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Master's Programme in Aalto Advanced Energy Solutions

Modelling of a lime kiln using renewable fuels and study of oxyfuel combustion

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Abstract

In kraft pulp mills, lime kilns are used in one of the processes to complete the chemical recovery cycle. The calcination reaction inside the lime kiln requires heat, which has been traditionally provided by combustion of fossil fuels. Due to tightening environmental regulations, the pulp and paper industry has started to implement more renewable fuels in pulp mills. This trend has led to more interest on renewable fuel integration into the lime kiln.

The aim of this thesis is to construct a process simulation model of a lime kiln. The lime kiln is modelled using natural gas and four different renewable fuels. Two different combustion processes are implemented in the model as well: a traditional combustion process with air, and an oxyfuel combustion process. The model gives the user results such as fuel consumption and amount of carbon dioxide emissions.

The model is created by using the process simulation software Aspen Plus. The literature review is used to choose appropriate boundary conditions and initial values for the model. The results provided by the model are also compared to similar models created in other studies and data from real lime kilns. An overview of economic feasibility for different renewable fuels is done shortly to compare the fuels outside of the model results.

The results from the model showed that the model works well in predicting most operating parameters, but some emissions are not calculated properly. While renewable fuels can have some adverse effects on the combustion process in the lime kiln, the overall process efficiency is comparable to using natural gas. It was concluded by the model results and the economic feasibility analysis that gasification of wood residues is one of the best alternatives to implement a renewable fuel for the lime kiln. Oxyfuel combustion works well in decreasing fuel consumption in the lime kiln but implementing the combustion process can come with high investment and running costs.

Keywords Lime kiln, Oxyfuel combustion, Aspen Plus, Renewable fuels

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Tiivistelmä

Sulfaattisellutehtaissa meesauunia käytetään tehtaan kemikaalikierron täydentämiseksi. Meesauunin sisällä tapahtuva kalsinointireaktio vaatii lämpöä, joka on perinteisesti tuotettu fossiilisia polttoaineita polttamalla. Kiristyvän ympäristösääntelyn takia paperi- ja selluteollisuus on alkanut käyttämään enemmän uusiutuvia polttoaineita sellutehtaissa. Tämä trendi on johtanut suurempaan kiinnostukseen uusiutuvien polttoaineiden käytössä meesauunissa.

Tämän diplomityön tarkoituksena on rakentaa prosessisimulointimalli meesauunista. Meesauunia mallinnetaan maakaasun sekä neljän uusiutuvan polttoaineen kanssa. Myös kaksi erilaista polttoprosessia asetetaan toimimaan malliin: perinteinen polttoprosessi ilman kanssa, sekä happipolttoprosessi. Malli antaa käyttäjälleen erilaisia tuloksia operointiparametreista, kuten polttoaineen kulutuksesta sekä hiilidioksidipäästöjen määrästä.

Malli luodaan käyttämällä prosessisimulointiohjelmaa Aspen Plus. Kirjallisuuskatsausta käytetään valitsemaan sopivat rajaehdot ja aloitusarvot mallille. Mallien tuottamia tuloksia vertaillaan muissa töissä tehtyihin malleihin sekä oikeiden meesauunien käyttödataan. Tässä työssä tehdään myös lyhyt yleiskuva uusiutuvien polttoaineiden taloudelliseen soveltuvuuteen meesauunia varten.

Mallin tulokset esittivät, että meesauunimalli toimii hyvin useimpien käyttöparametrien ennustamiseen, mutta osaa päästöistä ei lasketa oikein. Vaikka uusiutuvilla polttoaineilla voi olla joitain huonoja vaikutuksia meesauunin polttoprosessiin, niin prosessin kokonaishyötysuhde on verrattavissa maakaasuun polttoon. Mallin tulosten sekä taloudellisen katsauksen perusteella voidaan päätellä, että puujätteen kaasutus on yksi parhaista vaihtoehdoista uusiutuvaksi polttoaineeksi meesauuniin. Happipolttoprosessi toimii hyvin polttoaineen kulutuksen vähentämisessä, mutta prosessin käyttäminen voi vaatia suuria investointi- ja käyttökustannuksia.

Avainsanat meesauuni, happipolttoprosessi, Aspen Plus, uusiutuvat polttoaineet

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Helsinki, 19.5.2021

Olli Vainikainen

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Symbols and abbreviations

Symbols

E_c	Energy required for the calcination process (MJ)
E_d	Energy required for the drying of lime mud (MJ)
E_{in}	Sum of all lime kiln energy input (MJ)
ΔG	Standard Gibbs free energy change (MJ/mol)
h_f	Lover heating value of fuel (MJ/kg)
$\dot{m}_f$	Mass flow rate of fuel (t/d)
η_{lk}	Energy efficiency of a lime kiln
P_{CO_2}	Partial pressure of carbon dioxide (bar)
P_{sys}	Pressure of the system (bar)
$\dot{Q}_{sh}$	Shell heat losses (MW)
R	Universal gas constant (MJ/mol·K)
T_c	Calcination temperature (K)

Abbreviations

ASU	Air separation unit
BECCS	Bioenergy with carbon capture and storage
$CaCO_3$	Calcium carbonate
CAGR	Compound annual growth rate
$Ca(OH)_2$	Calcium hydroxide
CaO	Calcium oxide, lime
$CaSO_4$	Calcium sulfate
CCS	Carbon capture and storage
CFB	Circulating fluidized bed
CH_4	Methane
CO_2	Carbon dioxide
CO	Carbon monoxide
CTO	Crude tall oil
ESP	Electrostatic precipitator
FGR	Flue gas recirculation
GHG	Greenhouse gas
H_2S	Hydrogen sulfide
H_2SO_4	Sulfuric acid
HFO	Heavy fuel oil
LHV	Lower heating value
Mt	Megatonnes (million metric tons)
N_2	Nitrogen molecule
Na_2CO_3	Sodium carbonate
Na_2SO_4	Sodium sulfate
NaOH	Sodium hydroxide
Na_2S	Sodium sulfide

NCGs	Non-condensable gases
NO_x	Nitrogen oxides
NPE	Non-process element
O_2	Oxygen molecule
OC	Oxyfuel combustion
SO_2	Sulfur dioxide
TC	Traditional combustion
TOP	Tall oil pitch
TRS	Total reduced sulfur
UN	United Nations

1 Introduction

1.1 Overview of the pulp and paper industry

The pulp and paper industry produces a variety of products all around the world. The industry uses wood as the raw material to produce paper, paperboard or pulp. The paper produced is mostly for printing and writing purposes. Paperboards can be used for packaging purposes. In Finland, around 10.5 megatonnes (Mt) of paper and paperboard was produced in 2018 (Suorsa 2020). In the same year, the global production of paper and paperboard was around 420 Mt. The biggest producers of these products were large countries, such as China and USA. (Tiseo 2021) Considering the population of these countries compared to Finland, it is noticeable that Finland produces a high amount of paper and paperboard per capita.

The pulp and paper industry is a vital part of Finland's economy. In 2017, the pulp and paper industry had a share of 13 % of all manufacturing output in Finland. This led to the pulp and paper industry having a share of 15 % of all exports. (Suorsa 2019) The forest industry as a whole is important for Finland, and changes in the industry have a major impact on the economy. The biggest companies in this sector in Finland include UPM, Stora Enso and Metsä Group.

Figure 1 shows the compound annual growth rate (CAGR) of the global paper and paperboard market during recent years. Although the use of paper for printing and writing purposes has been on decline in recent years, the use of paper and paperboard globally has been on slight increase. This is mostly due to increase in the need for packaging materials. The tissue market has also been on the rise since the 1990s. (Berg & Lingqvist 2019) The projections of Statista support these projections made by McKinsey: the global demand for paper will keep on increasing in the future while the demand for printing and writing paper will decrease (Tiseo 2021).

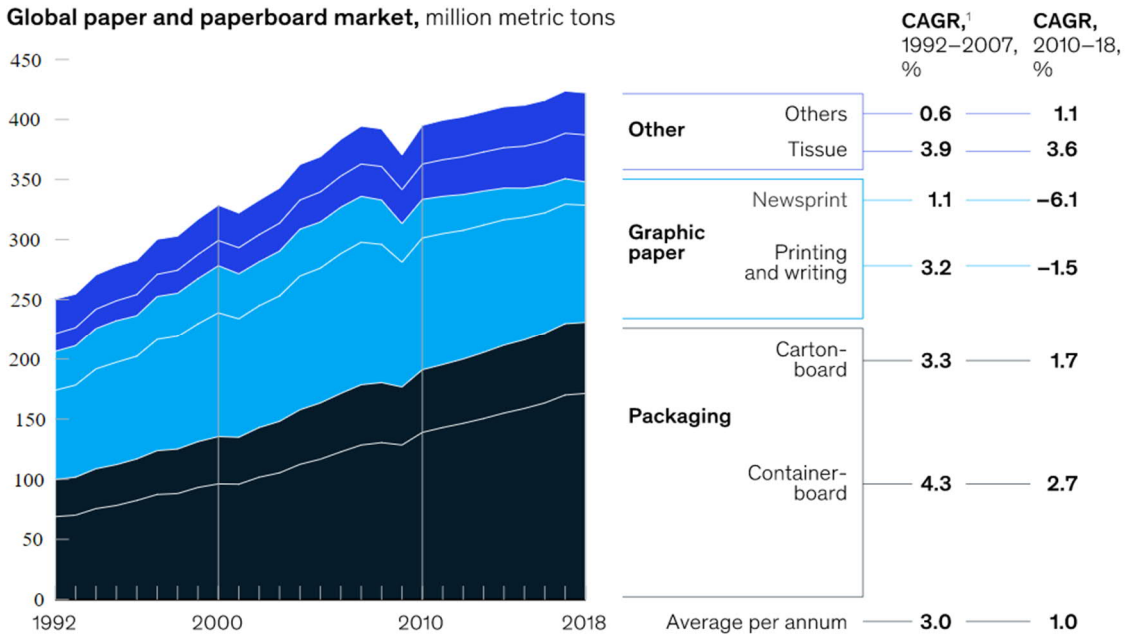


Figure 1: The growth of the paper and paperboard market during 1992–2018 (Berg & Lingqvist 2019).

The megatrend of climate change and resource depletion drives companies in the pulp and paper industry to increase their sustainability. In addition to increasing sustainability in the processes due to stricter environmental regulations, companies can improve their image and make the sustainability of the company profitable by providing new products and solutions. Decreasing the use of fossil fuels is crucial for many companies to cut down on emissions, but it can also help to increase profits due to increasing fossil fuel prices.

Pulp mills, which are used in the pulp and paper industry to convert wood materials into pulp, use a large share of bioenergy in their production. This bioenergy can be gained from biomass during the chemical recovery process in the mill. This is why pulp mills are mostly independent in terms of electricity and heat demand. However, some components in the mill still use fossil fuels for power production. Fossil fuels are used during startups or shutdowns, but these are only temporary operations. Traditionally, the only component that uses fossil fuels in regular operation is the lime kiln. (Kuparinen & Vakkilainen 2017)

Lime kilns are used in many different industries to convert calcium carbonate ($CaCO_3$) into lime (calcium oxide, CaO). In the pulp industry, the lime kiln is needed to complete the chemical recovery cycle in a pulp mill. Figure 2 shows a rotary lime kiln, which are used as the lime kiln in pulp mills. The lime kiln has a high heat demand, which is why fossil fuels have been convenient as a fuel for many pulp mills. In recent years, some pulp mills have started to use more renewable fuels in lime kilns. In addition to increasing sustainability, using renewable fuels produced at the mill can increase the self-sufficiency of power demand. (Syamsudin & Susanto 2016)

Figure 2: A rotary lime kiln in a pulp mill (Valmet 2021).

In a news article by EU Science Hub (2018), it is stated that “pulp and paper industry is the fourth most energy-intensive in Europe”. Although most of the energy use in the industry is bio-based, components, such as the lime kiln, still mostly use fossil fuels in regular operation. Therefore, implementing renewable fuels into the lime kiln could bring major reductions to emissions in the industry. The news article published by EU Science Hub (2018) ratifies this statement: switching fuels from fossil

fuels to biofuels in the pulp and paper industry would cut down most emissions of any measure. Implementing carbon capture and storage (CCS) across the industry would reduce emissions even more. With effective CCS and the use of captured carbon dioxide (CO_2) as a raw material to produce a variety of products, the pulp and paper industry could become theoretically carbon negative (Santos et al. 2021). This would fulfill the definition for bioenergy with carbon capture and storage (BECCS), which has been seen as one of the leading strategies to mitigate climate change in recent years (Kuparinen et al. 2019).

In addition to CO_2, pulp mills generate other emissions as well. Just lime kilns can release nitrogen oxides (NO_x), sulfur dioxide (SO_2), total reduced sulfur (TRS) and particulate matter (PM) emissions during normal operation. The amount of each emission can vary greatly between operating conditions, such as the fuel used or the operating temperature of the kiln. These emissions have a variety of adverse effects on the environment. For example, NO_x and SO_2 can cause acid rains, while TRS and PM emissions can decrease the quality of air in residential areas. Therefore, attention should be paid to all emissions instead of only CO_2 levels. (Dahl & Hynninen 2008)

The pulp and paper industry uses biomass from forests as feedstock for products and as an energy source. If unregulated, the industry's use of biomass and bioenergy in production can lead to various harmful effects. In recent years, deforestation and biodiversity decline has been noted by the United Nations (UN) as serious risks facing the world. The UN has set sustainable forest management as one of the UN's sustainable development goals (The United Nations 2021). If fossil fuels are switched completely to bioenergy in the pulp and paper industry, the change has to made with these types of sustainable goals in mind.

Environmental regulations are tightening all the time across the world. The Paris agreement in 2015 and the IPCC report in 2018 aim for global warming of 1.5 °C above pre-industrial levels (IPCC 2018). Finland aims to be carbon neutral by 2035 and carbon negative in the coming years after that (Finnish Government 2019). Along with these obligations to reduce the amount of CO_2 emissions, other emissions released in industrial processes are regulated in increasing amounts to improve the health of humans and the environment. These are ambitious goals that need ambitious measures in all parts of society. For the pulp and paper industry, the lime kiln is one of the most significant components, where improvements can be made to cut down on emissions.

1.2 Thesis objectives, research questions and research scope

The main objective of this thesis is to study the use of renewable fuels in a lime kiln located in a kraft pulp mill. The analysis of these renewable fuels is done with results gained from an Aspen Plus model. The model aims to study the effect of different fuels with process variables, such as fuel usage and emission levels. The results gained from the model are supported by the literature review, which also gives an overall view on pulp mills and the lime kiln as a component.

Secondary objectives include studying an oxyfuel combustion process with the lime kiln model, and comparison of selected renewable fuels by their financial aspects. By implementing oxyfuel combustion to the lime kiln, it is possible to determine if the change in the combustion process would have significant improvements to the process. The model only gives results related to process variables, which is why renewable fuels are compared also on financial and logistical aspects. However, this

comparison is made broadly and without any real data on costs. The optimal fuel choice for a lime kiln should always be made specifically for each pulp mill.

Based on these objectives, three research questions and hypotheses can be applied for this thesis:

1) *What effects does different renewable fuels have on the combustion process in a lime kiln?*

   Hypothesis: Fossil-based CO_2 emissions are decreased when compared to fossil fuels. However, problems may arise with low heating values and fuel impurities, which are typical properties for biomass-based fuels.

2) *How can oxyfuel combustion affect the lime kiln process compared to using a traditional combustion process?*

   Hypothesis: Oxyfuel combustion will improve thermal efficiency, which will lead to decreased fuel usage. It also makes possible to easily capture CO_2 from flue gases. However, overall process efficiency might not improve, because separating oxygen from air is an energy intensive process.

3) *Can renewable fuels be implemented in lime kilns without major financial and logistical challenges?*

   Hypothesis: Financial and logistical challenges will most likely arise if the fuels need to be imported outside of the mill. Renewable fuels also need new equipment related to fuel pretreatment and changes in the combustion process, which will likely increase costs even more. In some cases, renewable fuels can be created from surplus materials or energy from the pulp mill, what could prove to be a more cost-effective solution than using fossil fuels.

The research scope of this thesis is restricted to mostly concentrate on the lime kiln and the Aspen Plus model created for it. Other pulp mill processes are briefly introduced in the literature review, but most attention is paid to the lime kiln and fuels used in it. The literature review does not go into detail with mechanical aspects of the lime kiln, such as building materials, and lime kiln process controlling strategies. Instead, the literature review concentrates on lime kiln process variables and the effects these variables have on the process. The Aspen Plus model has multiple restrictions, which are done to simplify the model. These restrictions are detailed in Chapter 3.

1.3 Outline of the thesis

Chapter 1 of the thesis presents a small introduction to the pulp and paper industry. The latest trends in the industry are introduced to give importance to the chosen thesis subject. The thesis objectives, research questions and research scope are also explained. In Chapter 2, which acts as the literature review of the thesis, an overview of pulp mill processes is first presented. The focus of the literature review then moves on to the lime kiln, which is the main topic of the thesis. The lime kiln is mainly studied by the aspects that are relevant in constructing the model. Different lime kiln fuels as well as the oxyfuel combustion process are shortly presented at the end of the chapter.

The lime kiln model is described in detail during Chapter 3 to provide all the necessary information for the reader to understand the results provided by the thesis. The most important model settings are presented while also explaining the restrictions that the model has. The results of the model are then presented in Chapter 4. The chapter consists of studying the cases created for the model and three different sensitivity analyses. Some of the results are also compared to other suitable literature. Chapter 5 includes discussion of the results gained in Chapter 4. Also, financial aspects of oxyfuel combustion and studied renewable fuels are examined briefly. Chapter 6 presents conclusions of the thesis, answers the research questions, and gives suggestions for future work.

2 Literature review

2.1 Introduction to pulp mills

In a pulp mill, the main purpose of the process is to liberate fibers from the wood or plant material. This fibrous mass gained in the process is referred to as pulp and it can then be used to manufacture different types of paper products. The general term 'yield' is used to describe how much pulp is gained from the raw material by mass percentage. The pulping process used to manufacture pulp affects the properties of the produced paper. The most important properties are strength and printability, and these properties affect mostly in what application the paper is used. (Brännvall 2009)

There are many different pulping processes used globally to manufacture pulp. Different pulping processes can be classified broadly into four different categories: mechanical, chemical, semichemical and chemimechanical. Mechanical pulping uses mechanical energy to convert wood into pulp. In the process, wood is grinded against a wetted surface at high speeds to release fibers from the wood material. It produces a high yield of pulp (92–96 %) but requires a lot of energy. Chemical pulping uses chemicals and heat to produce pulp. The chemicals and wood are cooked together to dissolve most of the lignin away from the wood material. The chemicals also dissolve some of the fibers in the wood, which reduces the pulp yield to around 50 %. In chemical pulping, much less energy is needed to create pulp when compared to mechanical pulping. Chemimechanical and semichemical pulping processes combine mechanical and chemical pulping to produce pulp with higher yield than with chemical pulping. (Bajpai 2018)

Table 1 shows global virgin pulp production by different grades of pulp annually. It can be seen that chemical pulping is the most used process to produce virgin pulp globally with kraft pulp leading the line. However, kraft pulp is not the most produced pulp product globally. According to Smook (2016), over 230 Mt of recycled pulp is produced every year. The amount of recycled pulp can only be estimated to grow in the coming years with circular economy and recycling growing in importance each year.

Table 1: Global virgin pulp production by grade of pulp (Smook 2016).

