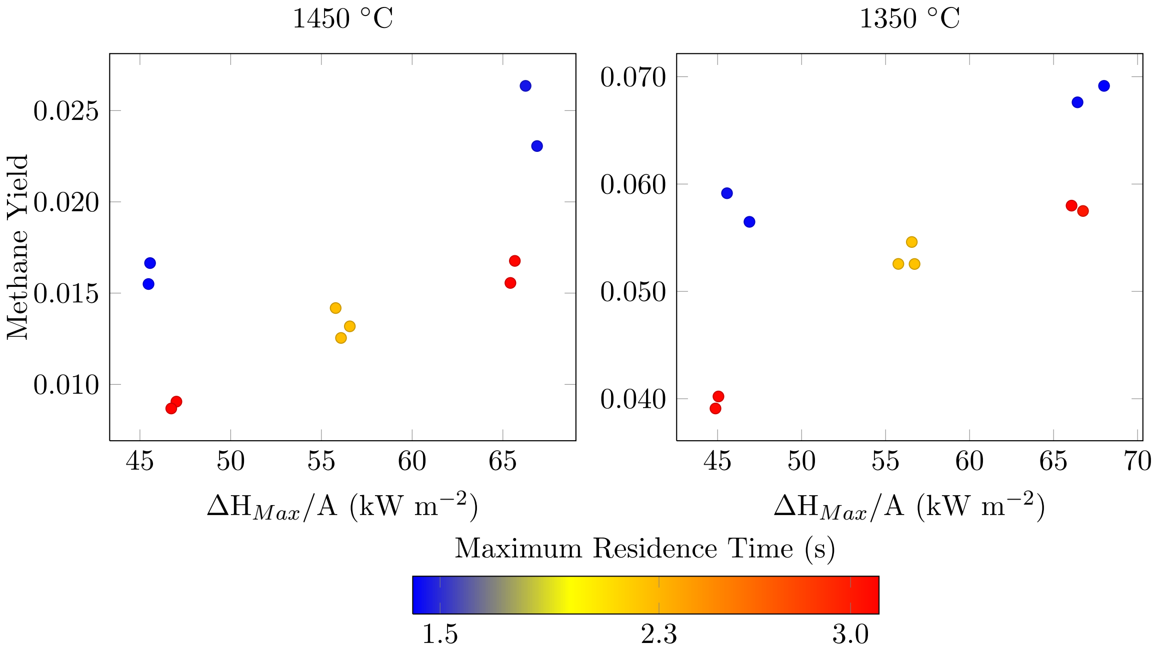

Figure 16: Blah blah blah blah SDPFOICJPFOIJD

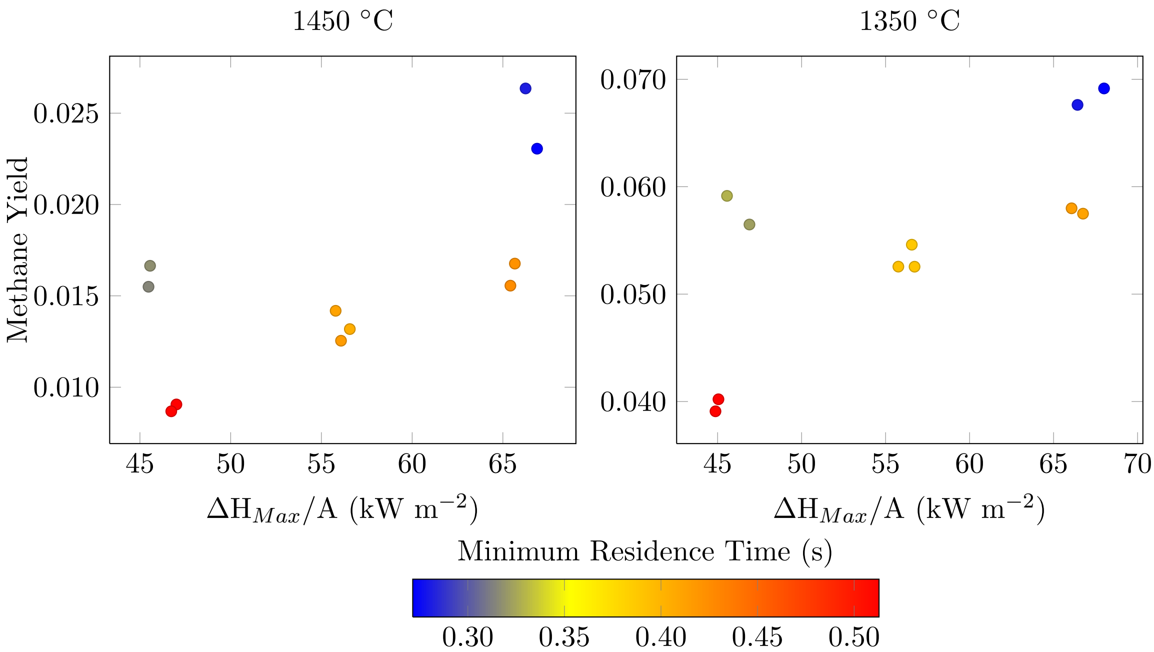

Figure 17: Blah blah blah blah SDPFOICJPFOIJD

E Experimental Set Points

Table 5: Setpoints for enthalpy vs. space time experiments. Steam temperature is at 500 °C for all runs, and argon flow is 2 SLPM.

Target $\Delta H_{max}/A$ ($kW\ m^{-2}$)	Target Max Res Time (s)	Temp. (°C)	Biomass (lb/hr)	Ent. N_2 (SLPM)	Ent. CO_2 (SLPM)	Makeup N_2 (SLPM)	Steam (g/min)	Pressure (psig)
45	1.6	1450	2.1	6.7	6.0	1.4	19.3	34
45	3.1	1450	2.2	9.3	3.8	11.1	12.0	64
55.5	2.35	1450	2.6	10.5	4.9	14.4	15.7	61
66	1.6	1450	3.5	14.3	6.4	0	20.3	41
66	3.1	1450	3.6	17.9	3.8	4.5	12.2	67
45	1.6	1350	2.1	6.3	6.3	7.9	20.2	40
45	3.1	1350	2.0	8.3	3.9	19.1	12.6	75
55.5	2.35	1350	2.8	11.6	4.9	14.5	15.8	62
66	1.6	1350	3.7	15.6	6.4	1	20.6	42
66	3.1	1350	3.8	18.9	3.9	7.0	12.5	72

F Experimental Results

Table 6: Selected results from the experimental campaign.

Run ID	Temp. (°C)	Max Res Time (s)	Min Res Time (s)	$\Delta H_{max}/A$ ($kW\ m^{-2}$)	Carbon Yield	Carbon Release	Tar Loading ($mg\ Nm^{-3}$)	CH_4 Yield
