Modeling Calcination in a Rotary Kiln using Aspen Plus

Summa Cum Laude Honors Thesis

Michelle Feole
Advisor: Dr. Spyros Svoronos
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Executive Summary

In order to treat water hardness a water softening process called lime softening is commonly employed. In this process quick lime (calcium oxide) is added to water to precipitate out calcium carbonate in the form of a residual (or a slurry stream of predominantly calcium carbonate solids and water). An issue common to water treatment plants that employ this process is how to reuse this residual. On potential reuse option is in a process called calcination. Here calcium carbonate is decomposed into quicklime and calcium carbonate by the following reaction: $CaCO_3 (s) \rightarrow CaO (s) + CO_2 (g)$. Calcination is an endothermic reaction that begins to take place at approximately 875°C. Typically, rotary kilns are used for this process. These kilns are typically operated at 1100°C or more in order to allow for consistent yields of CaO. The primary aim of this thesis was to generate a model of the calcination process in a rotary kiln to predict the optimal fuel requirements for various moisture contents of residual. Aspen Plus was used in order to create a one-dimensional model the rotary kiln. Aspen Plus was chosen because of its ability to handle solids reactions. In order to model the rotary kiln, the kiln was split into three stages. These stages correspond to different processes in within the kiln. Both PFR and equilibrium based reactors were used to develop simulation of calcination in a rotary kiln. Initially, the simulation was based on kinetics using PFR reactors. The kinetics for both the combustion and calcination reactions was found through literature. However, upon inconclusive modeling in Aspen Plus, a new approach was taken using equilibrium based reactors. Equilibrium data for the calcination reaction was inputted. Plots were generated for both the conversion of calcium carbonate based on fuel input as well as moisture content. Following the predictions made by Aspen Plus, a preliminary financial analysis was provided to examine the feasibility of adding a rotary kiln into a water treatment plant. Overall, this thesis provides a rudimentary model to the calcination process. Further work must be completed on this model in order to generate better predictive results if this were to be used in an industrial setting, including modeling the rotary kiln as CSTRs,

Introduction

There are many industries that can utilize quick lime (CaO) in their processes. For example in mining and water treatment plants lime is used for pH adjustment and also as a water purification method. However, the cost of lime is directly related to fuel cost (Bes, 2006) .

Lime is commonly used in water treatment plants in a process called Lime Softening to remove the hardness in the water. One byproduct of this process is the generation of Calcium Carbonate residual (or a slurry stream of predominantly calcium carbonate solids with various levels of moisture content). This residual can be reused in the water treatment process by converting the calcium carbonate back to calcium oxide by the following reaction:

$$CaCO3\ (s) \rightarrow CaO\ (s) + CO2\ (g)$$

This process is termed the calcination reaction. Typically this endothermic reaction begins to take place at approximately 875°C. Kilns are used in order to conduct the thermal decomposition of calcium carbonate. They are typically operated at 1100°C or more in order to allow for yields of CaO (Bes, 2006).

There are several different types of kilns available calcination. This paper deals with the traditional rotary kiln. A rotary kiln rotates at small angle to the horizontal. Figure 1 shows a schematic of a rotary kiln. Typically a rotary kiln is 3 meters in diameter and 90 meters in length. (M. Georgallis P. N., 2005).

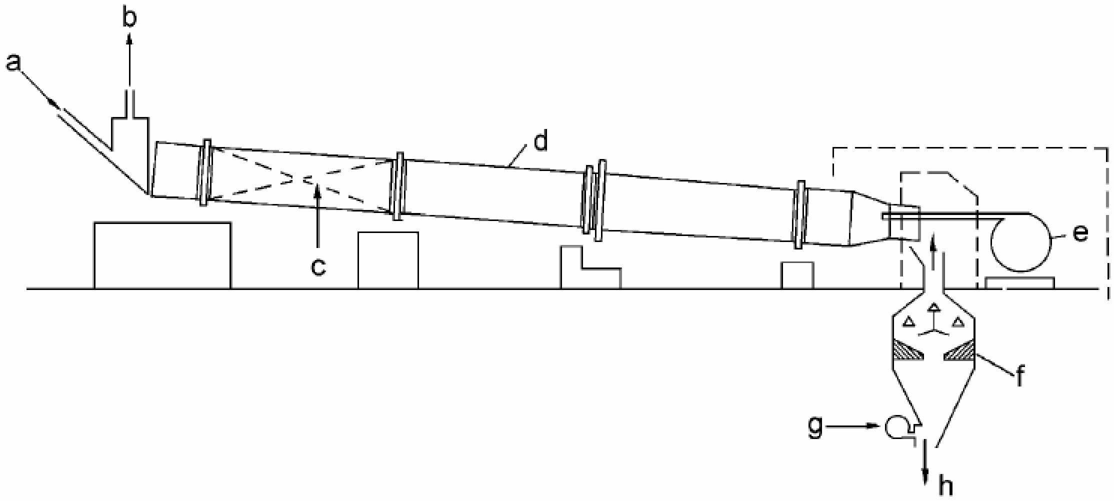


Figure 1: Schematic of traditional Rotary Kiln. a.) slurry input; b.) exhaust gases; c.) refractory trefoils; d.) kiln shell, e.) fuel + secondary air; f.) lime cooler; g.) cooling air; h.) quicklime product. From (Bes, 2006)

Objectives

This paper aims to present a study of a rotary kiln in order to find the optimal operating parameters for various moisture contents of the residual

Simulation Design

Aspen Plus was used in order to create a one-dimensional model the rotary kiln. Aspen Plus was chosen because of its ability to handle solids reactions. In order to model the rotary kiln, the kiln was split into three stages as seen in Figure 2. These stages correspond to different processes in within the kiln. The first stage is where the combustion reactions occurs generating temperatures to approximately 1000°C. In stage 2, the decomposition of the calcium carbonate begins to occur until the temperature reaches about 900°C. Depending on the residence time of the calcium carbonate, most of the calcium carbonate can dissociate before leaving the kiln. The third stage of the kiln is the cooling stage. Here secondary air can be pre-heated by the vapor exhaust product stream as well as the heated lime stream to be recycled back into the calcination process.