Grade of pulp	Production (Mt per year)	Type of pulping process
Kraft	151.3	Chemical
Bleached Chemimechanical	8.2	Chemimechanical
Thermomechanical	8.2	Mechanical
Dissolving	7.2	Chemical
Soda	6.2	Chemical
Sulfite	5.7	Chemical
Neutral Sulfite Semichemical	5.3	Semichemical
Groundwood	5.0	Mechanical
TOTAL	**280.9**	

As shown in Table 1, the kraft process is the most used chemical pulping process used globally. It accounts for approximately 90 % of chemical pulp and for over half of all virgin pulp produced annually around the world. In the kraft process, wood is cooked together with sodium hydroxide

(NaOH) and sodium sulfide (Na_2S) to dissolve approximately half of the wood material. This cooking process leaves behind a solution, which consists of pulp and weak black liquor. The pulp is separated from the weak black liquor by washing and can then be used to produce paper products. The weak black liquor can be recovered to be used in the kraft process again as chemicals and as power to produce heat and electricity for the plant. This high amount of chemical recovery is one of the main benefits of the kraft process. Around 97 % of chemicals can be recovered during the process. Other benefits of the kraft process are high strength of pulp produced and the flexibility of the process to use many species of hardwood and softwood as raw materials. (Tran & Vakkilainen 2016)

In a kraft pulp mill, the whole process of pulp production is based around the kraft recovery process. The kraft recovery process aims to recycle the inorganic cooking chemicals used in the process so that less chemicals need to be fed into the process each cycle. Other objectives of the kraft recovery process are to generate heat by burning the organic materials gained from the wood material, and to reduce water and air pollution. The kraft recovery process can be summarized into four main steps:

1. Concentration of weak black liquor
2. Combustion of high dry solids black liquor
3. Preparation of white liquor from green liquor
4. Burning lime mud to recover lime

After white liquor is prepared from green liquor in the causticizing plant, it can be used once again to cook wood. (Bajpai 2018) Figure 3 shows the kraft recovery process cycle in simplified process diagram. The following paragraphs will shortly describe these four main steps of the recovery process in more depth.

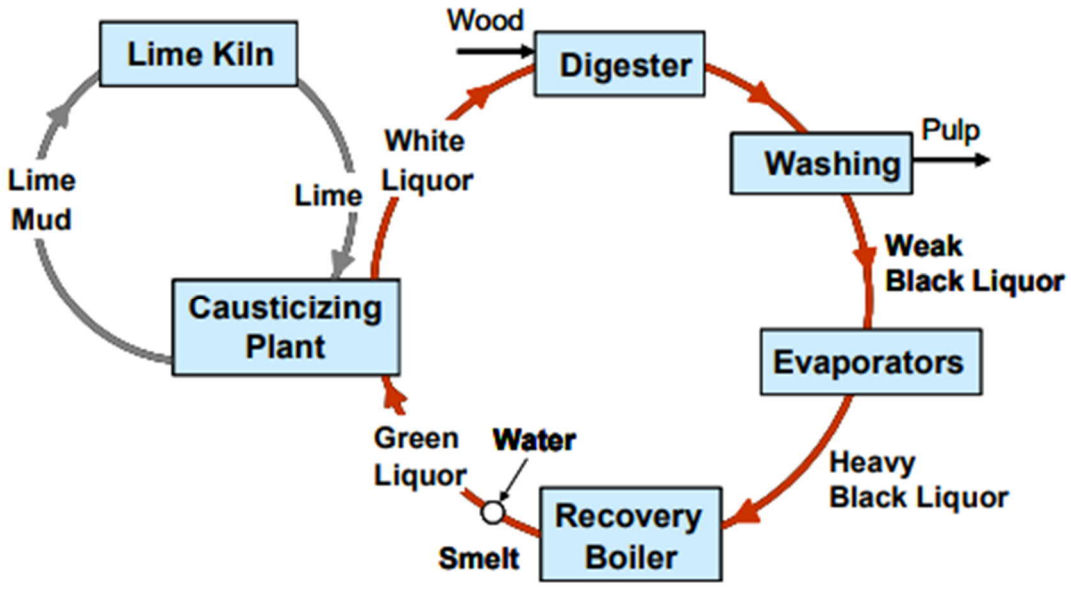


Figure 3: The kraft recovery process diagram (Tran & Vakkilainen 2016).

1. Concentration of weak black liquor

After the washing process, weak black liquor has a solids content of 13–17 %. Burning a fuel with this low of a solids content is not an optimal way of producing power. Therefore, weak black liquor is concentrated by evaporating water away. This increases the solids content of the black liquor to around 50 %. Most of the evaporation process is done in multiple-effect evaporators, which a series of evaporators operating at different pressure levels. Multiple-effect evaporators are advantageous because of their high steam economy; each evaporator's vapor is led to the next evaporator as steam supply. After the multiple-effect evaporators, concentrators are typically used to increase the solids content to 75–85 % to make the black liquor suitable for combustion. (Smook 2016)

2. Combustion of high dry solids black liquor

High dry solids (or heavy) black liquor is combusted in the kraft recovery process to achieve two objectives: to gain heat power for steam and power generation for the pulp mill and to recover the inorganic chemicals in the black liquor as smelt. The combustion process happens in a recovery boiler, which makes it possible to achieve these two different objectives. High dry solids black liquor is sprayed into the furnace and the droplets combust either completely or partially during flight. Remaining droplets fall down to the char bed, where remaining char in the droplets is oxidized. The main inorganic reaction for the droplets is the reduction of sulfates into sulfides. These inorganic compounds are then recovered from the bottom of the boiler as molten smelt and are transported into the smelt dissolver, where smelt is dissolved in water to form green liquor. (Theliander 2009a)

3. Preparation of white liquor from green liquor

Green liquor, which consists mostly of sodium carbonate (Na_2CO_3) and Na_2S, is transported into the causticizing plant. In the causticizing plant, Na_2CO_3 in the green liquor is converted into NaOH. Na_2S does not react with any compounds during the process. The product solution, which consists mostly of NaOH and Na_2S, is known as white liquor. White liquor contains all the necessary chemicals to cook wood with to create pulp at the digester. (Tran & Vakkilainen 2016)

The causticizing plant contains two main chemical reactions, which convert Na_2CO_3 into NaOH. The first reaction is known as the slaking reaction:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (1)$$

In this reaction, CaO coming from the lime kiln reacts with water in high temperature to create calcium hydroxide ($Ca(OH)_2$). $Ca(OH)_2$ can then be used in the second reaction, called the causticizing reaction, to create NaOH:

$$Ca(OH)_2 + Na_2CO_3 \rightarrow 2\,NaOH + CaCO_3 \quad (2)$$

$CaCO_3$ together with some impurities and moisture creates a substance, which is referred to as lime mud. This lime mud must be separated from white liquor before white liquor can be transported into the digester to cook wood. The clarification of white liquor can be done in settling tanks by sedimentation and with various filters. (Bajpai 2018)

4. Burning lime mud to recover lime

Lime mud created in the causticizing reaction (2) can be converted back into lime at the lime kiln. In this way, also lime can be recovered and reused in the causticizing plant. Before lime mud is transported to the lime kiln, it is washed to remove residual white liquor that was not separated earlier in white liquor clarification. Inside the lime kiln, the calcination reaction takes place when temperature is high enough:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{3}$$

If the calcination process is done properly, more than 90 % of lime can be recovered to be reused in the causticizing plant. (Smook 2016) The next chapter will go more in depth with lime kiln operation and the calcination reaction inside the lime kiln.

2.2 The lime kiln

The process of lime reburning happens in a lime kiln. The lime kiln is a counter-flow heat exchanger in which heat from the combustion gases is transferred to the lime particles directly in the same environment. The hot combustion gases are produced in a burner by combusting a suitable fuel. The rotary lime kiln is the most used component for lime reburning globally. There are some other alternative systems for lime reburning, but the rotary lime kiln has been favored due to its superior heat economy. (Engdahl et al. 2008)

The rotary lime kiln is a long tube-style heat exchanger that is constantly rotating at a slow speed and is set at a slight angle in the horizontal direction. Lengths of rotary lime kilns vary from 50–120 m and diameters from 2.4–4 m. Lime mud enters the kiln from the top and is moved to the other end of the kiln because of rotation and angle of the rotary lime kiln. Simultaneously the temperature of lime is increased due to the burner located in the lower end of the kiln. (Bajpai 2018) A schematic of a typical rotary lime kiln can be seen in Figure 4.

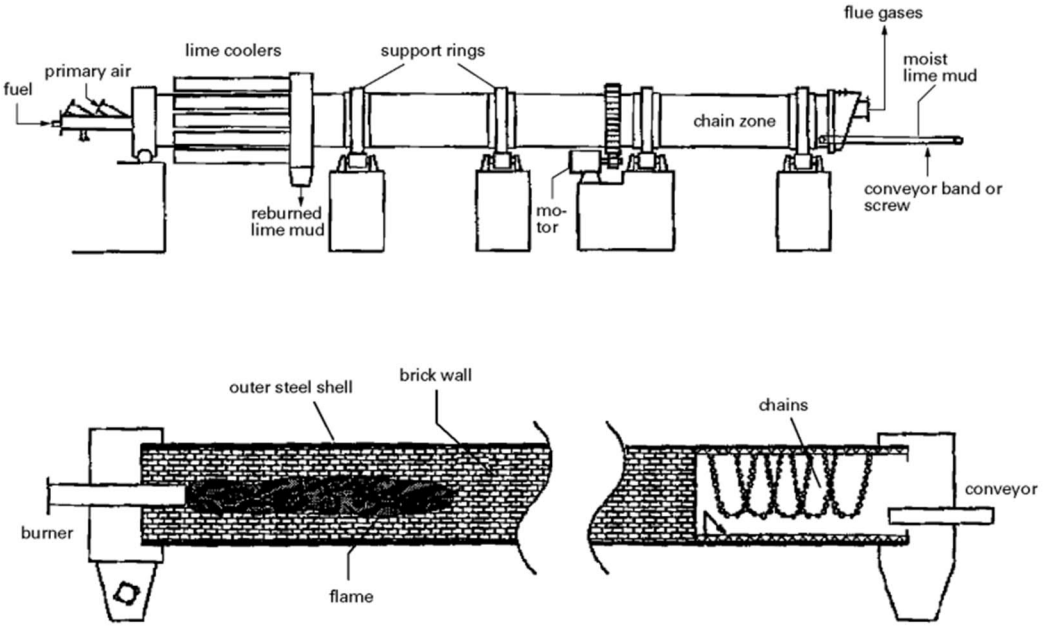


Figure 4: The interior and exterior schematic of a typical rotary lime kiln (Theliander 2009b).

The lime reburning process in a rotary lime kiln can be divided into four different zones: drying, heating, calcination, and sintering. In the drying zone, wet lime mud is dried with heat from the hot combustion gases. A chain system is typically implemented in the drying zone to increase heat transfer between the combustion gases and lime mud. After the drying process, lime is heated to a proper calcination temperature in the heating zone. When the calcination temperature is reached at the start of the calcination zone, the calcination reaction (3) starts to take place. The temperature does not increase drastically during this zone, because heat is needed for the endothermic calcination reaction. Finally, the temperature of lime is increased again in the sintering zone. Sintering describes the process, where smaller particles combine to form bigger particles due to the high temperature of the sintering zone. Bigger particles are created in the sintering zone when the rate of sintering is increased. Particle size affects the easiness of filtration for recycled lime after the causticizing plant; smaller particles are more difficult to filter. However, bigger particles react more slowly during slaking and causticizing reactions. Therefore, the rate of sintering should be optimized in the lime kiln to avoid too small or too large lime particles. (Theliander 2009b) The different zones of the rotary lime kiln are presented in Figure 5. The temperatures in the graph are typical for rotary lime kilns, but actual operating temperatures can vary with different operational parameters.

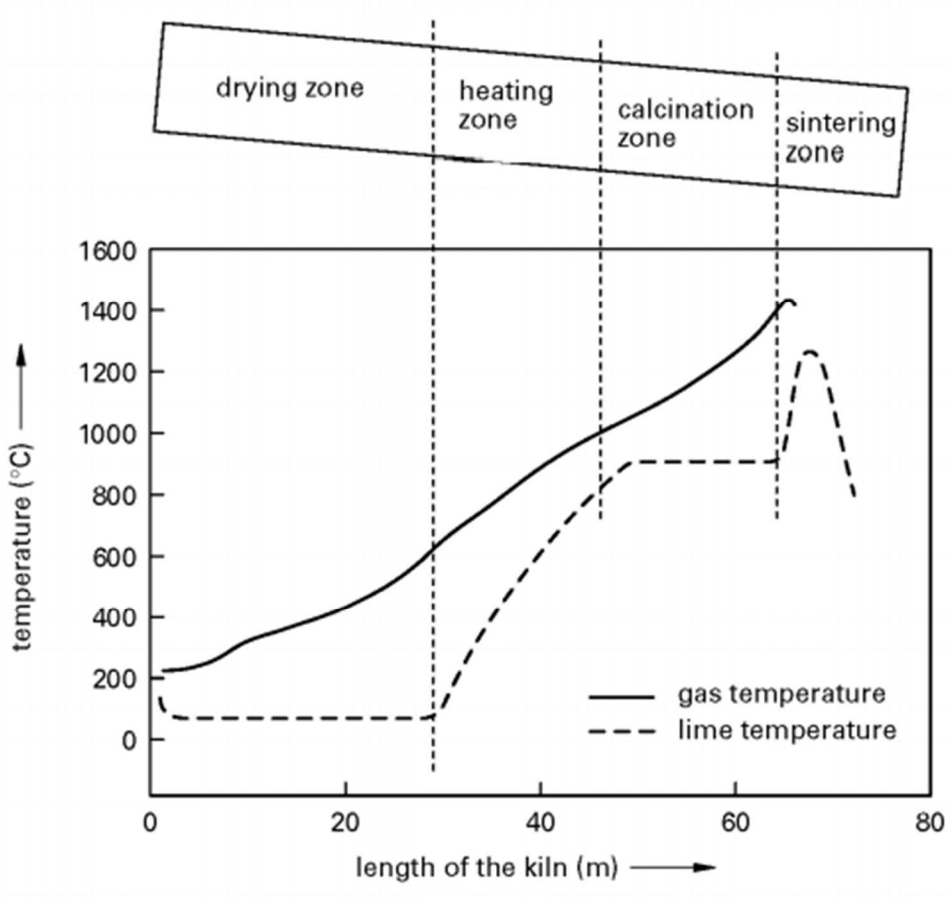


Figure 5: Different zones of the lime reburning process in a rotary lime kiln (Theliander 2009b).

Smook (2016) states that typically calcination temperature in a rotary lime kiln is around 800 °C, and sintering zone temperatures vary between 1150–1250 °C. However, Theliander (2009b) specifies that calcination temperature depends on the CO_2 concentration of the combustion gases and the type of

equipment used in the kiln. The correlation of CO_2 concentration and calcination temperature can be expressed with the following equation:

$$T_c = \frac{-\Delta G}{R \ln\left(\frac{P_{CO_2}}{P_{sys}}\right)} \tag{4}$$

where T_c is the calcination temperature, ΔG is the standard Gibbs free energy change for the reaction, R is the universal gas constant, P_{CO_2} is the partial pressure of CO_2, and P_{sys} is the pressure of the system. This equation can be determined by using the definition of the equilibrium constant for the calcination reaction.

An example of energy balance for the rotary lime kiln is shown in Figure 6. The heat values shown in the figure were calculated with a mathematical model by Shahin et al. (2016), which was created to analyze the thermal energy distribution in the kiln. The model included a preheater and a cooler for lime product. It can be seen that most of heat inserted into the process goes to the calcination reaction. Most heat is lost with flue gases leaving the kiln. Shell heat losses and losses of heat from reburned lime were both around 5 % of total heat input.

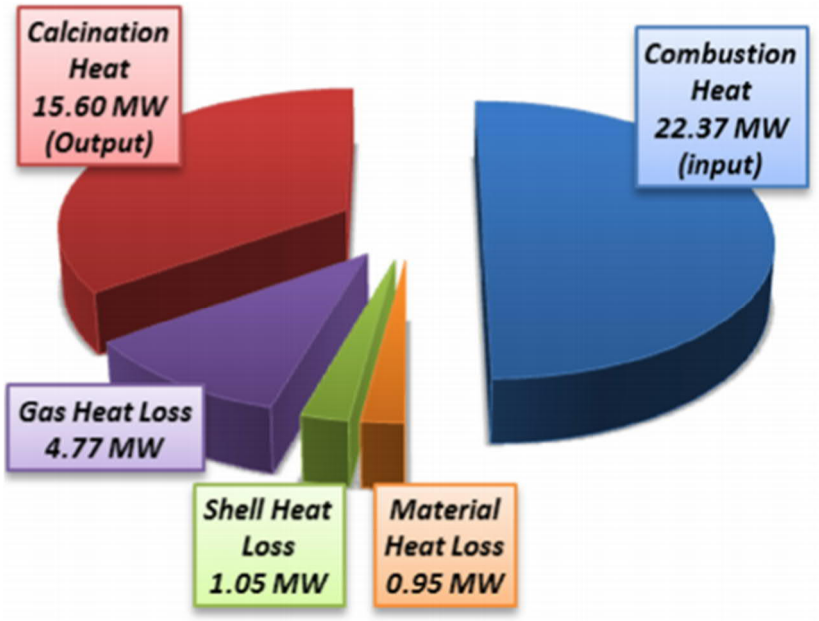


Figure 6: A pie diagram of the energy balance in a rotary lime kiln (Shahin et al. 2016).

The energy balance of a lime kiln is dependent on multiple factors. First, more energy is consumed in the kiln if lime mud has a low dry solids content, because more moisture needs to be evaporated. Also, more energy is consumed if lime mud contains a lot of impurities instead of a higher $CaCO_3$ content. Second, the oxygen content in the combustion gases needs to be optimized to achieve optimal heat consumption. If the oxygen content is too low, the combustion process in the burner will be incomplete. This will lead to formation of unwanted emissions, which will consume surplus energy during these chemical reactions. If the oxygen content is too high, air is supplied to the lime kiln in excess and more energy is lost to the combustion gases than necessary. Finally, the reburned lime quality is dependent on energy input. Heat is needed to convert $CaCO_3$ to CaO by the calcination

reaction in the calcination zone. If $CaCO_3$ content in the reburned lime is kept low, then more energy needs to be fed into the process. (Engdahl et al. 2008)

Modern lime kilns use two substantial modifications to the lime reburning process described earlier. The first one of these modifications is the use of flash dryers to dry the wet lime mud. The flash dryer often replaces the drying zone in the rotary lime kiln. In these kilns, drying is handled outside the kiln and only heating, calcination and sintering happens inside the kiln. (Theliander 2009b) The energy for drying the wet lime mud comes from the hot combustion gases that leave the kiln. The combustion gases have a higher temperature than typically because no energy was lost from the gases to dry the lime mud inside the kiln. The benefits of flash dryers are that they can increase the production capacity of a rotary lime kiln and make it possible to have a significantly shorter lime kiln in the pulp mill. (Bajpai 2018) The second modification for modern lime kilns is the use of coolers to capture the heat from lime leaving the kiln. Normally the reburned lime leaves the kiln at around 950 °C. With these coolers, heat can be transferred from the lime to the combustion air entering the kiln. After the coolers, lime is transported to the causticizing plant at around 350 °C. One type of cooler, the integral tube cooler, is shown in Figure 7. The use of coolers for reburned lime significantly improves the energy efficiency of a rotary lime kiln. (Smook 2016) A survey in 2008 conducted by Francey et al. (2011) shows that of 67 lime kilns included in the survey around 80 % had installed coolers for lime product and around 40 % had installed separate dryers for wet lime mud.