515	1450	1.62	0.314	45.5	0.831	0.862	28.2	0.0155
516	1450	1.66	0.281	66.3	0.741	0.785	118	0.0264
517	1450	3.09	0.421	65.7	0.734	0.767	7.93	0.0168
518	1450	1.65	0.271	66.9	0.774	0.813	20.2	0.0231
519	1450	2.36	0.403	56.6	0.783	0.816	11.9	0.0132
520	1450	3.10	0.425	65.4	0.730	0.761	6.12	0.0156
521	1450	2.37	0.415	56.1	0.751	0.783	3.77	0.0125
522	1450	1.62	0.317	45.6	0.816	0.848	13.1	0.0166
523	1450	3.10	0.513	47.0	0.777	0.805	1.92	0.0091
524	1450	2.37	0.410	55.8	0.772	0.806	6.27	0.0142
525	1450	3.10	0.512	46.7	0.778	0.806	2.93	0.0087
526	1350	3.11	0.599	44.9	0.707	0.770	22.3	0.0391
527	1350	3.04	0.469	66.8	0.649	0.727	657	0.0575
528	1350	2.35	0.444	55.8	0.671	0.746	248	0.0526
529	1350	3.13	0.473	66.1	0.659	0.738	627	0.0580
530	1350	1.60	0.290	68.0	0.644	0.745	2150	0.0691
531	1350	2.35	0.439	56.6	0.682	0.761	376	0.0546
532	1350	1.61	0.299	66.4	0.635	0.734	2040	0.0676
533	1350	1.61	0.355	46.9	0.695	0.775	443	0.0565
534	1350	3.11	0.600	45.1	0.708	0.771	64.1	0.0402
535	1350	1.63	0.362	45.6	0.705	0.789	526	0.0591
536	1350	2.35	0.442	56.7	0.662	0.737	412	0.0526