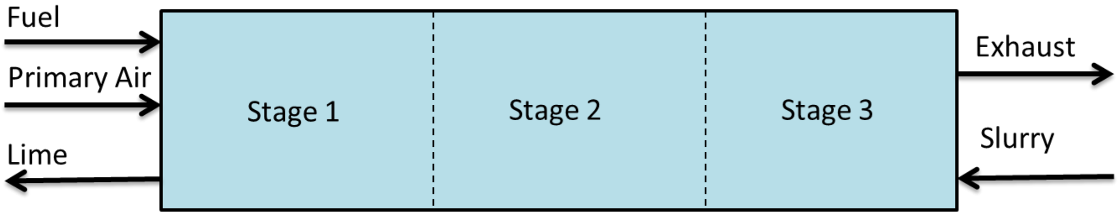


Figure 2: Example of Simulation Design. To emulate the different aspects of the rotary kiln, the simulation was split into three stages with each stage containing a reactor.

In order to simulate the cross-flow of vapor and solids stream, a splitter was used after each reactor to perfectly separate the solids stream from the vapor stream. The vapor stream proceeded to the proceeding reactor while the solids were directed to the preceding reactor. Both PFR and equilibrium base reactors were used to develop simulation flow sheets as seen in the following sections.

Assumptions and Limitations

There are several parameters that can be adjusted to model the calcination process in the rotary kiln such as feed rate of fuel, air and slurry, rotational speed, volume of kiln, kiln incline, and slurry solids particle size. However, this model is limited in scope as it only can change stream flow rates and compositions of each stream.

More rigorous modeling found in literature encompasses computational fluid dynamics. There are several models that use the shrinking core model (Hrvoje Mikulcic, 2012). There are several assumptions made in generating this model including that uniform conditions exist and the reactors are well mixed at any given point in the reactor. Furthermore, the natural gas was assumed to be almost pure methane. Splitters were used as artificial separation processes in to simulate perfect separation of both the vapor and solid/liquid product.

Equilibrium Based Reactors

There are two types of equilibrium based reactors in Aspen Plus: Equilibrium and Gibbs Equilibrium. Neither of these reactors takes into account kinetics or various volume specifications for the reactor. The delta Gibbs formation energy, 28.8614 kcal/mol, for calcium carbonate must be added to component parameters in order for the reactors to work. Gibbs reactors were chosen as the reactors; however, the calcination reaction was not based on the minimization of Gibbs free energy. Within Aspen, if equilibrium data is known, that data can be inputted into the simulation. Thus, the calcination reaction was based off of equilibrium data and the combustion reaction was not. No equilibrium data for the combustion reaction was inputted.

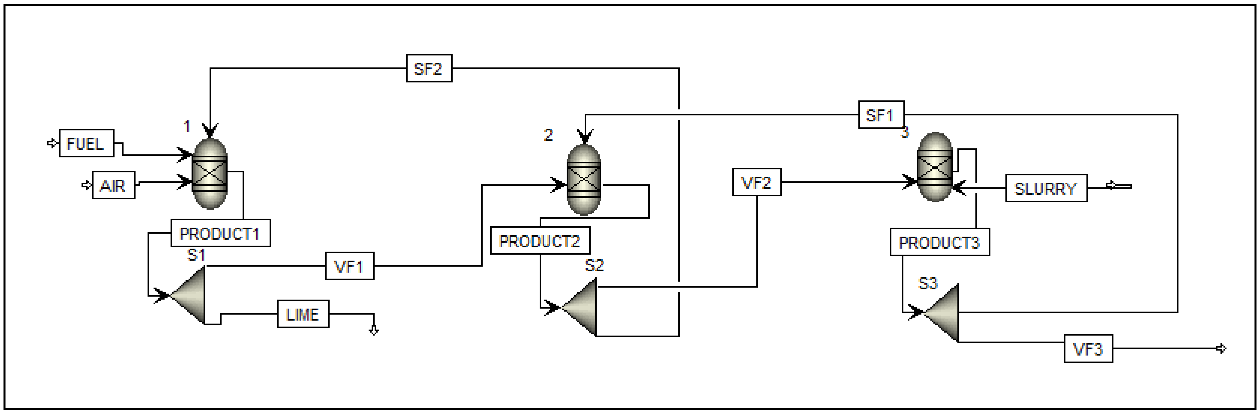


Figure 3: Screenshot of Equilibrium Based Reactors. These are Gibbs reactors, however, equilbrium data for the calcination reaction is inputted. No equilibrium data is inputted for the combustion reaction.

Dayton's Rotary Kiln Temperature Distribution

Dayton's Water Treatment Plant performed a CFD model on the calcination in the rotary kiln (David Cornwell, 2012). The temperature distribution they found is shown in Figure 4. The temperatures in this distribution were specified in the Equilibrium Based Reactor scheme. However, the PFR scheme was run adiabatically. This was done in order to monitor the temperature changes within the kiln.