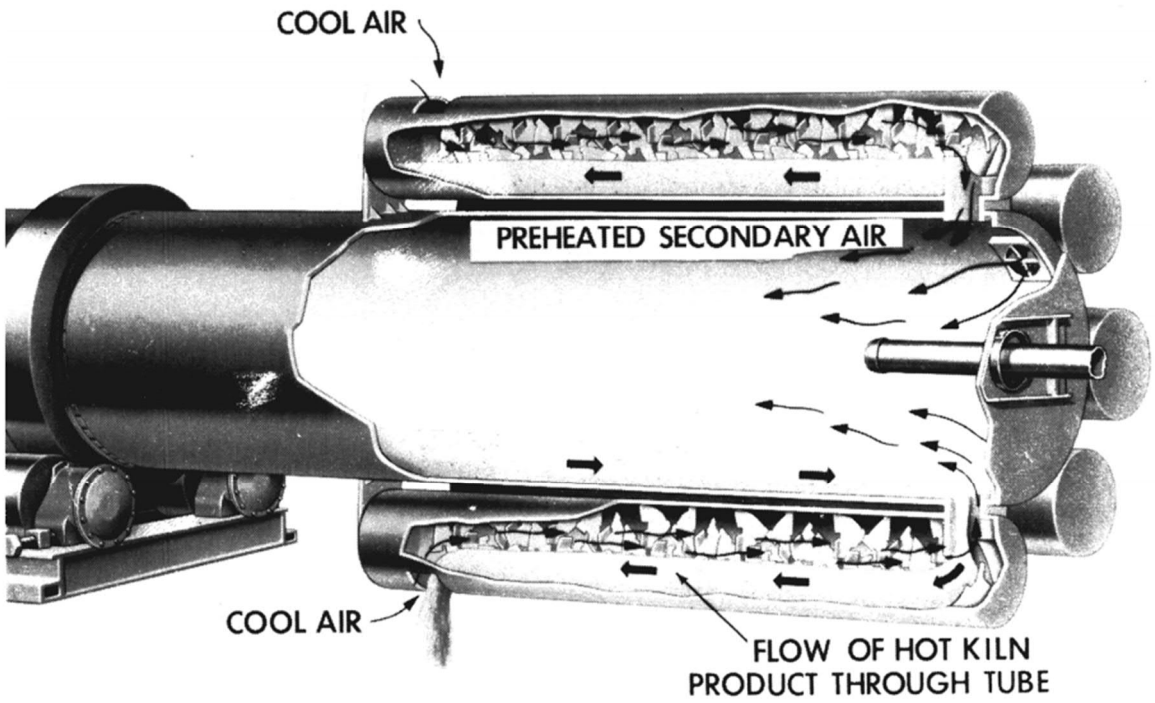


Figure 7: Integral tube coolers attached to a rotary lime kiln (Smook 2016).

One of the main objectives of a lime kiln is to produce good quality lime to be used in the causticizing plant. Reburned lime quality can be evaluated by three attributes: residual $CaCO_3$ content, lime availability and lime reactivity. Residual $CaCO_3$ content in reburned lime should be kept low (1.5–2.5 wt-%) to make sure that reactive lime is produced. $CaCO_3$ content can be controlled by adjusting the temperature near the burner. Lime availability describes the amount of CaO in reburned lime.

However, it is not simply the complement of residual $CaCO_3$ content. Reburned lime also contains various impurities, such as different sodium compounds, that were transferred from the lime mud. This is why lime availability can be used to describe the number of impurities in reburned lime as well as the amount of CaO. Lime availability ranges typically from 85–95 % in kraft pulp mill lime cycles. Lime reactivity expresses how quickly reburned lime reacts in the slaking reaction (1) at the causticizing plant. It is affected by lime availability and specific surface area of reburned lime. (Tran 2007) The specific surface area can be adjusted by controlling the sintering zone parameters in the rotary lime kiln like described earlier in this chapter.

Typical problems and emissions related to rotary lime kiln operation

Ring formation is one of the most severe problems related to rotary lime kiln operation. It can decrease the production capacity of the kiln by limiting the effective radius. In extreme cases, the kiln may need to be shut down to remove the rings. (Eriksson et al. 2019) Ring formation can happen in various parts of the rotary lime kiln due to different agglomeration processes. In general, ring formation happens when lime particles stick to the walls of the kiln or the chains in the chain system. Ring formation becomes more severe in the lower end of the kiln when the rings are strengthened due to recarbonation of CaO. The recarbonation reaction of CaO takes place when temperature in the rings drops below 800 °C due to temperature fluctuations:

$$CaO + CO_2 \rightarrow CaCO_3 \quad (5)$$

This reaction helps to grow the rings layer by layer. With more temperature fluctuations happening the kiln, the ring grows thicker each time with new lime particles adhering themselves to the ring's $CaCO_3$ layer. The strength of the inner layers is maintained, because the external layers work as insulation to maintain the temperature under 800 °C. In addition to the recarbonation reaction, a high SO_2 concentration in the kiln can lead to the sulphation reaction of CaO:

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \quad (6)$$

However, this reaction happens in a small temperature range (900–1200 °C) and is relevant only if high sulfur content fuels are used, because in most cases CO_2 concentration in the kiln is much larger than the SO_2 concentration. Ring formation in a rotary lime kiln can be decreased by minimizing the temperature fluctuations and by increasing the lime mud dry solids content to make the lime particles less adhering to the walls. Also, sodium left in the lime mud after washing helps ring formation, so more thorough lime mud washing before the lime kiln decreases ring formation. (Tran 2007)

Dusting in the lime kiln takes place when lime mud is rotated and transported through the kiln. Dust particles from lime mud create a dust stream that moves out of the kiln with the combustion gases. Typically, 5–20 % of dry lime mud feed is lost through these dust streams. Most of the lime mud dust can be captured by a scrubber or electrostatic precipitator (ESP) and recycled back to the kiln. (Tran 2007) The most important factors affecting the rate of dusting are the particle sizes of solids moving through the kiln and gas velocity in the kiln. Dusting can have various negative impacts on the operation of the lime kiln. First, dusting at the hot end of the kiln has an adverse effect on heat transfer near the burner, what can affect the general performance of the kiln. Second, the quality of reburned lime is affected due to lower reactivity of reburned lime. (Dernegård et al. 2017) Finally, dust can in

certain conditions stick to the walls of the kiln and in this way contribute to ring formation. These 'dust rings' are relatively weak and normally fall down by themselves, but the recarbonation reaction (6) can help make these rings stronger if temperature fluctuates under 800 °C. (Gorog & Leary 2016)

The GHG emission, which is most abundantly produced in lime kilns, is CO_2. It is released to the flue gases mainly in the calcination reaction and in the burning process of carbon-based fuels. The CO_2 that is released in the calcination reaction is typically more significant in terms of amounts of CO_2 released into the atmosphere. Kraft pulp mill lime kilns in the US released 9.6 Mt of CO_2 to the flue gases due to the calcination reaction, while 4.9 Mt of CO_2 was released in the burning process of fuels during the year 1995. Although close to twice as much CO_2 is released in the calcination reaction, the carbon released in this CO_2 is of biomass origin. The carbon in biomass turns into CO_2 during combustion in the recovery boiler, reacts with sodium compounds in the recovery boiler to form Na_2CO_3, converts into $CaCO_3$ during causticizing (2), and is released from $CaCO_3$ as CO_2 in the lime kiln. (Miner & Upton 2002) Therefore, the effect of this CO_2 can be regarded as carbon neutral in terms of the atmosphere. More attention should then be paid to CO_2 released in burning carbon-based fuels. In most lime kilns around the world, only fossil fuels are burned to produce heat. Out of 67 lime kilns included in the survey by Francey et al. (2011), only four do not use fossil fuels at all. If renewable fuels and effective CCS would be implemented, the calcining process in the lime kiln could become theoretically carbon negative. Thereby, the process of BECCS would be realized for the lime kiln.

Table 2 presents all the other emissions released in a lime kiln to air with some typical emission concentrations. In addition to these emissions, some amounts of carbon monoxide (CO) and volatile organic compounds are released from the lime kiln to the atmosphere. However, these emissions are usually relatively low when the kiln runs with excess air. (Engdahl et al. 2008)

Table 2: Typical emissions of a lime kiln (Dahl & Hynninen 2008).

Emission	**Condition**	**Concentration (mg/m^{3}n)**
SO_2	oil firing without NCGs	5–30
	oil firing with NCGs	150–900
PM	after ESP	20–150
	after scrubber	200–600
NO_x (as NO_2)	oil firing	240–380
	gas firing	380–600
TRS (as H_2S)		< 50

SO_2 emissions are released mainly during the oxidation of sulfur in the fuel or in non-condensable gases (NCGs). These NCGs are collected from other processes in a kraft pulp mill and are combusted to recover the energy in the gases. NCGs contain reduced sulfur compounds, which oxidize into SO_2 during combustion. If NCGs are fed into the lime kiln, the SO_2 emissions grow significantly larger because of the large amounts of reduced sulfur compounds in NCGs. SO_2 emissions can be controlled by using a scrubber to capture sulfur from the flue gases and recycling it back to the chemical recovery cycle. With different types of scrubbers, around 80–95 % of SO_2 emissions can be captured. The combustion of fuels with low sulfur contents, such as natural gas and wood materials, also have a positive effect in reducing SO_2 emissions. (Dahl & Hynninen 2008)

Particulate matter released from the lime kiln to the flue gases consist of lime mud dust and condensed sodium compounds (Na_2SO_4 and Na_2CO_3). The reasons for dusting of lime mud were explained earlier in the chapter concerning dusting in the rotary lime kiln. Sodium compounds vaporize from the lime mud in the hot end of the kiln and condense into small particles during the cooler zones of the kiln. This cycle of sodium compounds can be seen in Figure 8. PM emissions can be captured from the flue gases by using a scrubber or an ESP. Scrubbers can capture most of the lime mud dust, but it does not work well with capturing the sodium compounds. If PM emissions want to be kept low, then also an ESP needs to be installed. (Engdahl et al. 2008)

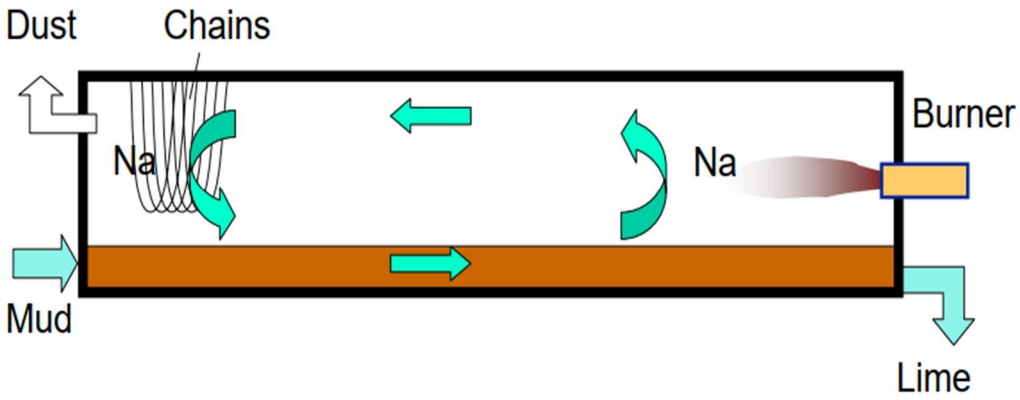


Figure 8: The cycle of sodium compounds inside the lime kiln (Tran 2007).

Various nitrogen oxides form during the combustion process in the lime kiln. These emissions can be released in two ways: as thermal NO_x and as fuel NO_x. Thermal NO_x is formed from nitrogen (N_2) and O_2 in the combustion air by the simplified global reaction:

$$N_2 + O_2 \rightarrow 2\,NO \tag{7}$$

However, this reaction becomes significant only in temperatures of 1300 °C and higher. Because the temperature in the lime kiln rarely reaches this high, thermal NO_x is not the major reason for large NO_x emissions. Fuel NO_x originate from the reaction between the nitrogen compounds in the fuel and oxygen in the combustion air. This reaction starts to happen at a much lower temperature (650 °C), which makes it a more viable path for releasing NO_x emissions. The nitrogen content of the fuel has significant effect on the amount of fuel NO_x released. This can be seen as well in Table 2: firing natural gas, a nitrogen rich fuel, instead of oil increases NO_x emissions drastically. In addition to the fuel choice, optimizing the burner in terms of the flame shape and air distribution help to minimize the forming of fuel NO_x. (Engdahl et al. 2008) Like with SO_2 emissions, inputting NCGs into the kiln increases NO_x emissions. NO_x emissions can be eliminated from the flue gases using selective non-catalytic reduction or selective catalytic reduction. Both of these methods involve using chemicals, such as ammonia and urea, to convert NO_x into N_2. (Dahl & Hynninen 2008)

TRS emissions are released from the lime kiln mainly as hydrogen sulfide (H_2S). TRS emissions cause foul odor problems even at low concentrations that can be a problem for residential areas near kraft pulp mills. H_2S emissions from the lime kiln originate mainly from residual Na_2S content, which

has been left in the lime mud by the white liquor. In the low temperatures of the drying zone, Na_2S breaks down to form H_2S according to the following reaction:

$$Na_2S + CO_2 + H_2O \rightarrow H_2S + Na_2CO_3 \quad (8)$$

However, in higher temperatures H_2S reacts quickly with O_2 to produce SO_2:

$$2\,H_2S + 3\,O_2 \rightarrow 2\,SO_2 + 2\,H_2O \quad (9)$$

Therefore, the chemical reaction determined by (8) is only relevant in the cold end of the lime kiln. H_2S can also be formed in the hot end of the kiln through sulfur if not enough air is brought into the combustion process. The sulfur originates from the use of fuels with high sulfur content or from NCGs. Excess air in both ends of the kiln helps to ensure that reaction (9) converts H_2S to SO_2, which then can be collected away from the flue gases by a scrubber. In addition of using excess air in the kiln, TRS emissions can be decreased by limiting the amount Na_2S fed into the kiln. This can be achieved by better operation of the lime mud filters. (Järvensivu et al. 1999)

2.3 Fuels used in lime kilns

Lime kilns require a lot of heat to convert $CaCO_3$ to CaO. An average lime kiln requires 5–8 GJ of heat per tonne of produced CaO. (Francey et al. 2009) This heat is provided by the burner in which various fuels can be combusted. Traditionally only fossil fuels, such as heavy fuel oil (HFO) and natural gas, have been combusted in lime kilns. These fuels have been cheap to use and have been readily available in various parts of the world. However, fossil fuel costs are increasing and there is a global drive to move away from using fossil fuels. This is why there is more interest in using various renewable fuels in lime kilns. (Manning & Tran 2015) This chapter presents multiple fossil and renewable fuels, which have been either used or researched for use in lime kilns. All of the fuels are shown in Table 3 at the end of this chapter with some fuel properties that are crucial for lime kiln operation.

Fuels in the lime kiln can be combusted by themselves or in conjunction with some other fuel using cofiring. Cofiring has been widely adapted in many lime kilns using traditional fossil fuels and waste streams from the kraft pulp mill. NCGs are one of these waste streams that are typically combusted in the lime kiln together with HFO and natural gas. However, NCGs have a low heating value that limits the use of NCGs to 15 % of total heat input. This is done to avoid temperature fluctuations in the kiln. (Engdahl et al. 2008) In addition to NCGs, different biomass waste from a kraft pulp mill or other renewable fuels can be used in cofiring. Also in these cases, careful attention needs to be paid to the properties of the fuels used in cofiring to avoid problems in combustion. (Manning & Tran 2015)

Natural gas

Natural gas is one of the traditional fuels used in lime kilns to provide heat power. According to the survey conducted in 2008, close to half of the lime kilns use natural gas as the main fuel (Francey et al. 2011). Natural gas has suitable thermodynamic properties to work as a fuel in the lime kiln. The lower heating value (LHV) and adiabatic flame temperature of natural gas are high enough to provide

stabile combustion in the kiln. Natural gas consists mostly of methane (CH_4), but it also has a relatively high nitrogen content that can lead to high amounts of NO_x emissions. (Engdahl et al. 2008) In Southern Finland, natural gas is widely available due to the gas transmission network that is connected to Russia (Gasgrid Finland Oy 2021). In areas such as this, connecting a kraft pulp mill to the natural gas supply is logistically easy and there is no need for separate transportation of fuels into the mill in terms of the lime kiln.

Heavy fuel oil

HFO has been traditionally used widely in shipping and in industrial burners, such as the lime kiln. It is the residual product of the oil refining process where more valuable components of crude oil are extracted to other fuel oils. This is why it has been a relatively cheap fuel to use and is still widely available around the world. However, HFO contains various contaminants that lead to high amounts of emissions and NPEs. These include some amounts of ash and compounds, such as vanadium and aluminum. (Vard Marine Inc. 2015) Most notably it has a high sulfur content, which leads to high amounts of SO_2 emissions. Although HFO has sufficient thermodynamical properties to work in the lime kiln, the chemical composition of HFO is not ideal for emission regulations in the world today. (Engdahl et al. 2008)

Wood residues

Substantial amounts of wood residue, such as bark, is produced in a kraft pulp mill. Wood residues can also be acquired from other factories in the forest industry. One example of this is sawdust from sawmills. This makes it a potentially cheap alternative to replace fossil fuels in the lime kiln. However, the economics of using wood residues as a fuel depends on transportation costs and the current use of wood residues. Transportation of wood residues in large amounts can be logistically challenging, because it has a lower heating value compared to natural gas and HFO. (Francey et al. 2009) Therefore, transportation can become costly in terms of money and emissions released during transportation. Wood residues are also already used in many kraft pulp mills to power steam boilers, which provide process steam to multiple pulp mill processes (Engdahl et al. 2008). Estimates of profitability and energy efficiencies need to be made to correctly assess the best use of wood residues.

Solid biomass fuels, such as various wood residues gained from the pulp mill, cannot be combusted in the lime kiln as they are without complications. Wood residues contain significant amounts of ash, which bring harmful non-process elements (NPEs) into the lime cycle. In addition, the moisture content of wood residues is usually high. (Engdahl et al. 2008) Extensive biomass pretreatment is required to improve the efficiency of wood residue combustion. The pretreatment processes include drying, chipping and grinding the biomass. Biomass drying is done to increase the heating value of the fuel, so that the adiabatic flame temperature can reach a high enough temperature. Drying can be achieved with hot flue gases leaving the kiln, but there is major fire risk if biomass is dried directly with flue gases. Therefore, hot water or steam gained from various heat sources in the mill is favored in the drying process. Chipping and grinding reduces the particle size of the biomass to a consistent size so that it can properly be used as a fuel. The particle size, which is aimed for during grinding, depends on the conversion process of the biomass for fuel use. (Kuparinen & Vakkilainen 2017)

After pretreatment, the wood residues can be directly combusted if they are pulverized completely during grinding. Pretreated wood residues can also be converted for fuel use through different conversion processes. There are three distinct conversion processes that have been either implemented in commercial lime kilns or tested in different research environments: gasification, torrefaction and fast pyrolysis.

Direct combustion of pulverized wood residues is a relatively simple process after biomass pretreatment. Grinding during pretreatment needs significant amounts of energy, because the wood particles need to be 1 mm in size on average. Specified pulverized fuel burners are used to combust pulverized wood residues in the lime kiln. Some problems of direct combustion of pulverized wood residues include fire hazards in the fuel feeding system and clogging of the grinders. (Kuparinen & Vakkilainen 2017) Because considerable amounts of ash remains in pulverized wood residues, lots of NPEs are also inserted into the lime kiln. This lowers reburned lime quality in terms of lime availability and increases the need of adding make-up lime into the lime kiln. (Francey et al. 2009)

Gasification turns dried biomass into a producer (or product) gas, which consists mostly of various combustible gases. This producer gas can then be fed into the lime kiln to be combusted. The gasification process is done usually in a circulating fluidized bed (CFB) gasifier through different thermochemical reactions. A schematic of a CFB gasification process implemented with a lime kiln is shown in Figure 9. Fuel flexibility is one of the advantages of gasification. It can accept various types of biomass with different particle sizes and heating values. This means that biomass pretreatment for gasification does not require as much energy as for pulverizing wood residues for direct combustion. Gasification also extracts most NPEs away from the biomass due to effective ash separation. (Taillon et al. 2018) The LHV of producer gas is relatively low, which leads to increased flue gases leaving the lime kiln. According to Hart (2020), this can lead to problems related flue gas capacity and increased dusting. Gasification is a proven technology that has been implemented in multiple kraft pulp mills (Taillon et al. 2018). One example of this is the Metsä Group bioproduct mill in Äänekoski, which creates producer gas from gasified bark to be combusted in the lime kiln (Metsä Group 2018).