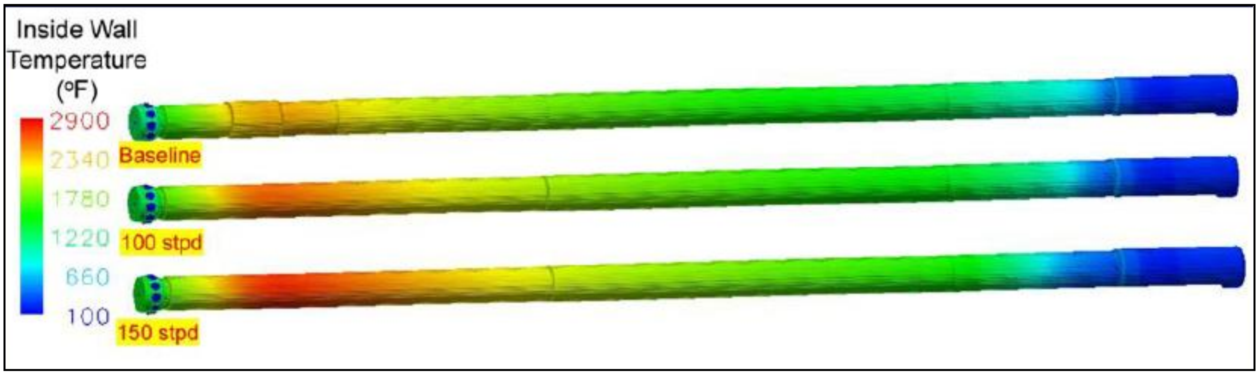


Figure 4: Temperature Distribution of Rotary Kiln determined by Dayton, Ohio water treatment plant

Plug Flow Reactor

Plug Flow Reactor is a kinetics based reactor block. This is a more rigorous method in determining rate-based reactions. One caveat with using the PFR is that only one feed stream is allowed. Because of this constraint, a mixer is used facilitate the use of PFRs. The reactor *must* consider both vapor and liquid as valid phases in order for the simulation to converge.

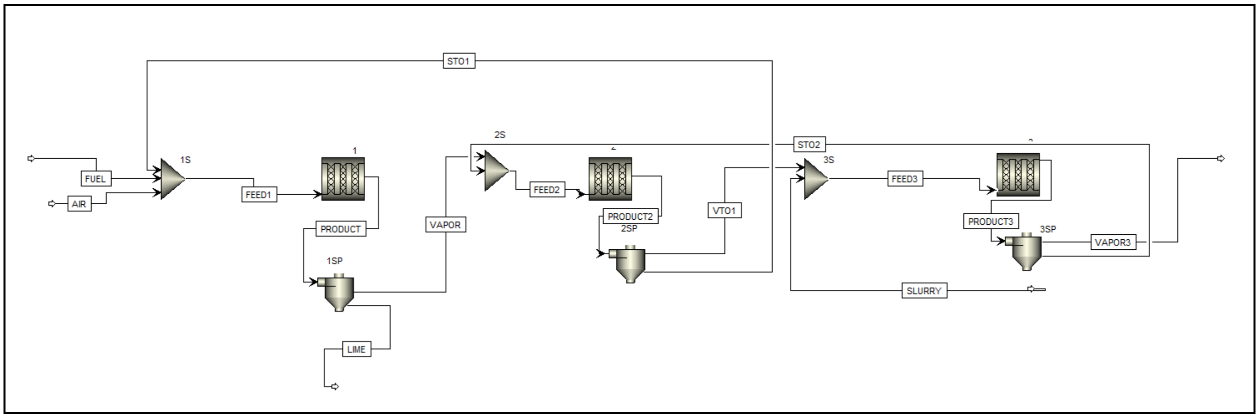


Figure 5: Screenshot of PFR scheme.

Input Parameters for the Kiln

The input parameters for this kiln were based off a water treatment plant (David Cornwell, 2012).

	Methane Fuel	Primary Air	Slurry Feed
Flow Rate (lb/hr)	1459.9	7742.2	15662.3
Temperature (° F)	65	65	90

Table 1: Input parameters for flow rates of feed streams

Compositions of Streams			
	Natural Gas (vol %)	Primary Air (vol %)	Slurry Feed (wt %)
CH4	95	--	--
N2	5	79	--
O2	--	21	--
H2O	--	--	40
CaCO3	--	--	60

Table 2: Input Parameters for feed streams compositions

The system pressure and stream pressures were all set to be 1 atm with no pressure drops in any of the process blocks. The thermodynamic model used was SYPSO. It was assumed the PFRs were adiabatic in order to monitor the temperature changes in the reactors. However, this assumption for a rotary kiln is not completely valid. Approximately 50% or more of the heat generated from the calcination process is dissipated to the surroundings. For the PFR reactors, in order to model each stage of the rotary kiln, the total volume of a kiln was split into thirds with a diameter of 6 meters and length of 77 meters each.

Reaction Kinetics for both methane combustion and calcination

The kinetics for both the combustion and calcination reactions was found through literature. Initially, the combustion was going to be modeled as a series of 19 reaction ultimately leading to the net reaction of $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$. However, there were several complications in Aspen including having to define HO2 which turned unsuccessful. Therefore kinetics was found for three consecutive-parallel combustion reactions of methane (Kryzsztof Gosiewski, 2009). The kinetics was also found for the decomposition of calcium carbonate (I. MArtinez, 2012).

The following kinetic parameters were used in the power-law reaction type. These parameters are for elementary reactions as followed by the Arrhenius equation. For equilibrium based reactors, Keq was used. Note that the equilibrium based components can also be inputted into the CSTR based reactors. The method of inputting the equilibrium data is by on the flowsheet section of Aspen, there is an option to input reactions. In the reactions tab, there is a choose between reaction kinetics or chemistry. By going to chemistry, the user can input the equilibrium data in the same mode as would be done for equilibrium based reactors.

Reaction	E (J/mol)	k_o (mol/m^3 * s)
$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$	127734	1.08×10^5
$2CO + O_2 \rightarrow 2CO2$	170952	7.61×10^7
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	306927	5.38×10^{13}
$CaCO_3$ (s) --> CaO (s) + CO_2 (g)	91700000	252015.2

,

Keq	**ΔG_{rx}** = 177,100-158T J/mol and T in K where **Keq=exp(-deltaGrx/(RT)**

Table 3: Input parameters for combustion kinetics and calcination equilibrium constants

Plots

Plug Flow Reactors

Sensitivity analyses were performed in order to study the effects of changing certain variables on characteristics such as temperature of the exit streams as well as conversion of CaO.

Mass Flow Rate of CaO vs. Fuel Flow Rate

In the PFR Reactor scheme, a model of the conversion of Calcium carbonate was generated. Figure 6 shows that the highest conversion the PFR scheme could attain was only 30%. This is grossly different from other models which depict near to complete conversion of calcium carbonate to calcium oxide. Upon receipt of this data, continued attempts at trying to fix the PFR scheme did not succeed in ever exceeding 30% conversion without error in the simulation.

With these results, a new reaction scheme was generated, this time with equilibrium based reactors.

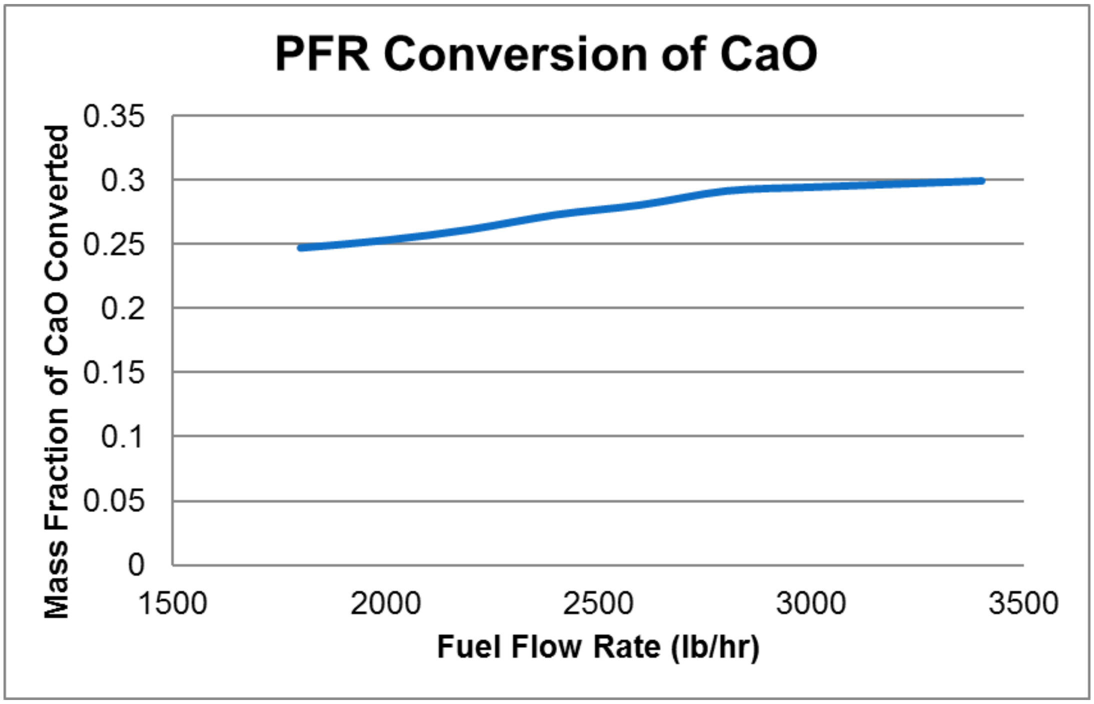


Figure 6: Conversion of $CaCO_3$ in the PFR simulation. Only 30% conversion could be achieved.

Temperature vs. Fuel Flow Rate

Figure 7 shows the temperature vs. fuel mass flow rate for a PFR reactor. The fuel and air flow rates were increased to observe how the temperature changes within the reactor. These temperature changes will ultimately affect the kinetic rates.