Torrefaction of wood residues involves a slow pyrolysis process, where biomass is upgraded in terms of LHV in the absence of oxygen. Biomass is pyrolyzed in temperatures of 200–300 °C during 0.5–2 hours. The properties of torrefied biomass resemble coal as it is hydrophobic and brittle. Therefore, it can be combusted in the lime kiln using pulverized fuel burners. Pulverization of torrefied wood residues is easier and takes less energy than with direct combustion of pulverized wood residues. Like with gasification, the torrefaction process is flexible and accepts wood residues of varying quality. However, NPEs are inserted into the kiln together with torrefied wood residues, so similar problems arise due to high ash amounts like with pulverized wood residues combustion. (Kuparinen & Vakkilainen 2017)

In fast pyrolysis, bio-oil is produced from wood residues in pyrolysis temperatures of around 400–500 °C. Bio-oil contains condensed volatile organic compounds, a high-water content of 20 wt-% and a low ash content. This is why bio-oil acts more similarly to natural gas in combustion than fuel oils, such as HFO. (Manning & Tran 2015) The conversion process of fast pyrolysis has usually a yield of 60–70 %. The by-products of fast pyrolysis can be combusted to provide heat for the pyrolysis process. (Hamaguchi et al. 2013) Tests in some lime kilns have shown that lime quality and emission levels with bio-oil are similar to natural gas. Possible problems can arise with fuel storage or injection

equipment due to viscosity and low pH level of bio-oil. (Francey et al. 2009) Bio-oil also has a relatively low adiabatic flame temperature compared to other lime kiln fuel alternatives (Lehto et al. 2014). This could lead to problems in the combustion process.

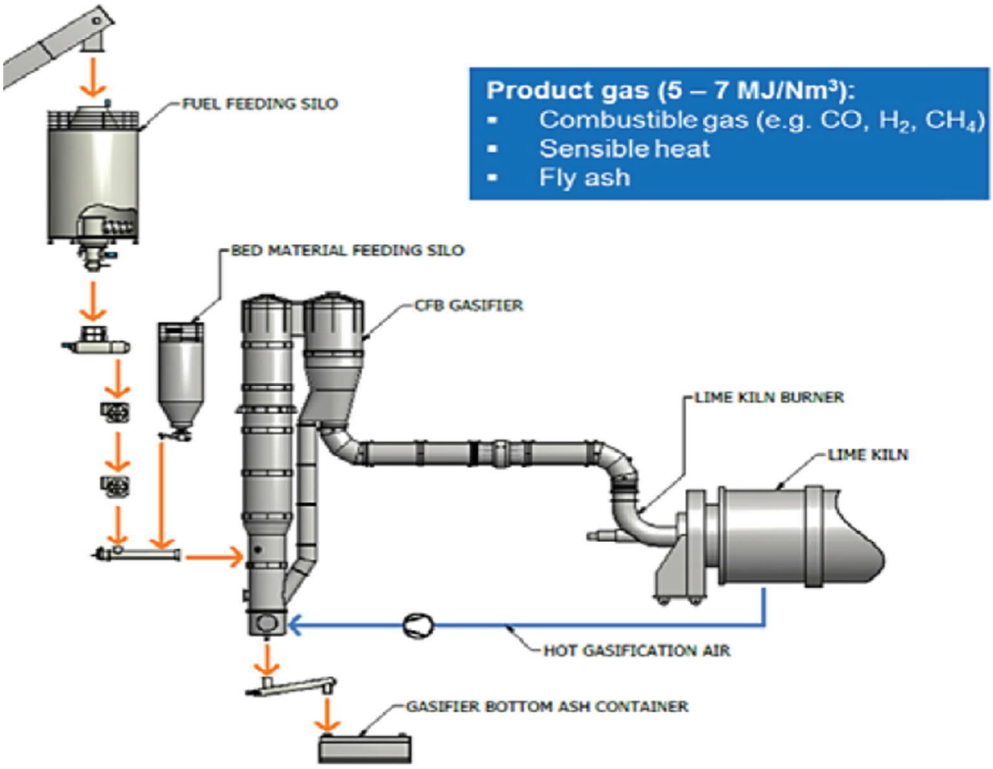


Figure 9: A schematic of a CFB gasifier for lime kiln fuel preparation (Taillon et al. 2018).

Lignin

Lignin can be separated from black liquor during black liquor evaporation. Separated lignin can be then used as a fuel in the lime kiln. One way of lignin separation is the LignoBoost process, where CO_2 and sulfuric acid (H_2SO_4) is used to precipitate lignin. CO_2 for the LignoBoost process can be acquired from lime kiln flue gases instead of importing it from outside the kiln to lower the costs of the process. The lignin needs to be dried and pulverized before combustion in the lime kiln. Tests of lime kilns running only on dried lignin as the fuel have been successful. The LHV is similar to other biofuels and the ash levels are relatively low. (Tomani et al. 2011) Lignin acquired from a kraft pulp mill does have a high sodium content, which is why lignin needs comprehensive washing to avoid problems with ring formation and chemical losses (Francey et al. 2009).

Separating lignin from black liquor affects the energy production in the recovery boiler. The carbon content of black liquor is decreased, which leads to a lower energy production in the recovery boiler. However, kraft pulp mills usually produce surplus electricity that needs to be sold elsewhere. In addition, lignin separation decreases flue gas production in the recovery boiler, what can be a limiting factor in most kraft pulp mills. Therefore, lignin separation can be used to increase pulp production in the mill. (Kuparinen & Vakkilainen 2017)

Alternatively to combusting lignin in the lime kiln, lignin can be sold to different industries, which can then use lignin to produce different products with more value. Lignin acquired from a kraft pulp mill can be used to produce different products, such as carbon fibers and resins, or various chemicals, such as vanillin and aromatics. (Bajwa et al. 2019) Combusting lignin in the lime kiln might not always be the most economical solution for a kraft pulp mill.

Hydrogen

Hydrogen can be produced through the electrolysis of water. The electrolysis reaction breaks down the water molecules into hydrogen and oxygen. The hydrogen produced in the reaction can be fed straight into the lime kiln to be combusted. In addition to purified water, the reaction requires electricity. This electricity can be gained from the surplus electricity that is produced in a kraft pulp mill. Electrolysis of water can be executed by three different technologies: alkaline electrolysis, polymer electrolyte membrane electrolysis, or solid oxide electrolysis. The first two are already commercial technologies with efficiencies of 40–60 %. Solid oxide electrolysis can have a higher efficiency of around 80 %, but it requires a much higher temperature compared to other water electrolysis technologies. Solid oxide fuel cells are mostly still in the research stage and are not ready for wide commercial usage. (Buttler & Spliethoff 2018) The water electrolysis process needs to be cooled with cooling water, which can then be used as a heat source around the mill. In one case study of a Brazilian pulp mill, water heated by water electrolysis produced a third of the pulp mills hot water demand (Hart 2020).

The combustion of hydrogen is a clean process, where no harmful emissions are released into the atmosphere and no NPEs are inserted into the lime cycle. Hydrogen also has suitable thermodynamic properties, in terms of LHV and adiabatic flame temperature, to reach the necessary operating levels required in lime reburning. The oxygen produced in the electrolysis of water can be used in the pulping process, where pure oxygen is needed in the chemical reactions. Leftover oxygen can also be used in the combustion process of the recovery boiler to increase the flue gas capacity of the boiler. While hydrogen has many positive aspects, it is still rather expensive for most kraft pulp mills to invest in. Investment costs of electrolysis equipment are relatively high, and no profits are gained by selling the surplus electricity produced in the mill. This is why hydrogen usage can be profitable only when electricity price is low or alternative lime kiln fuels are expensive. The equipment costs are likely to decrease in the future, what would make hydrogen usage more profitable. (Kuparinen & Vakkilainen 2017)

Crude tall oil & Tall oil pitch

Kraft pulp mills produce crude tall oil (CTO) by separating soap from black liquor before and during black liquor evaporation. Separation of soap from black liquor helps with process stability and pulp quality. When soap is acidulated in sulfuric acid, CTO is produced. CTO is a valuable byproduct, which is often sold to tall oil distillers who refine it further. It can alternatively be combusted in the lime kiln as a fuel. During the refinement process of CTO, tall oil pitch (TOP) is left as a byproduct. TOP also has favorable combustion properties, which is often why kraft pulp mills transport TOP from the refineries back to the kraft pulp mills to be used as a fuel in the lime kiln. (Laxén & Tikka 2008)

The thermodynamic properties of CTO are relatively close to HFO. The sulfur content of CTO is relatively low compared to HFO and other fuels with high sulfur content. Kiln operation is handled in similar ways than with HFO. However, CTO is highly acidic, so specially made equipment is needed for fuel management in the lime kiln. Fluctuation in fuel quality must be kept to a minimum in order to have a steady combustion in the kiln. This includes keeping the viscosity and LHV as constant as possible. (Manning & Tran 2015) TOP has similar attributes compared to CTO in terms of thermodynamic properties and low sulfur content (Forchem 2011).

Table 3: Properties of fuels that can be used in lime kilns.

Fuel	LHV (MJ/kg)	Adiabatic flame temperature (°C)	Contaminants
Natural gas	50	2050	None
HFO	41	2210	Some
Pulverized wood residues	12–19	1950	Substantial
Producer gas	6–7 [a]	1870	Some
Torrefied wood residues	20–30	1840	Substantial
Bio-oil	13–18 [b]	1400–1700 [b]	Some [b]
Lignin	17–26	1980	None
Hydrogen	120	2210	None
CTO & TOP	35–40 [a]	2200–2250 [c]	None [c]

Note. All of the data is from Kuparinen and Vakkilainen (2017) unless labelled with letters a–c. Other sources: [a] Manning and Tran (2015); [b] Lehto et al. (2014); [c] Laxen and Tikka (2008). No information in sources in which conditions the adiabatic flame temperatures were obtained at.

2.4 Oxyfuel combustion and carbon capture in a lime kiln

In order to limit CO_2 emissions from different combustion processes, multiple carbon capture and storage (CCS) technologies have been developed. With CCS, around 85–90 % of CO_2 emissions can be reduced from various sources. This is particularly efficient with singular sources that have significant emissions, such as power plants and large factory complexes. CCS technologies have been researched extensively during the last years and they are already available on the market. However, these technologies are still very costly and usually come with a significant decrease in the energy efficiency of the combustion process. (Leung et al. 2014)

Oxyfuel combustion is one of these CCS technologies that have been developed to limit CO_2 emissions. In oxyfuel combustion, combustion air is replaced with pure oxygen. This decreases the amount of flue gases drastically because air contains mostly nitrogen, which stays largely inert during the combustion. The oxygen for combustion can be produced in an air separation unit (ASU). The flue gases consist of mostly of water, CO_2 and other emissions depending on the fuel. After combustion, CO_2 can be easily separated from the flue gases by compression. The water in flue gases condensates in high pressures, while other gases can be separated from the CO_2 stream in a separate purification unit. The purified CO_2 can then be either stored or used in other processes to produce various compounds. (Toftegaard et al. 2010) A schematic of oxyfuel coal combustion with CCS can be seen in Figure 10. A similar configuration could be implemented for the lime kiln.

When combustion in the lime kiln is done with pure oxygen, the flame temperature increases drastically compared to using just air. Flue gas recirculation (FGR) is typically used to control the flame temperature to a proper level. Using FGR has two significant effects on the process. First, using FGR affects the energy balance of the lime kiln. The mass flow rate and composition of recirculated flue gases significantly affects the combustion process. Second, the CO_2 concentration of recycled gases are high, which increases the calcination temperature in the lime kiln. (Eriksson et al. 2014) The suitable level of FGR, which will give an optimal reburned lime quality and energy efficiency for the lime kiln, needs to be calculated for each separate kiln.

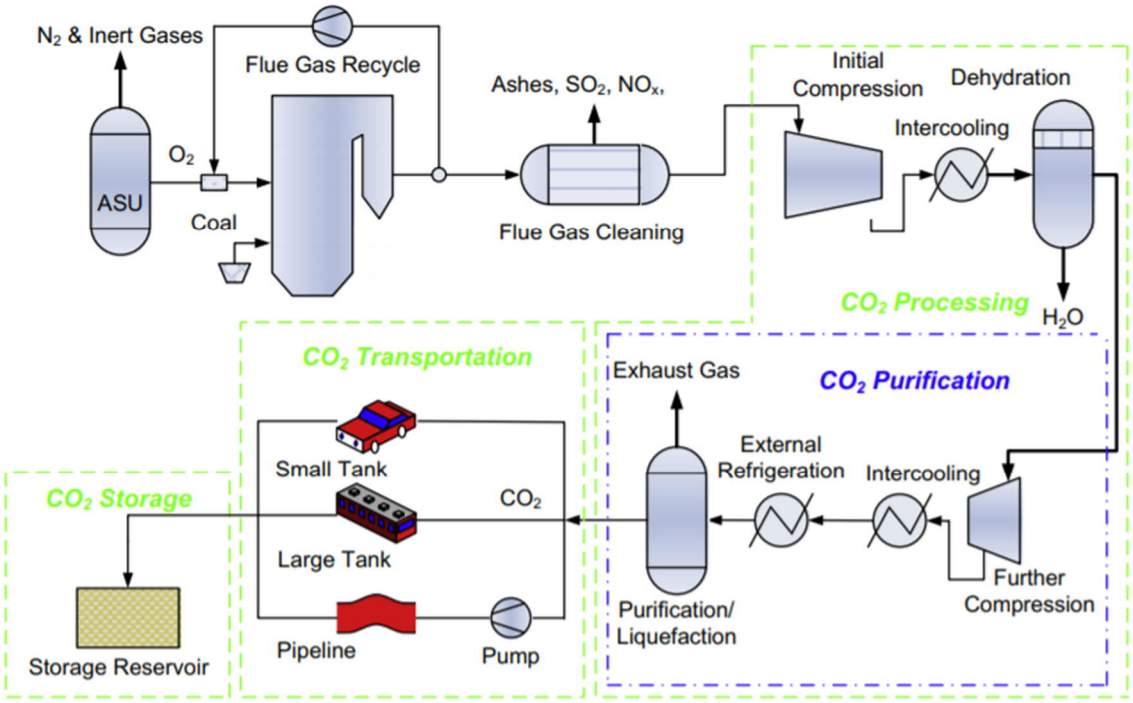


Figure 10: Process scheme of oxyfuel coal combustion and CCS (Li et al. 2009).

After CO_2 is captured from the flue gases, it needs to be either transported elsewhere or utilized at the mill as raw material. When CO_2 is transported away from the mill, it can be utilized for other industrial processes or moved to a geological storage. For example, CO_2 can be used to produce chemicals, such as ammonia and urea. Geological storage has been considered one of the most viable options for the storage of large amounts of CO_2, what will most effectively reduce the effect of climate change. (Leung et al. 2014) During their research of using CCS technologies in kraft pulp mills, Kuparinen et al. (2019) detailed three different processes of utilizing captured CO_2 at the mill. These processes include tall oil manufacture, precipitated calcium carbonate production, and lignin separation from residual black liquor. However, these processes need much less CO_2 than the lime kiln would emit as a whole. Kuparinen et al. (2019) concluded in their work that "utilization possibilities in pulp mills are minor compared with the capture potential".

The positive effects of using oxyfuel combustion in a lime kiln are most evident in reduced emission levels. With efficient CO_2 separation, most of CO_2 emissions can be controlled. NO_x emissions are also reduced due to the fact that no thermal NO_x reactions (7) happen in the kiln. Another positive side of oxyfuel combustion is the improved heat transfer from fuel to lime. Because there is less mass

entering the kiln in the form of N_2, less heat is loss to the flue gases. Also, the increased concentration of H_2O and CO_2 in the flue gases improve heat radiation inside the kiln. (Granados et al. 2015)

The negative sides of using oxyfuel combustion in a lime kiln are mostly with the financial aspects of the technology. Large amounts of pure oxygen are required for the combustion process and usually this oxygen needs to be separated from air. An ASU of this scale can consume significant amounts of energy, which can lead to major costs for the mill. The fuel choice effects the system as well. If the fuel has a high sulfur content, it may lead to corrosion problems in the system. (Leung et al. 2014) The kraft pulp mill will also need to invest in new equipment. These include the forementioned ASU, new piping and fans for the FGR system. (Eriksson et al. 2014)

Oxyfuel combustion in a rotary lime kiln, which is located in a kraft pulp mill, has not yet been studied extensively. Kuparinen et al. (2019) mention the lime kiln as a potential place to use oxyfuel combustion, but more attention is paid to the general effect of using CCS in a kraft pulp mill. Eriksson et al. (2014) and Granados et al. (2015) use modelling to study oxyfuel combustion for a lime kiln, but these studies concentrate on general lime production instead of the use of oxyfuel combustion in a kraft pulp mill. In a techno-economic analysis of CCS for different industries, Leeson et al. (2017) conclude that it could be difficult to integrate CCS to the pulp and paper industry due to the remote areas in which the mills usually are located in.

3 Description of the model

In this thesis, the model of a rotary lime kiln in a kraft pulp mill is modelled by using Aspen Plus V11 (version 11). Aspen Plus is a software created by AspenTech that is based on flowsheet simulation and is used to model chemical processes during various process steps. The process models created in the software are based on thermodynamical and mathematical models. With different balance equations and physical constraints placed on the model, Aspen Plus is capable of simulating complex chemical processes. A model in Aspen Plus consists of streams and blocks. The streams can be either material, heat or work streams. The blocks represent different components or processes, such as reactors and flow separators. Some blocks are used to manipulate the simulation by adjusting the values in streams or blocks. The streams and blocks are combined in the flowsheet to assemble the model. (Al-Malah 2017)

The objective of the lime kiln model is to provide a simple, yet effective method to study various fuels for a lime kiln. By assigning desired lime production, calcination zone temperature and excess oxygen level as boundary conditions, the model gives the user information about operating parameters, such as the consumption of fuel and oxidizer. The user can also study the composition of different streams in the model, such as the flue gases leaving the kiln.

Two major variations of the model are created in this thesis: a lime kiln with traditional combustion and a lime kiln with oxyfuel combustion. The traditional combustion (TC) model has a combustion process, where fuel is combusted with air in the burner. The oxyfuel combustion (OC) model uses pure oxygen instead of air as the oxidizer. The OC model also uses FGR to recycle a portion of flue gases back into the lime kiln.

3.1 Model restrictions, simplifications and assumptions

The model has multiple restrictions, which are done to narrow the scope of the model. First, the model has been restricted to contain only the lime reburning process inside the lime kiln. All of the blocks used in Aspen Plus are used to model the rotary lime kiln and adjacent components. Streams in the model only include streams that either enter, leave or are inside the lime kiln. Therefore, the model does not include processes, such as lime mud filtering or any type of fuel pretreatment. Any flue gas cleaning processes have also been disregarded. In the case of the OC model, air separation or CO_2 separation from flue gases have not been implemented in the model.

Second, the model does not provide in-depth thermodynamic analysis of a lime kiln in terms of heat distributions. This kind of thermodynamic analysis is outside the scope of this thesis. The model takes a simplistic approach to the thermodynamics of a lime kiln. Temperatures inside the lime kiln have been limited to few singular values in the model describing the most important temperature levels. More detailed thermodynamic models of lime kilns have been done previously in other studies: for example by Shahin et al. (2016). The model is in an equilibrium state, where the residence time of different components inside the lime kiln and reaction kinetics do not have an impact on the results.