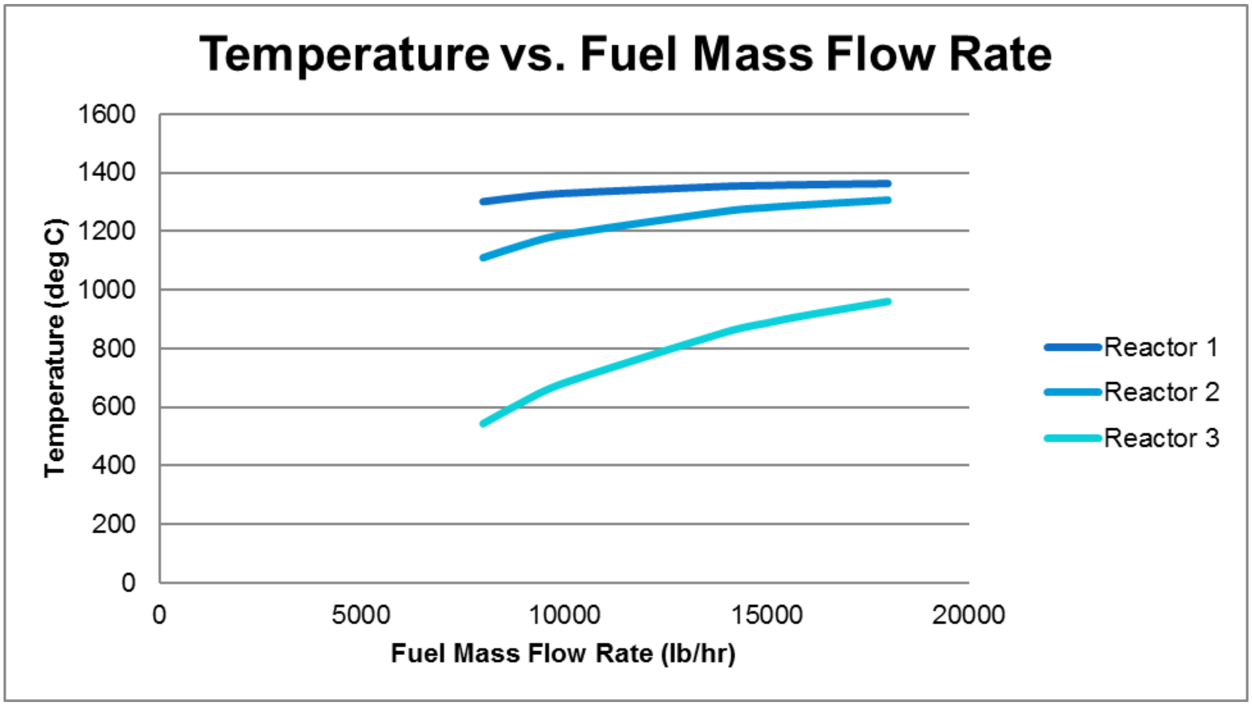


Figure 7: An adiabatic PFR scheme examining how the temperature changes in each reactor with increasing fuel rates.

Equilibrium Based Reactors

Conversion in Equilibrium Based Reactors

Figure 8 shows how the conversion of $CaCO_3$ depends on the fuel and air input streams. The x-axis is in kg/s based on previous attempts at creating the rotary kiln simulation.

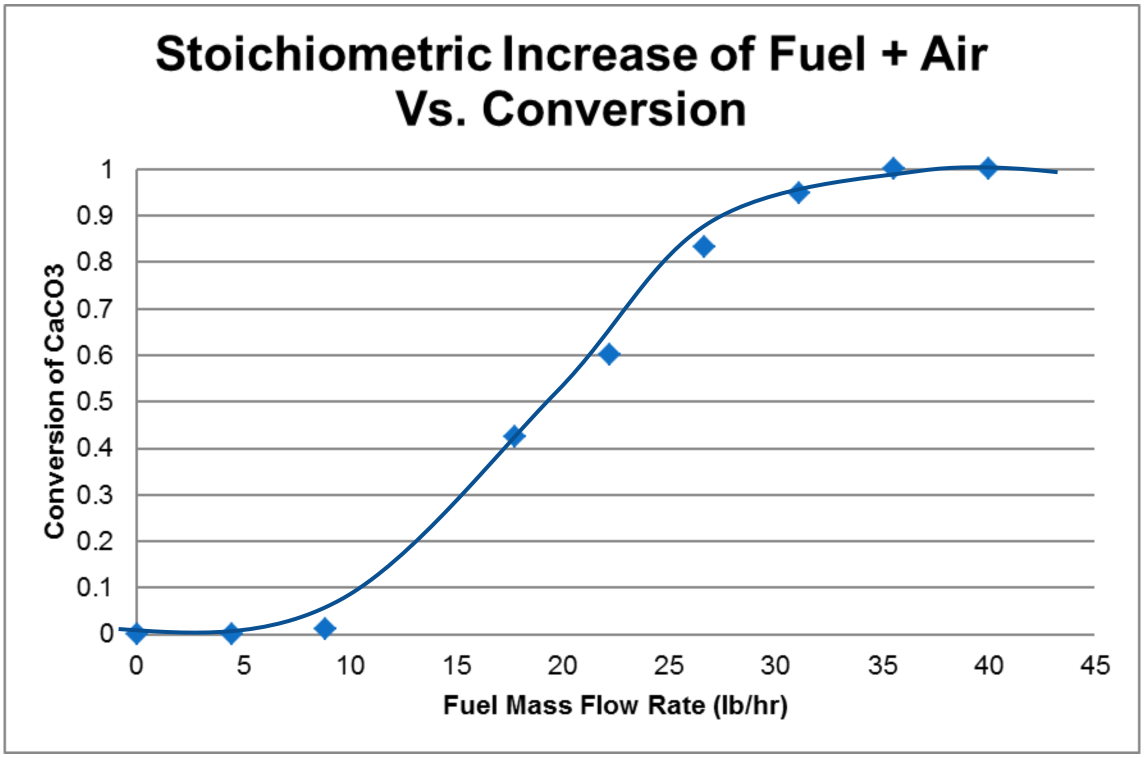


Figure 8: Sensitivity study completed on how the fuel and air input streams affect the amount of CaCO3 converted.

Moisture Content vs. Fuel Required

Figure 9 shows a sensitivity analysis done on determining the amount of fuel that would be required for various moisture contents in order to produce the required amount of CaO for a water treatment plant. Increased fuel would be needed as the moisture content of the residual increased as the rotary kiln would have less CaCO3 content in the input stream.

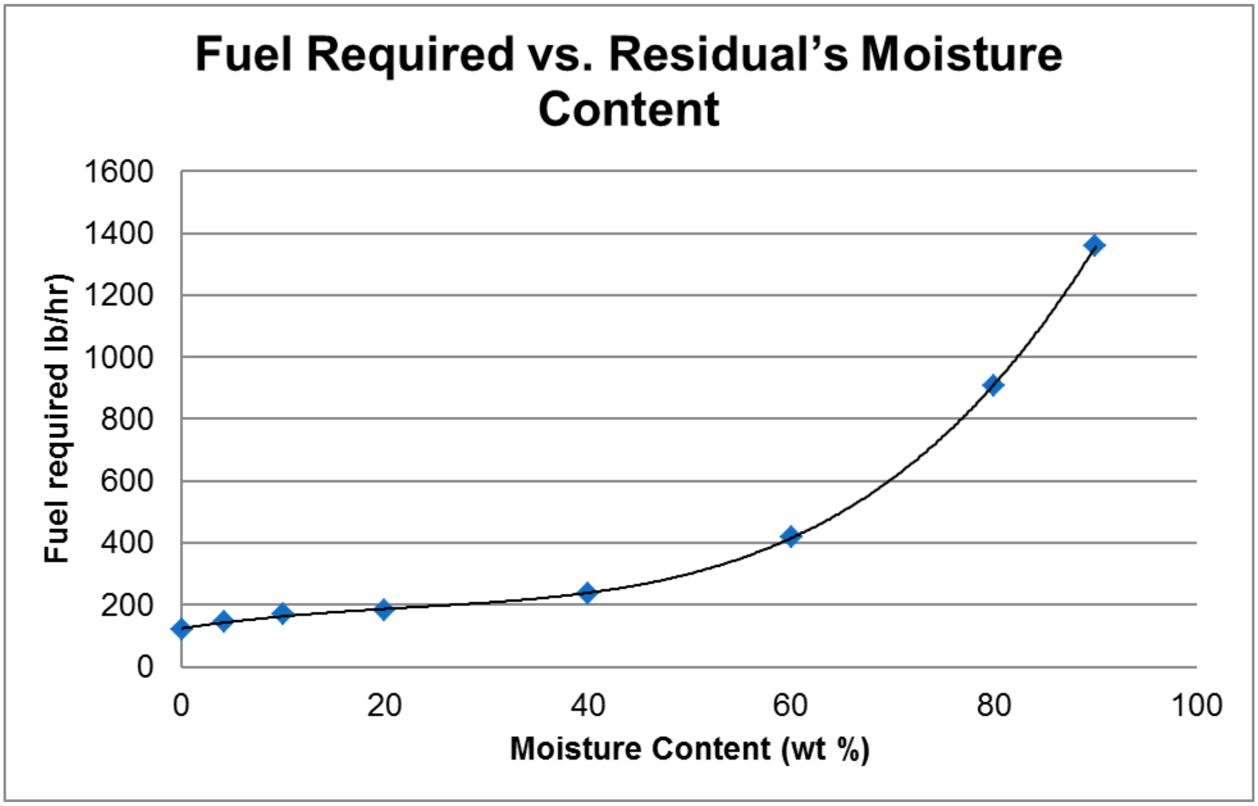


Figure 9: Plot showing fuel required for various moisture content of calcium carbonate residual

Complications within Aspen

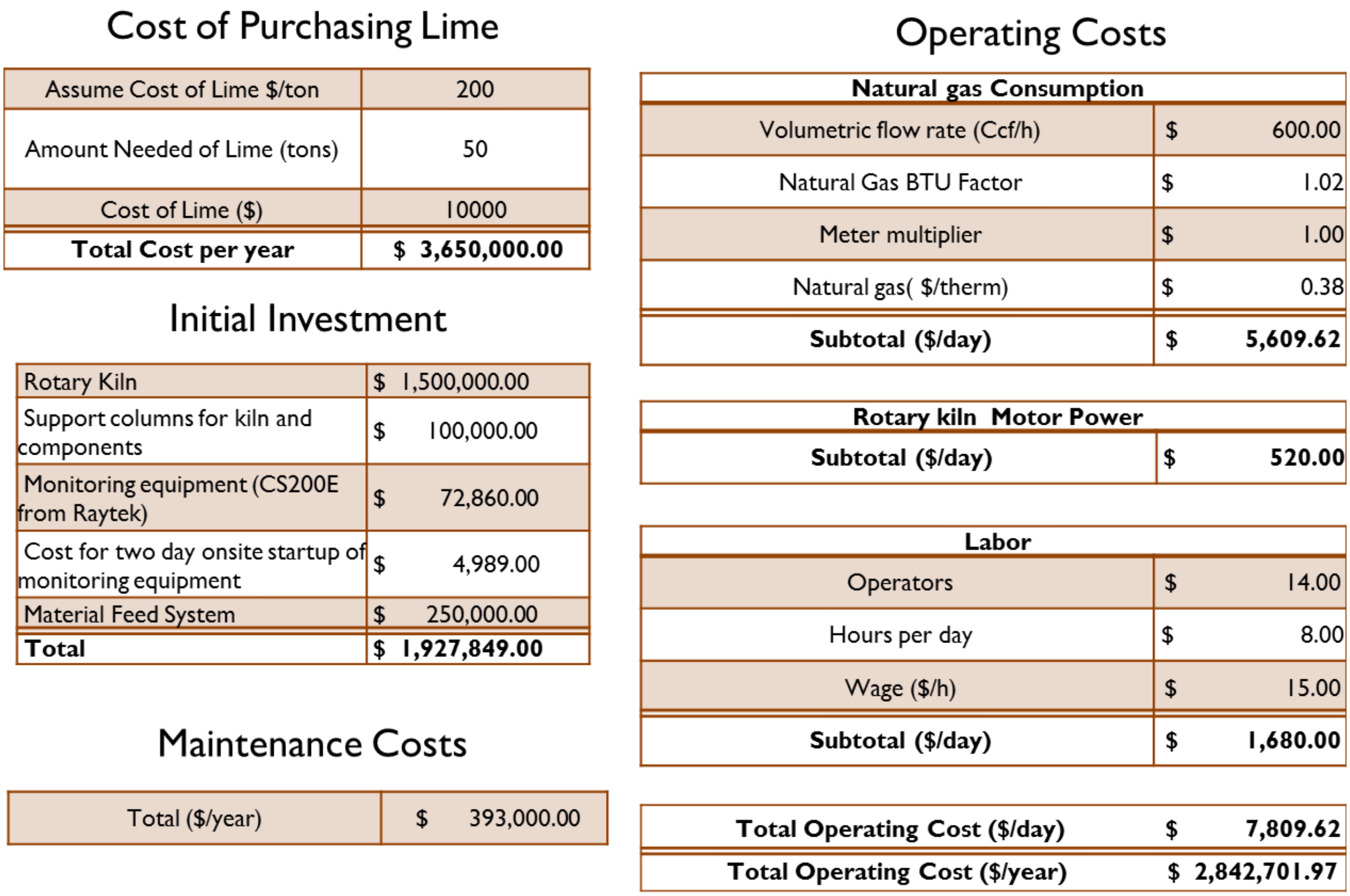
There were several attempts made in aspen to model solids. Initially, the first attempt was to use a series of CSTR reactors. This turned out unsuccessful. The reactors would achieve conversion but neither the calcination nor combustion reactions would go to completion. Furthermore, the temperatures in the reactors were below the temperatures required for conversion to occur.