Third, various physical properties of solids is not taken into consideration. Therefore, lime reactivity and the effect of the sintering zone cannot be studied through the model. Solid impurities in fuels and lime mud are set as inert. Finally, various lime mud dusting processes and co-firing of NCGs are not

implemented in the model. These aspects have not been added into the model to narrow the scope of the model to focus more on the combustion of different fuels.

Heat losses, which happen through the shell of a lime kiln, have been simplified in the model to account for 15 % of combustion heat that comes through the fuel. The shell heat losses $\dot{Q}_{sh}$ are calculated by the following equation:

$$\dot{Q}_{sh} = 0.15 \times \dot{m}_f h_f \tag{10}$$

where $\dot{m}_f$ is the mass flow rate of fuel and h_f is the heat of combustion of the fuel as LHV. The percentage of shell heat losses is based on the calculations done by Gorog et al. (2015). Because these heat losses include all heat leaving the kiln by radiation or convection, the other blocks in the model have no separate heat losses. These include the heat exchangers blocks, which have efficiencies of 100 % due to the same reason.

The model has a constant pressure of 1 bar throughout the system. The effect of pressure on calculations has been assumed to be negligible. Compositions of various materials have been simplified from the referenced sources. Components, which have a mass fraction of under 1 wt-%, have been left out in most cases. The mass fraction of larger components have been rounded up to fill the total composition.

3.2 Fuels analyzed in the model

Because there are two variations of the model, each fuel needs to be analyzed for both the TC and OC model. Therefore, the number of different cases is two times the number of fuels used in modelling the lime kiln. The number of fuels analyzed in the model has been restricted to five, which means there are ten different cases to compare in Chapter 4. This helps to keep focus on the comparison for the fuels chosen to be analyzed. All of the fuels presented in Chapter 2.2 are not analyzed in the model, but they could be easily implemented into the model for future research outside of this thesis.

The following fuels are analyzed by using the model: natural gas, hydrogen, lignin, producer gas, and pulverized wood residues. Natural gas is used in the model as a baseline comparison for renewable fuels. It is one of the most used fuels in lime kilns together with HFO (Francey et al. 2011). Comparing it to other renewable fuels in the model can show how the change from fossil fuels to renewable fuels would affect lime kiln operation. Hydrogen is an efficient and carbon-free fuel, which can be produced onsite with water electrolysis. This makes it an interesting alternative as lime kiln fuel. Lignin can be extracted from black liquor to be used as a fuel in the lime kiln using the LignoBoost process (Tomani et al. 2011). Implementing lignin extraction and usage in the lime kiln will increase the recovery of energy and chemicals in a pulp mill, which is why lignin can be an attractive choice to replace fossil fuels with.

From the four different ways of utilizing wood residues presented in Chapter 2.2, pulverized wood residues and producer gas produced by gasification of wood residues are analyzed with the model. Using wood residues produced at the mill or nearby wood mills reduces CO_2 emissions compared to fossil fuels and can be financially beneficial (Francey et al. 2009). In addition to comparing pulverized wood residues and producer gas to other analyzed fuels, comparison can be made between these two

alternatives to determine which biomass pretreatment method is the optimal way of using wood residues as a fuel.

3.3 Model settings

In Aspen Plus, the choice of the property method impacts the simulation significantly. Al-Malah (2017) describes property methods as "a set of models used to calculate thermodynamic, kinetic and transport properties". The property method used in this model is PENG-ROB. This property method is based on the Peng-Robinson equation-of-state model. The PENG-ROB property model works well with various hydrocarbons in all temperatures, which is why it was selected for the lime kiln model in this thesis. The full list of all components present in the model is presented in Appendix B.

The Aspen Plus flowsheet of the TC model is shown in Figure 11. In addition to the blocks visible in Figure 11, the model has three design blocks, which fulfill the boundary conditions for the model, and one calculator block, which calculates the shell heat losses according to (10).

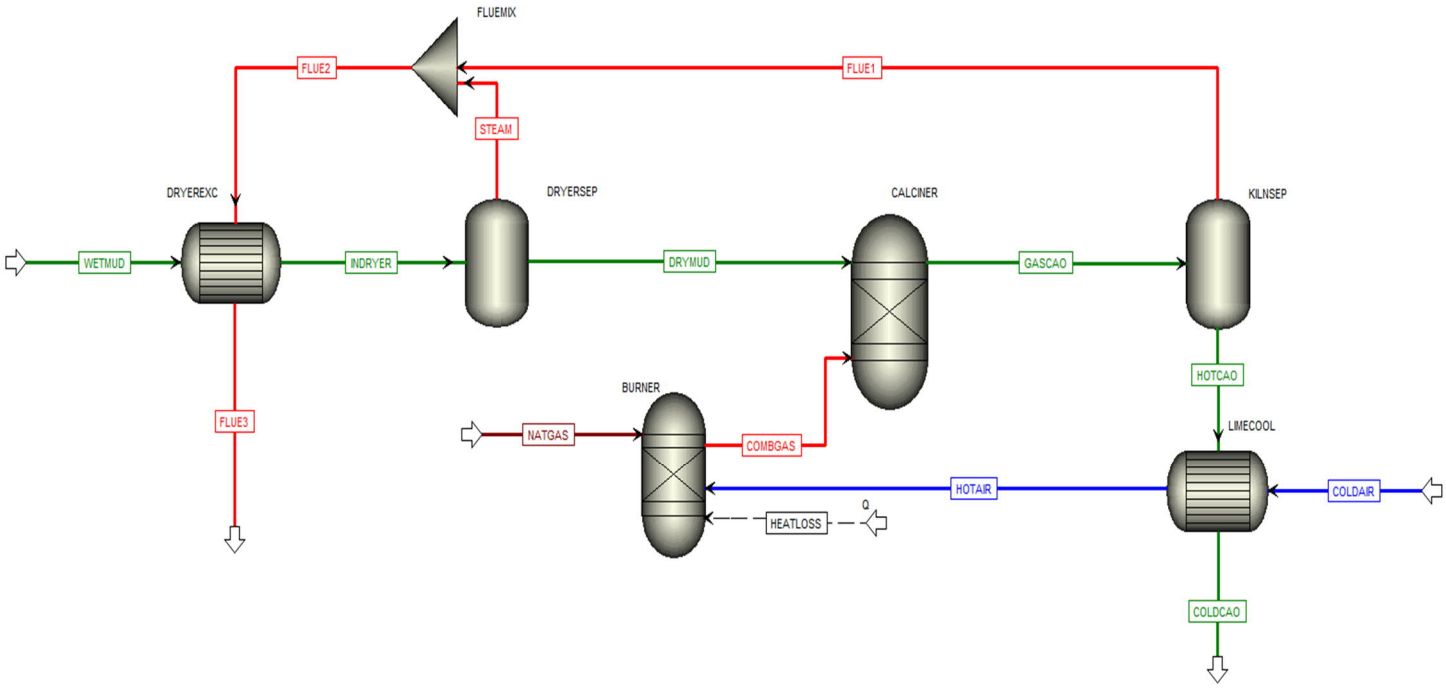


Figure 11: Aspen Plus flowsheet for the TC model.

The streams colored with green describe the conversion of $CaCO_3$ to CaO. The lime mud enters the lime kiln as stream WETMUD. After the drying process, which happens in blocks DRYEREXC and DRYERSEP, dried lime mud (i.e. stream DRYMUD) enters the block CALCINER. This is the block where the calcination reaction (3) happens. Finally, reburned lime is cooled in the block LIMECOOL and the stream COLDCAO leaves the lime kiln model.

The combustion process happens in the BURNER block, where fuel and oxidizer streams are connected to. The fuel and oxidizer streams are colored with brown and blue respectively in the model flowsheets. The oxidizer stream is preheated by reburned lime in the lime cooler before combustion. The shell heat losses are applied to the BURNER block by connecting the heat stream HEATLOSS into the block. After combustion of the fuel and the oxidizer, the combustion gases (i.e. stream

COMBGAS) are inserted into the CALCINER block, where the heat of the gases completes the calcination reaction.

The fuel stream enters the BURNER block directly in the case of most fuels. Fuels, which are biomass-based and solid, use nonconventional properties and need an additional block before the BURNER block to produce the correct yield for combustion. This block is named DECOMP in the model and it is modelled using the RYield unit in Aspen Plus. An additional heat stream COMBHEAT is used to carry the required heat for decomposition of the fuel between the blocks. The TC model for biomass-based fuels is shown in Figure 12.

The flue gases are colored with red in the flowsheet. Flue gases are produced in three processes in the model: during drying, during combustion and during calcination. The flue gases are separated from solid phases in separator blocks (DRYERSEP and KILNSEP) after the drying and calcination processes. Flue gases are combined in the block FLUEMIX, because in the real process there are no separate flue gas streams present inside the kiln. Finally, the flue gases are used for the drying of the lime mud in the block DRYEREXC. The stream FLUE3 represents the flue gases leaving the lime kiln.

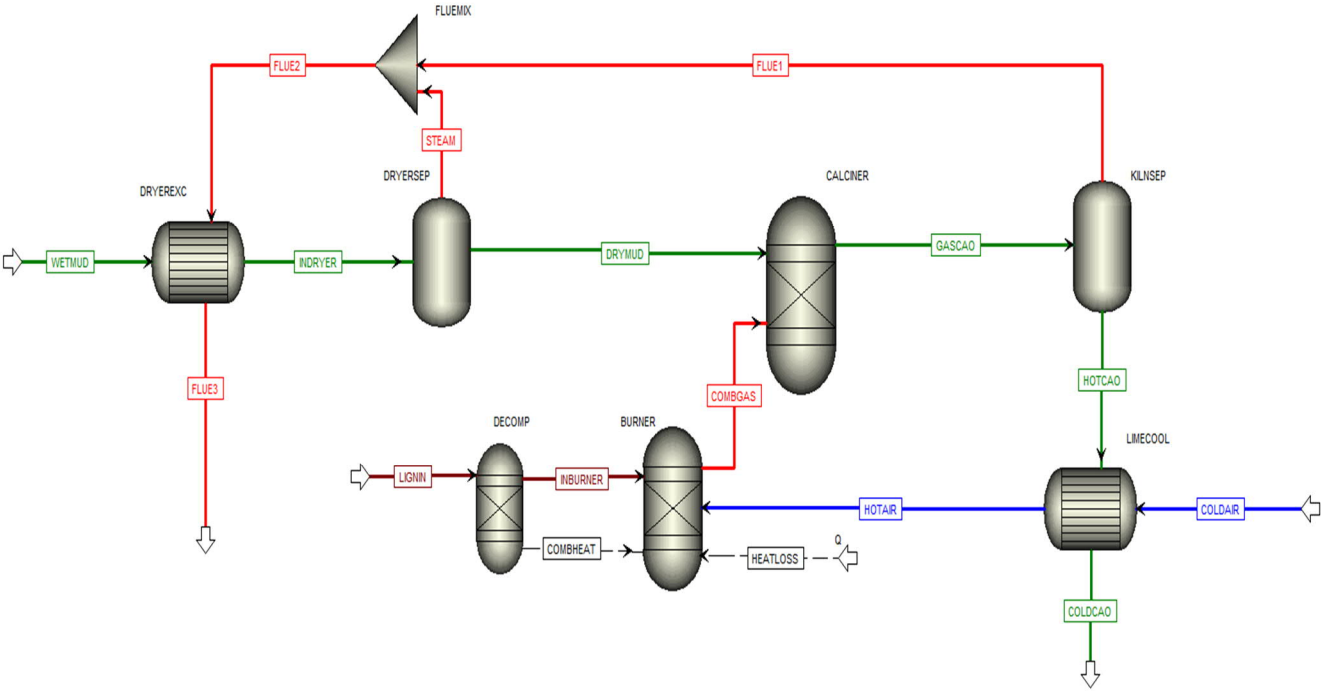


Figure 12: The TC model flowsheet with biomass-based fuel combustion.

Figure 13 shows the OC model, which has some additional blocks and streams compared to the TC model. The main difference is the use of FGR in the oxyfuel combustion process. In this model, flue gases leaving DRYEREXC block are split into two different flue gas streams. A portion of the flue gases are inserted back into the kiln by the stream FLUEFGR. The other flue gas stream (i.e. stream FLUE4) is transported outside the lime kiln, where CCS and other flue gas cleaning processes can be performed.

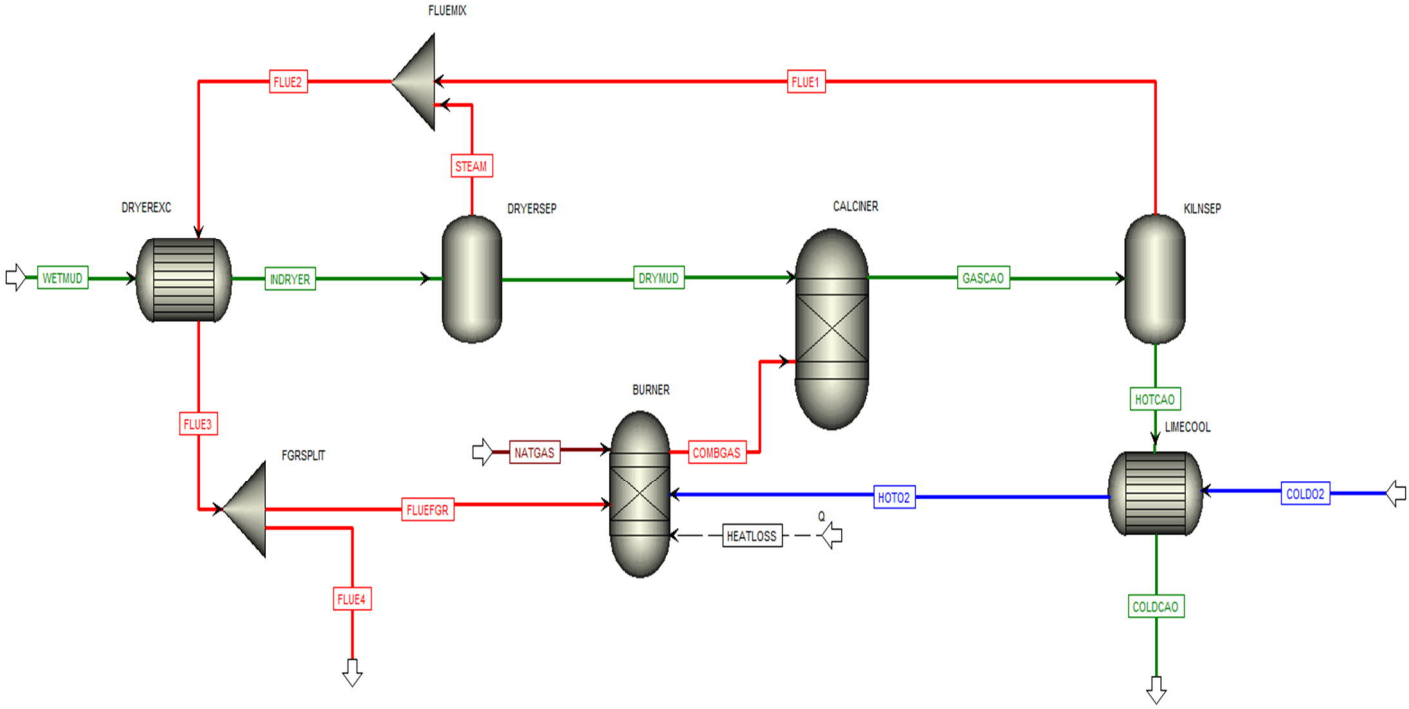


Figure 13: Aspen Plus flowsheet for the OC model.

The heat exchanger blocks used in the model are HeatX units, which work as two-stream heat exchangers. The units are used to model the drying zone in the lime kiln and the lime cooler at the discharge end of the kiln. The blocks adjust either the cold or hot stream outlet temperature to a specific value depending on the boundary conditions. Model fidelity in HeatX units are set to shortcut methods and calculation mode is set to “Design”. Default settings are used for all other options.

Of the two modifications to the lime reburning process presented in Chapter 2.2, the lime cooler is included in the model, but the flash dryer is disregarded. This is because implementing the flash dryer into this Aspen Plus model would not bring much additional value. The positive aspect of including flash dryers for lime kilns are to increase production capacity by decreasing the length of the kiln (Bajpai 2018). Because the model does not regard production capacity in terms of dimensions of the lime kiln, this positive aspect of the flash dryer would be negligible.

The calcination zone of the lime kiln and the burner are modelled in the model with the same Aspen Plus unit: the RGibbs reactor. The unit can model chemical equilibriums with multiple different phases present. Modelling in the unit is based on minimizing Gibbs free energy. Both blocks have specified pressure and heat duty. The pressure is set to 1 bar in both blocks like elsewhere in the model. The heat duty in the BURNER block is specified by the heat streams attached to it. The CALCINER block is set to be adiabatic.

3.4 Boundary conditions and initial values

The model has three main boundary conditions, which are shown in Table 4. These boundary conditions are handled in the model by using design blocks. Design blocks in Aspen Plus ensure that a specified target value of a selected parameter is fulfilled by varying another parameter in the model.

In the case of the first boundary condition in Table 4, the production of lime (i.e. the mass flow rate of the COLDCAO stream) is modified by varying the mass flow rate of lime mud entering the lime kiln. The target value is based on the average lime production found from the survey conducted by Francey et al. (2011).

Similarly, the second boundary condition of excess oxygen in flue gases is modified by varying the mass flow rate of oxidizer in the model. The oxidizer is air in the TC model and pure oxygen in the OC model. The target value for excess oxygen is the same value that has been used in a similar lime kiln model by Gribik et al. (2007). The boundary condition is set for the flue gas stream nearest to the CALCINER block: the stream FLUE1.

The third boundary condition sets the calcination zone temperature as 900 °C. The calcination zone temperature is set as the temperature of the stream leaving the CALCINER block in the model (i.e. the GASCAO stream). The calcination zone temperature is adjusted by varying the mass flow rate of fuel entering the kiln. A calcination zone temperature of around 800 °C could suffice for the TC model to fully complete the calcination reaction. However, the OC model has a higher concentration of CO_2 in combustion due to FGR, what increases the required calcination temperature like indicated by (4). Therefore, a high enough temperature of 900 °C is used in all cases to ensure total conversion of $CaCO_3$ to CaO in both variations of the model.

Table 4: The main boundary conditions of the model.

Condition	**Target value**	**Varied parameter**
Production of lime	320 tonnes/day	Mass flow rate of lime mud
Excess oxygen in flue gases	1.8 wt-%	Mass flow rate of oxidizer
Calcination zone temperature	900 °C	Mass flow rate of fuel

There are two additional boundary conditions, which modify the temperature of lime mud and cooled lime after the heat exchangers. These boundary conditions are set as outlet stream temperatures in the HeatX units instead of using additional design blocks. The temperature of lime mud (i.e. the stream INDRYER) after drying is set as 335 °C like in the model by Gribik et al. (2007). The temperature of cooled lime after the lime cooler is set as 350 °C, which is over the suggested minimum temperature of 320 °C (Bajpai 2018). The cooled lime temperature might remain over 350 °C if temperature crossover happens in the lime cooler. This can happen especially with oxyfuel combustion, where the mass flow rate of the oxidizer is lower than with traditional combustion.

The initial values used for streams entering the kiln model are shown in Table 5. The temperature of lime mud before drying (i.e. the stream WETMUD) is set as 90 °C. This is approximately the same value that is presented by Gorog (2002) and Theliander (2009b) for filtered lime mud. Ambient temperature of 20 °C is used for air and pure oxygen streams. The moisture content of lime mud before drying is set as 25 wt-%. This value is based on the average moisture content found from the survey by Francey et al. (2011). The chemical composition of lime mud and fuels analyzed in the model are shown in full in Appendix A.

Table 5 also presents the initial temperature values for all fuels analyzed using the model. The ambient temperature of 20 °C is used for natural gas, lignin and pulverized wood residues. It is assumed that

lignin and pulverized wood residues have been stored in ambient temperature before combustion. Natural gas is transported into the lime kiln without any pretreatment, such as fuel preheating. The temperature of hydrogen is set as 70 °C. This temperature is the average temperature of alkaline electrolysis indicated by Buttler and Spliethoff (2018), and it is assumed that hydrogen has this temperature when entering the kiln without hydrogen storage in between. Producer gas temperature is set as 700 °C, which is shown as the temperature for gasified wood residues by Manning and Tran (2015).

Table 5: The initial values for streams inserted into the kiln.

Parameter	**Value**
Temperature of lime mud	90 °C
Temperature of oxidizer	20 °C
Moisture content of lime mud before drying	25 wt-%
Temperature of natural gas, lignin and pulverized wood residues	20 °C
Temperature of hydrogen	70 °C
Temperature of producer gas	700 °C

4 Results

To study the fuels chosen for analysis in Chapter 3.2, ten different cases were simulated with the Aspen Plus model. These cases are referred to with specific case labels that are presented in Table 6. The first five cases use the TC model with different fuels fed into the lime kiln. Similarly, the last five cases use the OC model with the same fuels. All models use the settings, boundary conditions and initial values presented in Chapter 3. However, some of these settings are adjusted by sensitivity analyses later in this chapter.

One of the differences in the TC and OC models is the use of FGR. Using FGR affects multiple variables in the simulation, such as fuel and oxidizer mass flow rates, combustion temperature and flue gas composition. Therefore, the FGR split fraction (i.e. how much flue gases are recycled back into the process) needs to be decided for the OC model before comparing the cases between themselves. The split fraction is chosen for each fuel so that the combustion temperature is relatively constant between the TC and OC models. A sensitivity analysis of the FGR split fraction is done later in the chapter for two fuels to study the effects of the split fraction in more detail.

Table 6: The cases simulated with the model.

Case	Fuel	Combustion process	FGR split fraction	Color in graphs
TC-NG	Natural gas	Traditional combustion	–	Gray
TC-HY	Hydrogen	Traditional combustion	–	Blue
TC-LI	Lignin	Traditional combustion	–	Green
TC-PG	Producer gas	Traditional combustion	–	Orange
TC-WR	Pulverized wood residues	Traditional combustion	–	Yellow
OC-NG	Natural gas	Oxyfuel combustion	45 %	Gray
OC-HY	Hydrogen	Oxyfuel combustion	37 %	Blue
OC-LI	Lignin	Oxyfuel combustion	45 %	Green
OC-PG	Producer gas	Oxyfuel combustion	36 %	Orange
OC-WR	Pulverized wood residues	Oxyfuel combustion	45 %	Yellow

4.1 Studying the cases

The heat input from fuels in different cases is shown in Figure 14. Fuel mass flow rates as such are not compared here, because fuels have a large variance in heating values. Therefore, it is better to compare the total heat input that the fuel brings to the system. Fuel mass flow rates and other additional results can be seen in Appendix C. When comparing traditional combustion cases to oxyfuel combustion cases, it is evident that less heat input is required from a fuel with oxyfuel combustion. On average, 19 % less heat input needs to be fed with the fuel in the OC model compared to the TC model.

When comparing the fuels, it can be seen that hydrogen requires the least amount of heat input to satisfy the boundary conditions in both model variations. On the other hand, producer gas and pulverized wood residues need the most heat input through the fuel. The fuel heat input can be related to the amount of flue gases located in the kiln: a higher flue gas mass flow rate requires more heat input from the fuel. Mass flow rates of flue gases are shown in Figure 15. The same hierarchy between the

fuels can be recognized when comparing Figures 14 and 15. The only outlier in this comparison is the case TC-PG in Figure 14. Producer gas brings a substantial amount heat through its high temperature, and the temperature of fuel is not taken into consideration when calculating the heat losses (10). Therefore, cases with producer gas have relatively low heat losses, which decreases the needed heat input from the fuel.

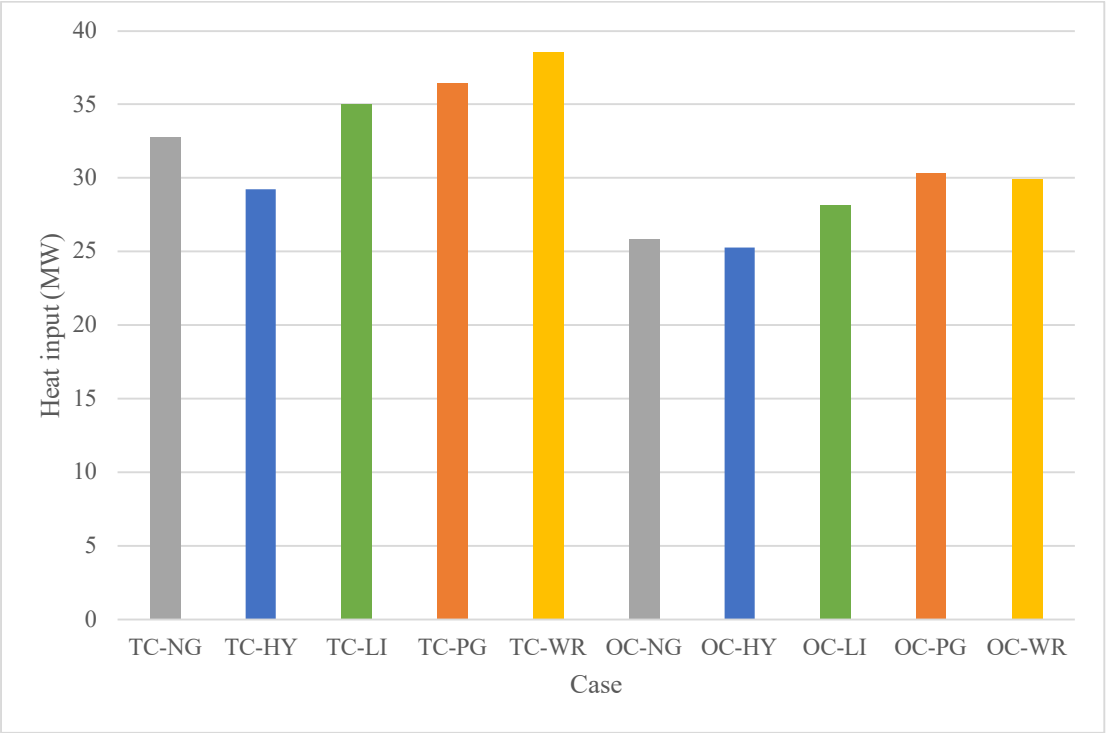


Figure 14: The total heat input of the fuel in different cases.

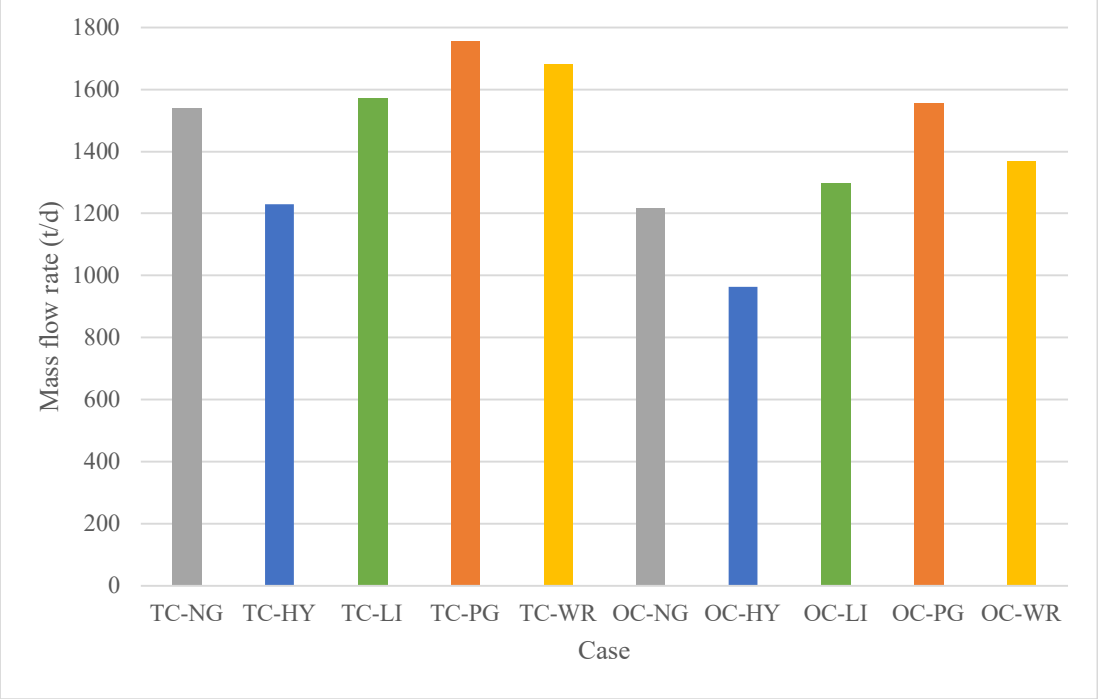
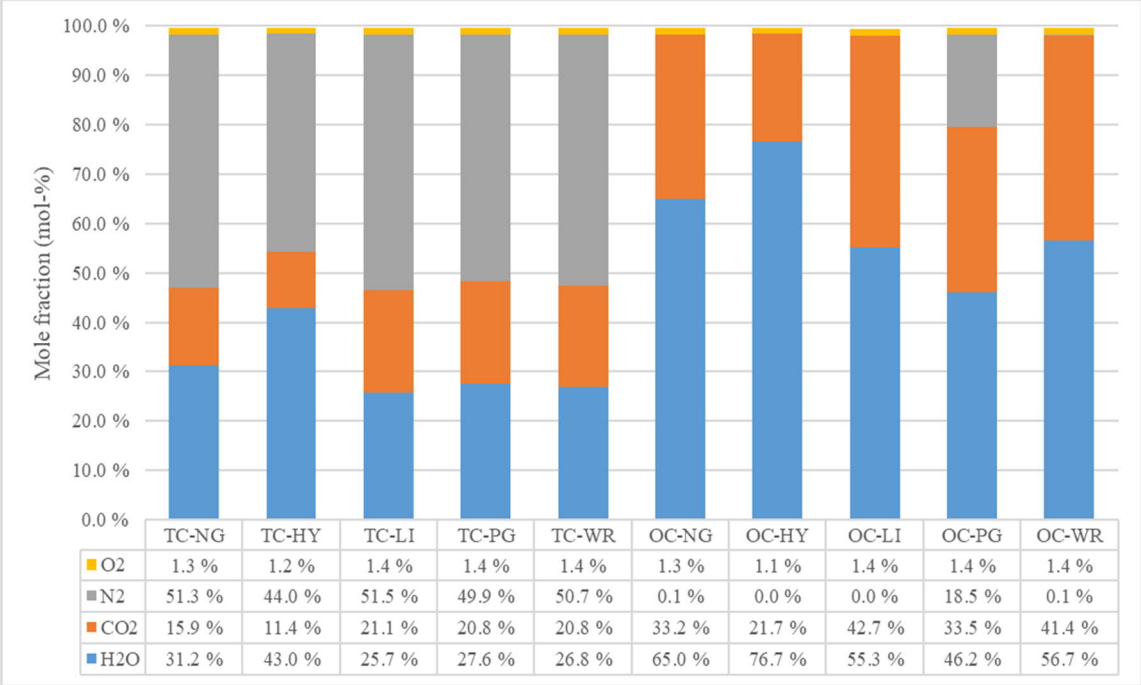


Figure 15: The mass flow rate of flue gases inside the kiln in different cases.

Figure 15 shows that less flue gases are generated with oxyfuel combustion. This is because no N_2 is inserted into the kiln with the oxidizer stream, and fuel mass flow rates are lower than with traditional combustion. Hart (2020) explained that decreased flue gas flow rates can be beneficial in lime kilns and flue gas handling systems limited by flue gas capacity. In the same article, Hart (2020) stated that increases in flue gas mass flow rates also leads to higher gas velocities inside the kiln, what can result in increased dusting.

The flue gas composition changes depending on the fuel and the model variation. This composition is same for the flue gases that are transported outside the kiln or recirculated back into the kiln. The composition can be seen for the most abundant flue gas components in Figure 16. The amount of N_2 decreases significantly between TC and OC models. Case OC-PG stands out from the OC models with its relatively high N_2 concentration, which is due to the high fraction of N_2 in producer gas. Because the OC model has flue gases that consist mostly of H_2O and CO_2, separation and capture of CO_2 from the flue gases is an easy and straightforward process (Granados et al. 2015).



	TC-NG	TC-HY	TC-LI	TC-PG	TC-WR	OC-NG	OC-HY	OC-LI	OC-PG	OC-WR
O2	1.3 %	1.2 %	1.4 %	1.4 %	1.4 %	1.3 %	1.1 %	1.4 %	1.4 %	1.4 %
N2	51.3 %	44.0 %	51.5 %	49.9 %	50.7 %	0.1 %	0.0 %	0.0 %	18.5 %	0.1 %
CO2	15.9 %	11.4 %	21.1 %	20.8 %	20.8 %	33.2 %	21.7 %	42.7 %	33.5 %	41.4 %
H2O	31.2 %	43.0 %	25.7 %	27.6 %	26.8 %	65.0 %	76.7 %	55.3 %	46.2 %	56.7 %

Figure 16: Flue gas composition in different cases.

Different amounts of CO_2 are produced in every case. Figure 17 presents how much CO_2 is exhausted per tonne of reburned lime (CO_2 t/CaO t). The results are same for both model variations: most CO_2 comes from using producer gas as a fuel and least from using hydrogen. CO_2 is produced in the combustion of a fuel and in the calcination reaction. The amount of CO_2 from the calcination reaction stays constant between all cases: around 0.75 CO_2 t/CaO t. Figure 18 shows how much CO_2 originates from the combustion of a fuel. More CO_2 is produced in the combustion process than during the calcination reaction in cases TC-LI, TC-PG, TC-WR, and OC-PG. Lignin, producer gas and pulverized wood residues produce more CO_2 than natural gas during the process, but the impact of these emissions can be thought to be less significant, because they come from biomass-based fuels.

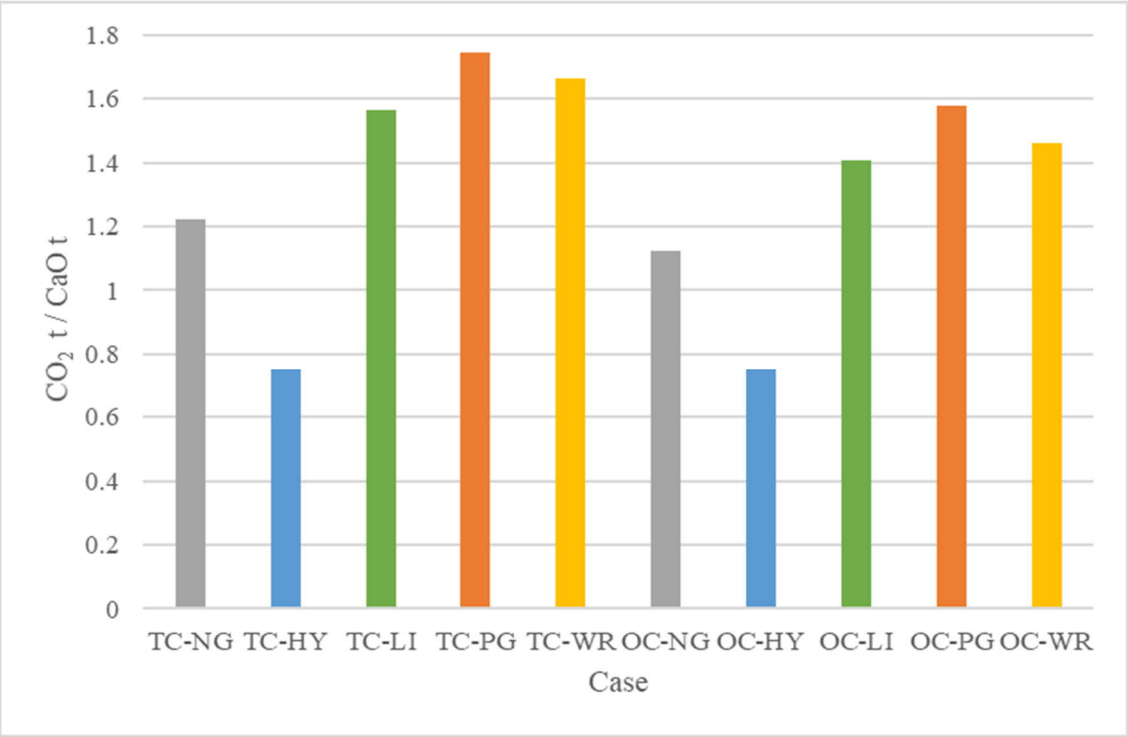


Figure 17: Tonne of CO_2 in flue gases per tonne of reburned lime in different cases.

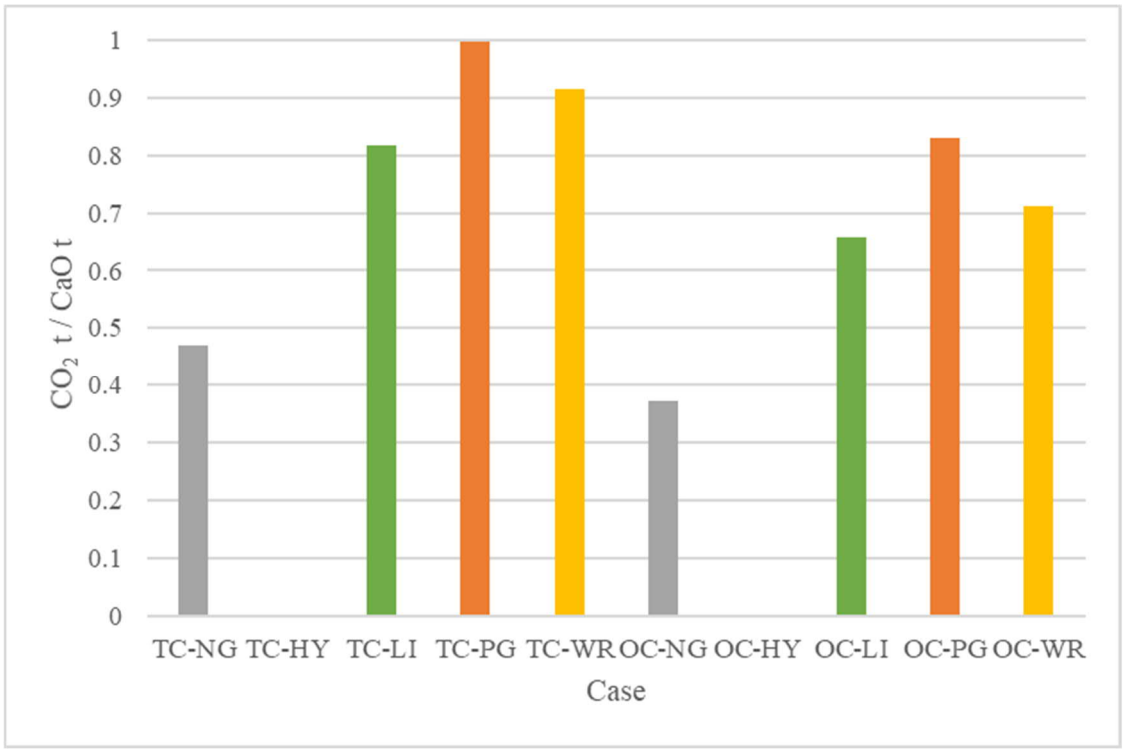


Figure 18: Tonne of CO_2 (from fuel) in flue gases per tonne of reburned lime in different cases.