With both the CSTR and PFR scheme, combustion kinetics were incorporated. Initially a total of 19 reactions were to be modeled (18 reactions for the combustion of methane and 1 for the calcination reaction). This proved unsuccessful. Furthermore, a component HO_2 needed to be user defined as Aspen Plus did not have this component in its library.

Summary of Costs

Table 4 shows the summary of costs associated with purchasing a rotary kiln. Table 5 shows a financial analysis. The assumptions for the business case are as follows:

1. The amount of lime needed is 50 tons per day
2. Lime costs $200 per ton
3. The plant already has land prior to the purchase and installation of the rotary kiln.



Cost of Purchasing Lime

Assume Cost of Lime $/ton	200
Amount Needed of Lime (tons)	50
Cost of Lime ($)	10000
Total Cost per year	**$ 3,650,000.00**

Initial Investment

Rotary Kiln	$ 1,500,000.00
Support columns for kiln and components	$ 100,000.00
Monitoring equipment (CS200E from Raytek)	$ 72,860.00
Cost for two day onsite startup of monitoring equipment	$ 4,989.00
Material Feed System	$ 250,000.00
Total	**$ 1,927,849.00**

Maintenance Costs

Total ($/year)	$ 393,000.00

Operating Costs

Natural gas Consumption	
Volumetric flow rate (Ccf/h)	$ 600.00
Natural Gas BTU Factor	$ 1.02
Meter multiplier	$ 1.00
Natural gas($/therm)	$ 0.38
Subtotal ($/day)	**$ 5,609.62**

Rotary kiln Motor Power	
Subtotal ($/day)	**$ 520.00**

Labor	
Operators	$ 14.00
Hours per day	$ 8.00
Wage ($/h)	$ 15.00
Subtotal ($/day)	**$ 1,680.00**

Total Operating Cost ($/day)	**$ 7,809.62**
Total Operating Cost ($/year)	**$ 2,842,701.97**

Table 4: Tables summarizing the various costs for installing and operating a rotary kiln

Financial Analysis

Year	End of Year	Initial Investment	dk, DDB	Cost of Purchasing Lime	Operating Costs + Maintenance Costs	Savings	Cash Flow	Cumulative Cash Flow	Discounted Cash Flow	Cumulative Discounted Cash Flow
2013	0	-1927.85	0.00	3650.00	3235.70	414.30	-1513.55	-1513.55	-1513.55	**-1513.55**
2014	1	0.00	30.00	3650.00	3235.70	414.30	414.30	-1099.25	376.63	**-1136.92**
2015	2	0.00	15.00	3650.00	3235.70	414.30	414.30	-684.95	342.40	**-794.52**
2016	3	0.00	30.00	3650.00	3235.70	414.30	414.30	-270.66	311.27	**-483.25**
2017	4	0.00	18.00	3650.00	3235.70	414.30	414.30	143.64	282.97	**-200.28**
2018	5	0.00	-7.20	3650.00	3235.70	414.30	414.30	557.94	257.25	**56.96**
2019	6	0.00	-4.32	3650.00	3235.70	414.30	414.30	972.24	233.86	**290.82**
2020	7	0.00	-2.59	3650.00	3235.70	414.30	414.30	1386.54	212.60	**503.43**

Table 5: This table shows a preliminary financial analysis of implementing a rotary kiln in the water treatment plant. According to this analysis at approximately 4.5 years, the plant would start to save money.

Future Work

Generating new reaction Scheme to Better Model the Calcination in a Rotary Kiln

Using better calcination models and also trying a scheme with yield reactors.

Particle Size Distribution Implementation

Future work includes creating a model that incorporates the particle size distribution. Samples of a particle size distribution from a local utility company can be used to further investigate the effect of varying particle size on the calcination process.