Table 7 presents concentrations of emissions in flue gases not including CO_2. NO_x emissions are represented only by NO emissions, because close to none NO_2 is formed during the reactions. Similarly, PM emissions are represented only by the condensed sodium component Na_2SO_4. No lime mud dusting processes were implemented in the model.

In terms of NO_x emissions, there is an evident change in emissions between the TC and OC models. Less NO_x emissions are generated with oxyfuel combustion because there is no N_2 coming into the lime kiln with the oxidizer stream. Only with case OC-PG there are relevant NO_x emissions due to the amount of N_2 in producer gas. However, there is not much deviation in NO_x emissions between the fuels in the TC model. The emission concentrations are also quite low compared to values presented by Dahl and Hynninen (2008) for typical lime kilns. It can be concluded that the chemical equilibrium approach in the model does not describe the nitrogen chemistry sufficiently. This can be due to the many restrictions of the model, such as the noncontinuous nature of the temperature distribution and the lack of proper reaction mechanisms. Therefore, the model at its current state cannot accurately predict NO_x emissions for a lime kiln.

SO_2 emissions are only observed when lignin is used as a fuel. This is due to the high amount of sulfur found in lignin. The emission concentration increases heavily between the TC and OC model. The recirculated flue gases in the OC model include sulfur compounds, which originate from lime mud. These sulfur compounds increase SO_2 emissions during combustion and calcination reactions. This eventually leads to increased concentration of SO_2 in flue gases of case OC-LI. Both cases TC-LI and OC-LI have an emission concentration that far exceeds the level of SO_2 during oil firing in the lime kiln (Dahl & Hynninen 2008). Therefore, it can be said that the model does not also simulate SO_2 emissions very accurately.

No H_2S is found in the flue gases in any of the cases although some residual white liquor content was inserted into lime mud. The reaction producing H_2S (8) is only relevant in the temperature range of 200–250 °C according to Järvensivu et al. (1999). In the model, the temperature of lime mud changes directly from 90 °C to 335 °C. Therefore, the Na_2S vaporized from the lime mud does not react with any other compounds in the flue gases during the drying process. The model could be improved to make the drying process more detailed so that TRS emissions could be properly modelled.

The PM emissions in the flue gases consisted only of sodium sulfate (Na_2SO_4). These emissions are produced during the calcination process by the following reaction presented by Tran (2007):

$$NaOH + SO_2 + \tfrac{1}{2} O_2 \rightarrow Na_2SO_4 + H_2O \quad (11)$$

In the TC model, NaOH comes from lime mud while SO_2 and O_2 come from the combustion gases. This is why PM emissions show up only with fuels that have sulfur in the TC model. However with the OC model, all cases produce these condensed sodium sulfate emissions. This is due to using different levels of FGR. The flue gases, which recirculate back into the kiln, contain relatively high amounts of NaOH, Na_2S and SO_3. These compounds lead to increased concentration of Na_2SO_4 in flue gases after multiple chemical reactions during combustion and calcination.

In real lime kilns, the concentrations of condensed sodium compounds in flue gases would not be this high. Most sodium compounds would cycle between vaporization out of reburned lime and condensation back onto the lime mud. This would decrease the amount of sodium compounds flying out of the kiln with the flue gases. Also, there would be more different types of PM emissions than just Na_2SO_4, such as lime mud dust and Na_2CO_3. (Tran 2007)

Table 7: The emission concentrations in flue gases as mg/m^{3}n.

Case	TC-NG	TC-HY	TC-LI	TC-PG	TC-WR	OC-NG	OC-HY	OC-LI	OC-PG	OC-WR
NO_x (as NO)	48	42	49	49	49	2	0	1	30	2
SO_2	0	0	676	0	0	0	0	5205	0	0
TRS (as H_2S)	0	0	0	0	0	0	0	0	0	0
PM (as Na_2SO_4)	0	0	4176	0	106	11681	9412	13769	6705	11382

Table 8 shows the share of energy input and consumption for all studied cases. The energy balance was constructed mostly from values gathered straight from the model. The energy for calcination was determined from the energy balance in such way that the net balance of incoming and outgoing energy is zero. In all cases, approximately 80 % of energy comes with the fuel. Lime mud also brings in a relatively high amount of energy due to the high moisture content, which increases the specific heat capacity for lime mud.

Energy is consumed in the lime kiln by the calcination and drying processes. The calcination process requires around 20–30 % of all energy input while drying lime mud takes up around 15–25 %. It must be noted that the drying process in this model includes heating the lime mud to 335 °C as well as vaporizing moisture out of the lime mud. If only the vaporization of moisture was included in the drying process, the significance of drying in total energy consumption would be smaller.

In terms of energy losses, a large share of energy goes out of the kiln with the flue gases. In the TC model, approximately 40 % of energy is lost with the flue gases. These losses are less significant with the OC model, because of lower flue gas mass flow rates, but still relatively high. According to these results, flue gas temperature should be aimed to be lower or the heat in flue gases should be extracted to improve energy efficiency of the process. Approximately 6 % of sensible energy is lost with re-burned lime and 12 % by shell heat losses.

Table 8: The energy balance of the process in different cases.

Case	TC-NG	TC-HY	TC-LI	TC-PG	TC-WR	OC-NG	OC-HY	OC-LI	OC-PG	OC-WR
IN										
Fuel	78 %	78 %	79 %	81 %	80 %	80 %	80 %	82 %	83 %	83 %
Oxidizer	9 %	7 %	8 %	6 %	8 %	2 %	1 %	2 %	1 %	2 %
Lime mud	14 %	15 %	13 %	13 %	12 %	18 %	18 %	17 %	16 %	16 %
OUT										
Calcination	23 %	28 %	26 %	21 %	26 %	30 %	33 %	32 %	24 %	33 %
Drying	19 %	21 %	18 %	17 %	16 %	24 %	25 %	23 %	21 %	22 %
Shell heat losses	12 %	11 %	12 %	9 %	12 %	12 %	12 %	12 %	10 %	12 %
Flue gases	42 %	34 %	40 %	47 %	42 %	27 %	22 %	27 %	38 %	28 %
Reburned lime	5 %	6 %	5 %	5 %	4 %	7 %	8 %	6 %	7 %	6 %

The energy efficiency for the lime kiln can be defined to be:

$$\eta_{lk} = \frac{E_c + E_d}{E_{in}} \tag{12}$$

where η_{lk} is the energy efficiency of the lime kiln, E_c is the energy required for calcination, E_d is the energy required for drying, and E_{in} is the sum of all energy input. By using this definition for the energy efficiency, Figure 19 was constructed. On average there is a 10 % increase in energy efficiency when comparing the TC and OC models. The best energy efficiency is achieved by using hydrogen as a fuel for the lime kiln. On the other hand, the worst energy efficiency is achieved by using producer gas. Lignin and pulverized wood residues have similar energy efficiency values as with natural gas.

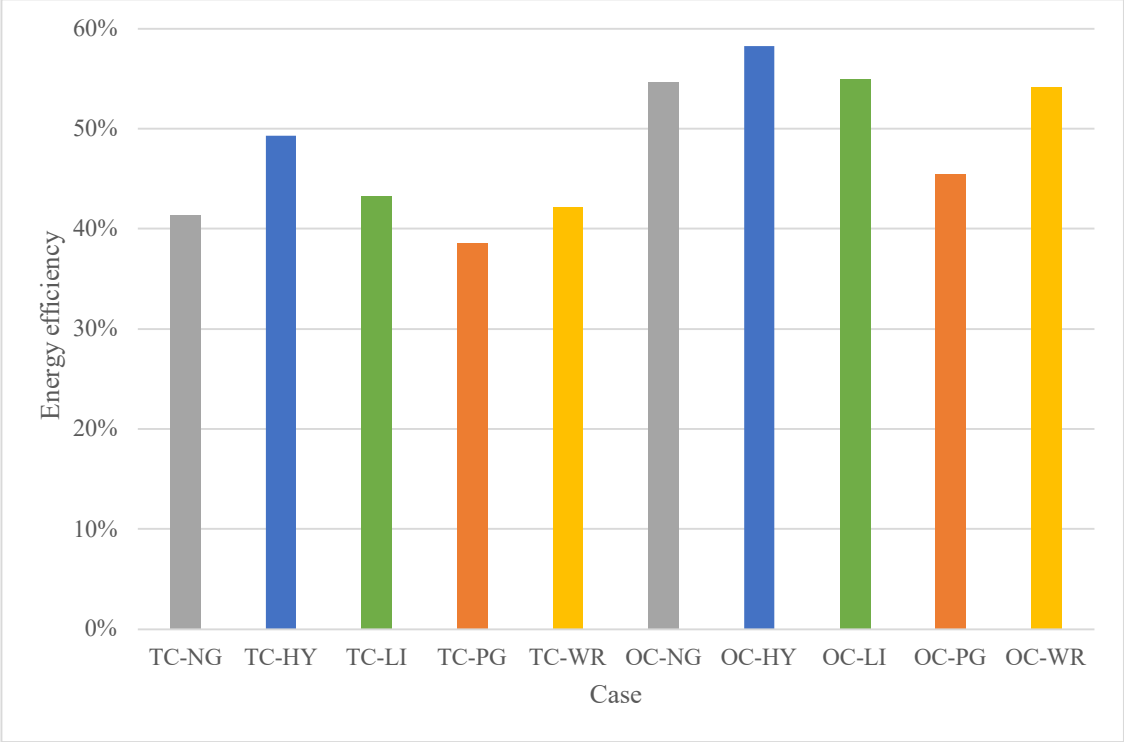


Figure 19: The energy efficiency of the lime kiln in different cases.

In terms of lime quality, the cases do not have a large variance in the results. This is due to model restrictions and initial values used in the analysis. The calcination zone temperature of 900 °C ensures that no residual $CaCO_3$ is left to reburned lime in any of the cases. The lime mud compositions are also the same for every case. The only difference in lime quality appears with small differences in the number of impurities in reburned lime. The change in impurity level is due to the amount of ash in a fuel. All of the ash in lignin and pulverized wood residues are transferred to the reburned lime. The amount of ash in lime depends on the fuel mass flow rate, which means that oxyfuel combustion produces slightly better-quality lime with biomass-based fuels.

4.2 Additional analyses

In this section, three sensitivity analyses are performed for selected cases. In the analyses, one chosen parameter is adjusted to study how changing the value for that parameter affects other parameters in the model. Other model settings, such as boundary conditions and initial values for input streams, are kept same as presented in Chapters 3 and 4.1. The parameters, which will be adjusted in each analysis, are explicitly explained at the start of the analysis. All of the cases are not implemented in every

sensitivity analysis, but the results can be assumed to be mostly similar between the cases and the fuels.

4.2.1 Effect of FGR split fraction

Natural gas and producer gas were selected for this sensitivity analysis. Both fuels are modelled using the OC model. The model parameter, that is adjusted, is the FGR split fraction. The objective of this analysis is to study the effect of FGR split fraction on multiple model parameters, such as combustion temperature and fuel heat input. The split fraction is adjusted between 0–80 %, while all the other model settings, such as calcination zone temperature and lime production, are kept same as detailed before.

Figure 20 shows how adjusting the FGR split fraction affects heat input gained from the fuel. It can be clearly seen that higher amounts of FGR increases the required fuel input. The increase in fuel heat input is approximately 0.15 MW per 1 % increase in FGR split fraction for both fuels. Using more FGR increases the total volume of gases in the lime kiln, which need to be heated by the fuel. The increase in flue gas mass flow rate can be seen in Figure 21. The mass flow rate of flue gases increases rapidly when FGR split fraction is increased above 60 %. Some lime kilns can be restricted by flue gas capacity, which is why using higher levels of FGR may be not possible.

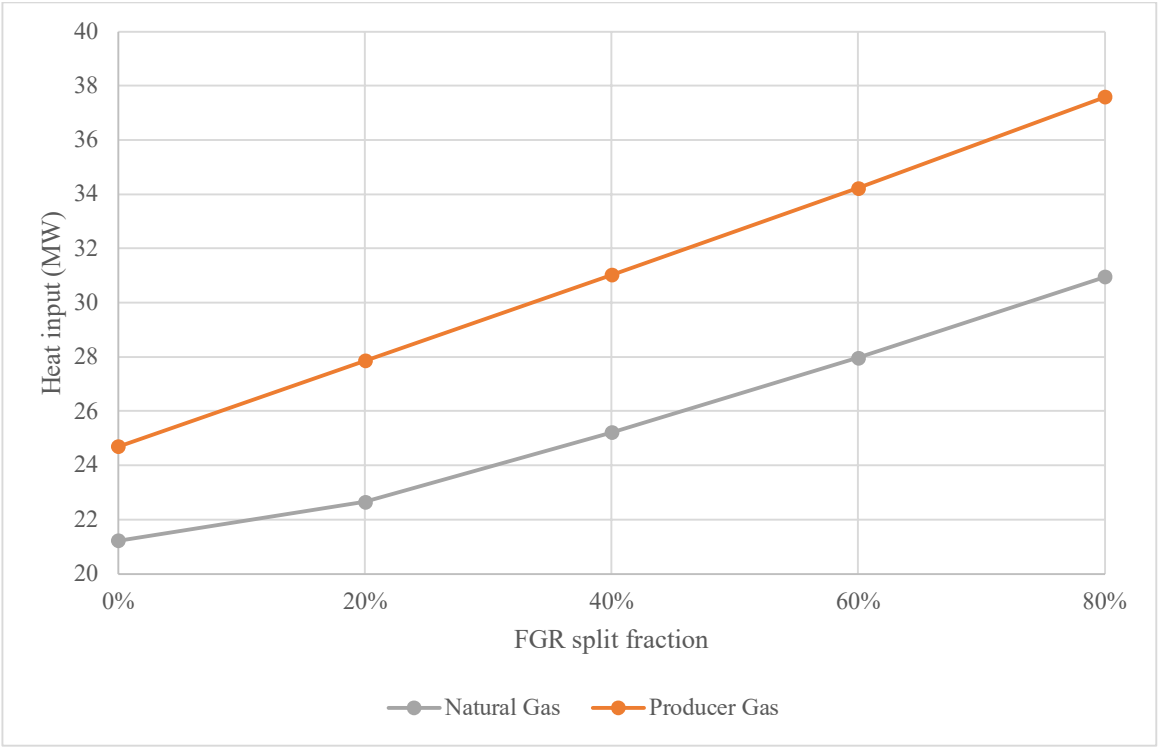


Figure 20: Effect of FGR split fraction on fuel heat input.

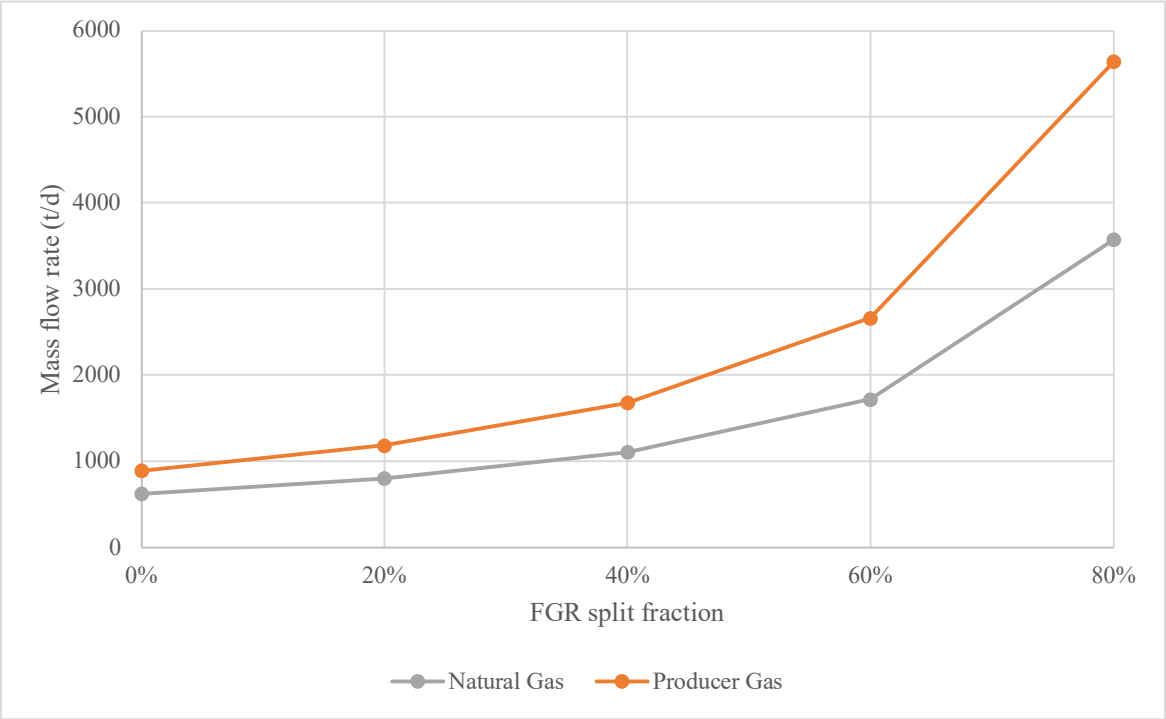


Figure 21: Effect of FGR split fraction on flue gas mass flow rate.

One of the main reasons mentioned in Chapter 2.4 for implementing FGR to oxyfuel combustion is to control combustion temperature. Controlling combustion temperature can be crucial for protection of the lime reburning process and kiln materials, such as refractory materials (Granados et al. 2015). Figure 22 shows how increasing FGR split fraction decreases combustion temperature in the lime kiln. Especially with low levels of FGR, small changes in the FGR split fraction have a great impact on the combustion temperature. The effect decreases with higher levels of FGR.

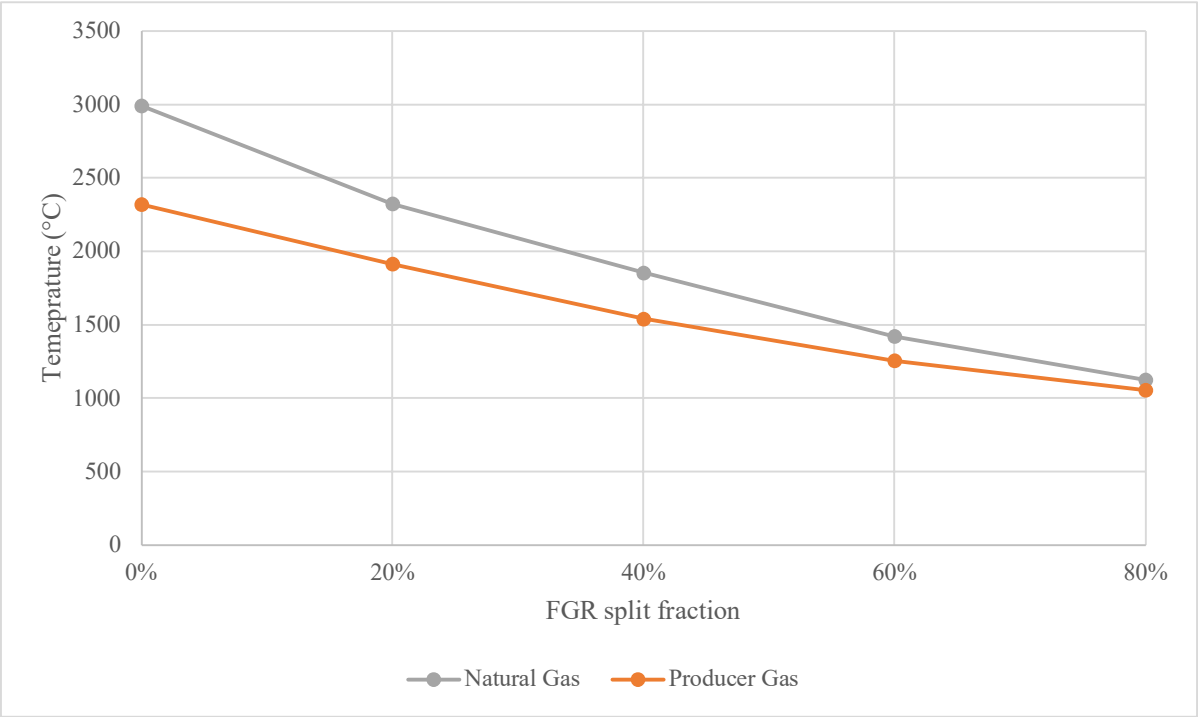


Figure 22: Effect of FGR split fraction on combustion temperature.