Rigorous Modeling of Combustion Kinetics

The combustion reactions of the fuel can be modeled more rigorously by modeling the mechanism of combustion as the kinetics can be readily found in literature. One complication in this study with modeling all 18 reactions was due to having an undefined component HO2. This variable must be user defined

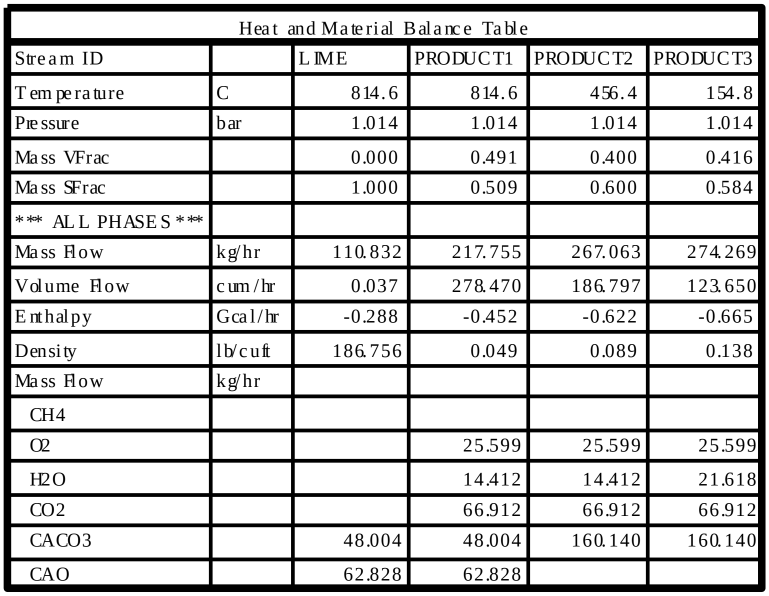
Recycle Streams/Waste Disposal/Emissions

Recycle streams can be added. In water treatment processes, the carbon dioxide emissions are used downstream of the calcination process in order to change the pH of the water. Recycle streams can be used as a way to heat secondary air streams from the produced lime product (Branko Rusic, 2006).

Appendix

Converged Aspen Diagram/Stream Results

Equilibrium Based Reactors



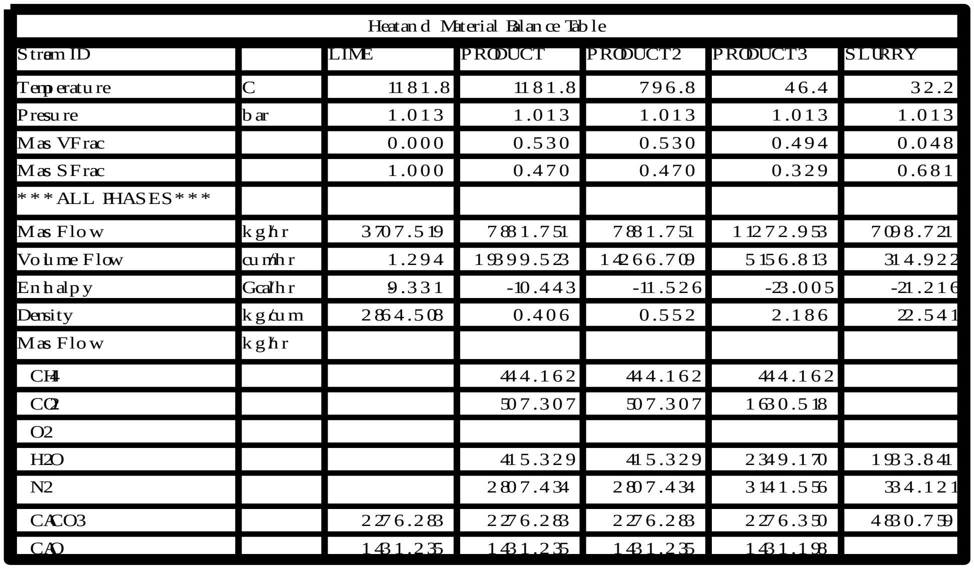
Heat and Material Balance Table

Stream ID		LIME	PRODUCT1	PRODUCT2	PRODUCT3
Temperature	C	814.6	814.6	456.4	154.8
Pressure	bar	1.014	1.014	1.014	1.014
Mass VFrac		0.000	0.491	0.400	0.416
Mass SFrac		1.000	0.509	0.600	0.584
*** ALL PHASES ***					
Mass Flow	kg/hr	110.832	217.755	267.063	274.269
Volume Flow	cum/hr	0.037	278.470	186.797	123.650
Enthalpy	Gcal/hr	-0.288	-0.452	-0.622	-0.665
Density	lb/cuft	186.756	0.049	0.089	0.138
Mass Flow	kg/hr				
CH4					
O2			25.599	25.599	25.599
H2O			14.412	14.412	21.618
CO2			66.912	66.912	66.912
CACO3		48.004	48.004	160.140	160.140
CAO		62.828	62.828		

Table 6: Product Streams for the equilibrium based reaction scheme

Plug Flow Reactors

The following charts show the results of a converged PFR reactor.



Heat and Material Balance Table						
Stream ID		LIME	PRODUCT	PRODUCT2	PRODUCT3	SLURRY
Temperature	C	1181.8	1181.8	796.8	46.4	32.2
Pressure	bar	1.013	1.013	1.013	1.013	1.013
Mass VFrac		0.000	0.530	0.530	0.494	0.048
Mass SFrac		1.000	0.470	0.470	0.329	0.681
*** ALL PHASES ***						
Mass Flow	kg/hr	3707.519	7881.751	7881.751	11272.953	7098.721
Volume Flow	cum/hr	1.294	19399.523	14266.709	5156.813	314.922
Enthalpy	Gcal/hr	-9.331	-10.443	-11.526	-23.005	-21.216
Density	kg/cum	2864.508	0.406	0.552	2.186	22.541
Mass Flow	kg/hr					
CH4			444.162	444.162	444.162	
CO2			507.307	507.307	1630.518	
O2						
H2O			415.329	415.329	2349.170	1933.841
N2			2807.434	2807.434	3141.556	334.121
CACO3		2276.283	2276.283	2276.283	2276.350	4830.759
CAO		1431.235	1431.235	1431.235	1431.198	

Table 7: Product streams for the PFR reactor scheme

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