Figure 23 shows how lime kiln energy efficiency determined using (12) decreases with increasing FGR split fraction. The energy efficiency decrease is due to two significant factors. First, more heat input is required from the fuel as shown in Figure 20. Second, although less flue gases leave outside the kiln when FGR split fraction is high, these flue gases have a high energy content due to high temperatures. The flue gas temperature is around 750–800 °C for both fuels at 80 % split fraction.

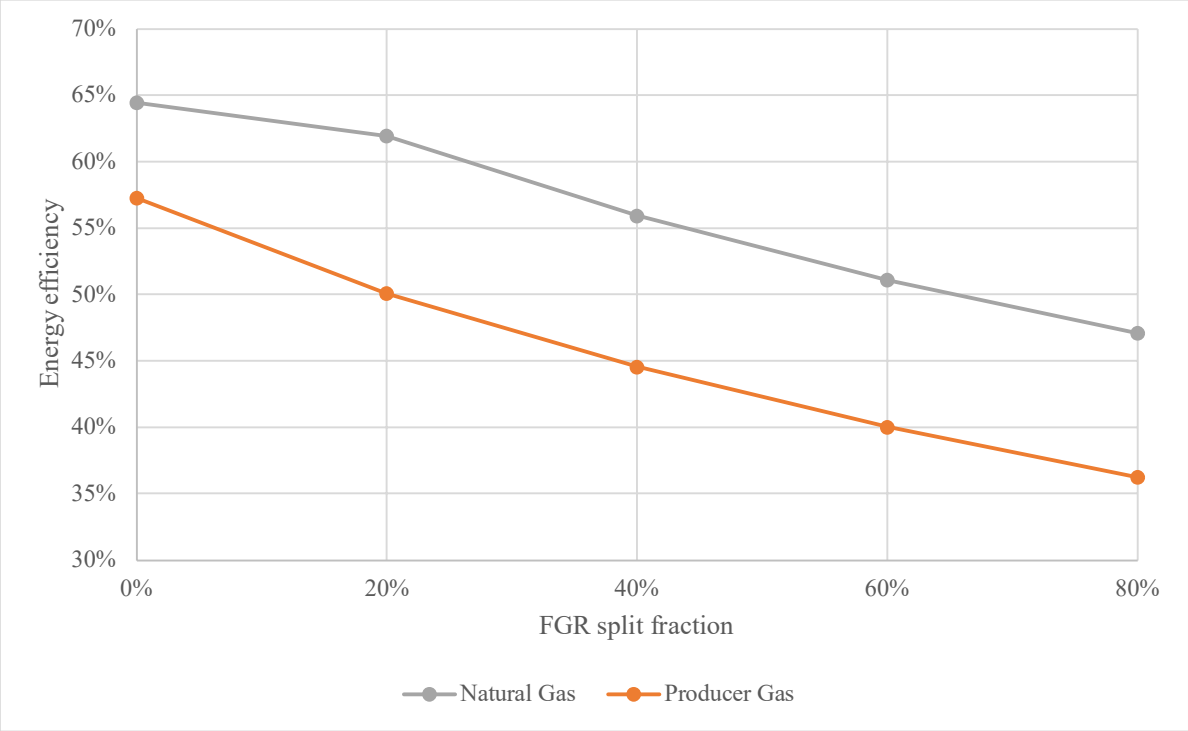


Figure 23: Effect of FGR on lime kiln energy efficiency.

According to the model and results obtained from this sensitivity analysis, increasing the level of FGR increases fuel and flue gas mass flow rates. The increase in FGR also results in the decrease of the system energy efficiency. The positive aspect of implementing FGR into oxyfuel combustion is to decrease the combustion temperature. Therefore, the optimal FGR split fraction should be determined to be as low as possible while keeping the combustion temperature at acceptable levels. No significant changes in flue gas compositions were observed between different FGR levels.

4.2.2 Effect of fuel mass flow rate

Fuel mass flow rate is adjusted in this sensitivity analysis to study the effect of fuel input on calcination zone temperature and lime quality. Fuels chosen for this analysis are hydrogen and lignin from both model variations. The fuel mass flow rate was adjusted approximately between -50–0 % of a reference value. The reference fuel mass flow rate was gained from the case analysis results for each specific case. The boundary condition for calcination zone temperature is not active in this analysis, which enables changing the fuel mass flow rate to achieve different calcination zone temperatures. Other boundary conditions and model settings are same as detailed in Chapter 3 and 4.1.

Figure 24 presents the analysis results on calcination zone temperature. The calcination zone temperature stays relatively constant while there is still $CaCO_3$ to be converted into CaO. After the calcination reaction has been fully completed, the temperature starts to increase with increased fuel heat

input. Therefore, the figure can be used to determine the temperature when the calcination reaction takes place for each case. The lowest calcination temperature is for hydrogen at around 760 °C in the TC model. In the OC model, the calcination temperature increases to approximately 790 °C. For lignin, the calcination temperature is at 790 °C in the TC model, and at 825 °C in the OC model. The cases have a large variance in CO_2 concentration of combustion gases, which is why the calcination temperature varies between the cases like shown by (4).

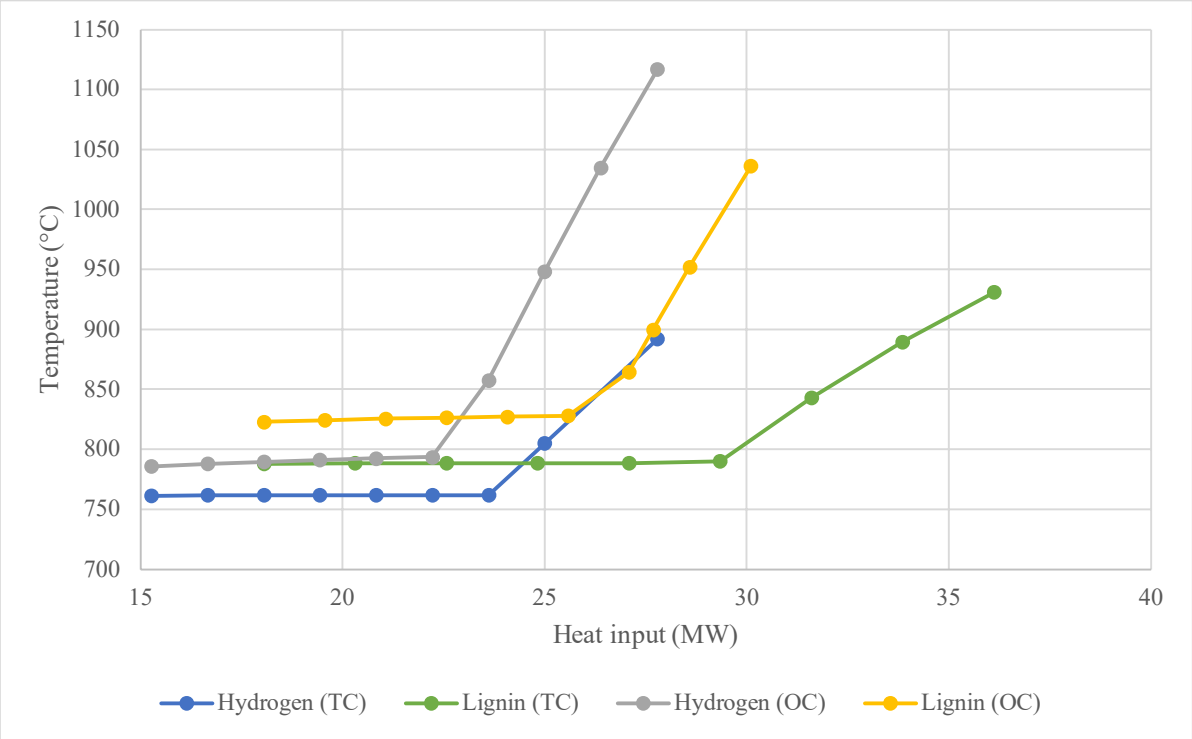


Figure 24: The effect of fuel heat input on calcination zone temperature.

The dependency of fuel heat input on residual $CaCO_3$ content is shown Figure 25. The graph shows that residual $CaCO_3$ decreases in the calcination zone when more heat is inserted to the kiln with the fuel. The required fuel heat input, where residual $CaCO_3$ is 0 wt-%, is around the same value in which the calcination zone temperature starts to heavily increase in Figure 24. Tran (2007) stated that residual $CaCO_3$ content should kept as low as 1.5–2.5 wt-% to ensure proper process efficiency during slaking. According to the model results, the difference in fuel mass flow rates is around 1 t/d for hydrogen and 3 t/d for lignin between 0–2.5 wt-% residual $CaCO_3$ contents. Heat is not evenly distributed in real lime kilns, like in this model, which is why surplus fuel heat input will most likely need to be inserted into the kiln if proper lime quality needs to be assured of.

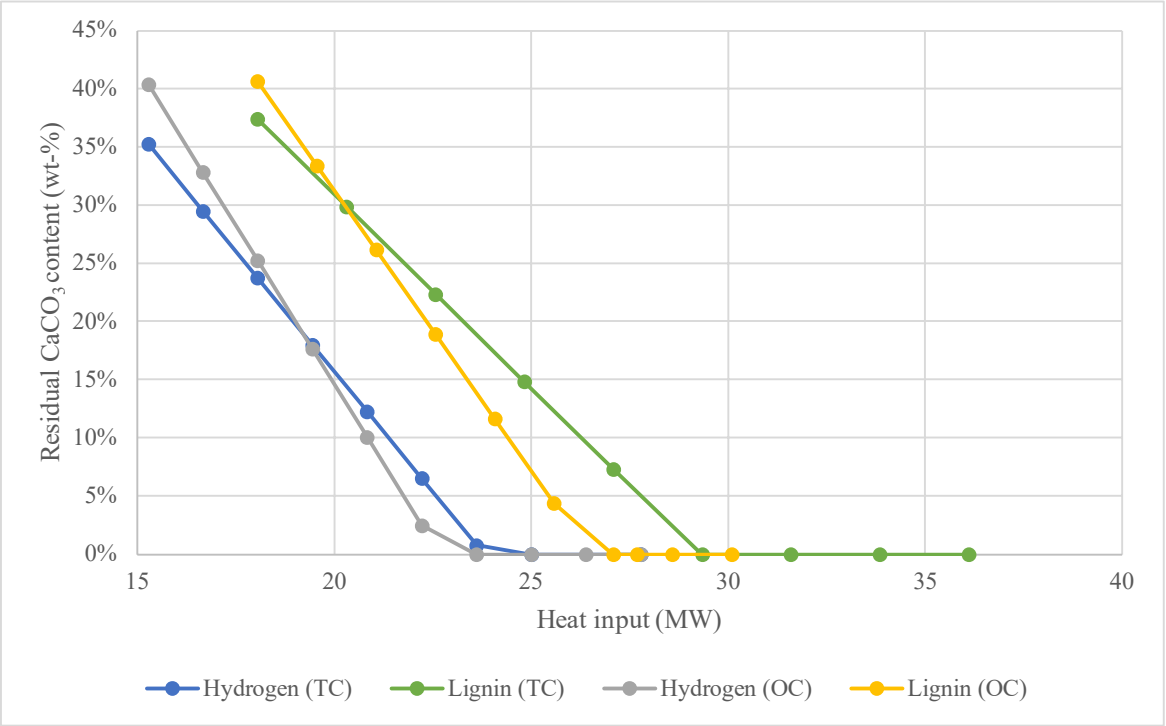


Figure 25: The effect of fuel heat input on residual $CaCO_3$ content.

4.2.3 Effect of lime mud moisture content

Hydrogen and producer gas from both model variations were selected for this sensitivity analysis. The objective of this sensitivity analysis is to study the effect of input lime mud moisture content on flue gas temperature and energy consumption. The lime mud moisture content was adjusted between 5–35 wt-% while other model settings were kept same as detailed in Chapters 3 and 4.1.

Figure 26 shows how the flue gas temperature changes after the drying of lime mud. A higher lime mud moisture content decreases the energy content of the flue gases leaving the drying zone. Therefore in all analyzed cases, the flue gas temperature decreases when the moisture content of lime mud has been set higher.

The dependency between total energy consumption and lime mud moisture content is shown in Figure 27. For the TC models, fuel heat input is not affected by the moisture content. The calcination reaction always requires a constant energy input to provide a sufficient calcination zone temperature with the set boundary conditions. This means that in the TC model, the calcination process is not dependent on energy consumption during the drying stage. Therefore, only energy content of the flue gases is affected by the lime mud moisture content. However in the OC model, FGR recycles a portion of flue gases back into the kiln. Recycled flue gases have an impact on the calcination process, and this is why more heat input is required from the fuel when lime moisture content increases in the OC model.

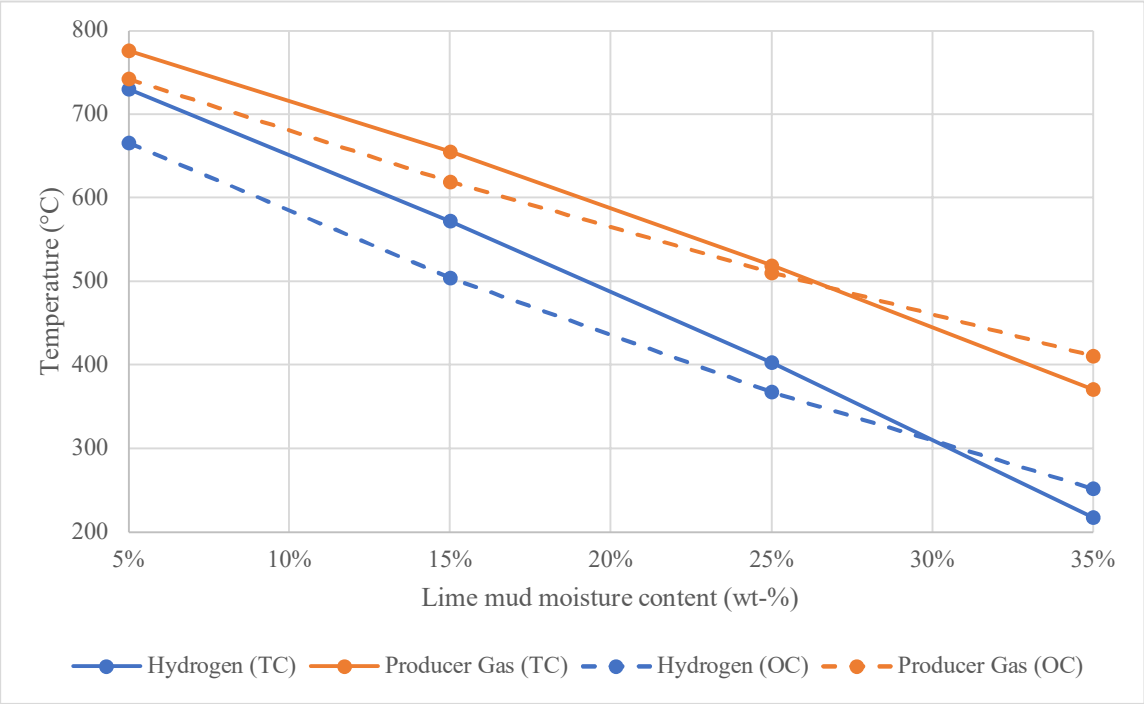


Figure 26: Effect of lime mud moisture content on flue gas temperature.

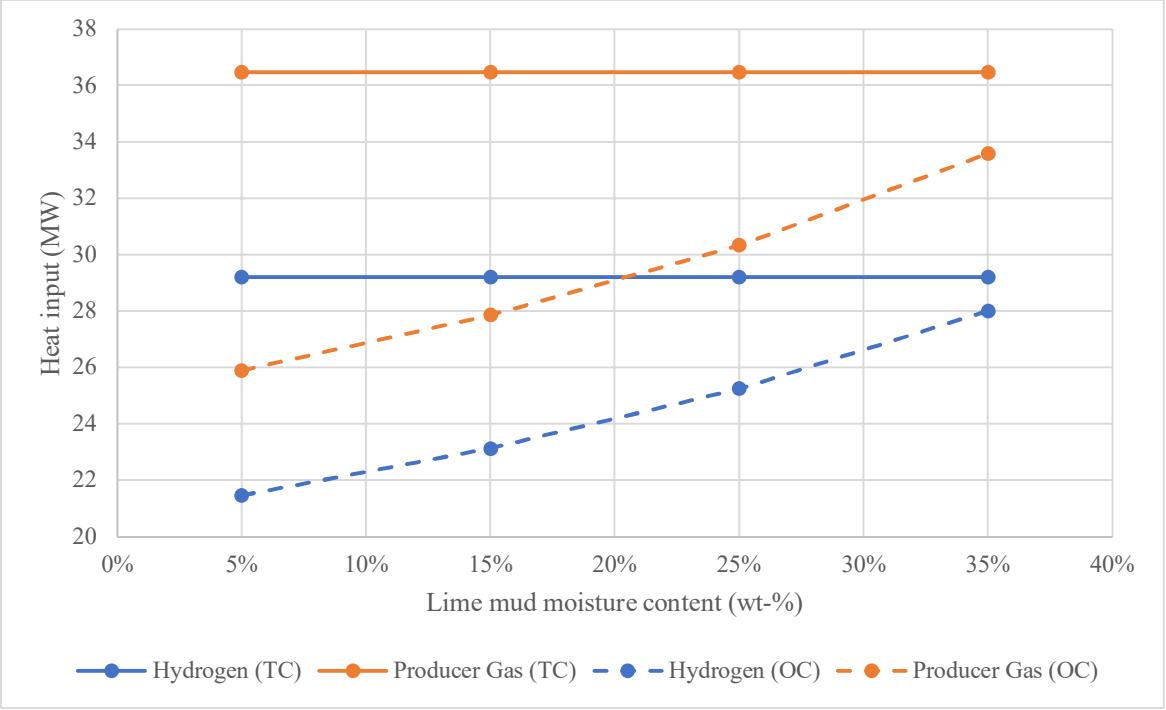


Figure 27: Effect of lime mud moisture content on fuel heat input.

According to these results, lime mud moisture content only affects fuel heat input when FGR is used. Figure 26 showed how the flue gas temperature decreases with the increase in the moisture content. Lime mud moisture content can be relatively high if flue gas temperature is not specified to a set limit. If flue gases have a minimum accepted temperature, for example 200 °C, then eventually more fuel heat input is needed to keep the flue gas temperature above the limit. Flue gases may also have a use after the lime kiln, such as in the gasification of biomass. In these cases, flue gas temperature

must be kept high and lime mud moisture content has to be regulated more strictly. Lime mud moisture content does also affect ring formation in the lime kiln. Lime mud with a higher moisture content makes lime particles more adhering to the wall of the kiln, what increases potential for ring formation (Tran 2007). Although particle sizes and particle transport inside the kiln is not modelled in this model, this is important to keep in mind when adjusting lime mud moisture content.

4.3 Comparison of the results to other studies

All of the results presented earlier in this chapter cannot be compared directly to other studies focusing on lime kiln modelling or oxyfuel combustion. These other studies have either used different fuels or different bases for modelling. Also, no studies were found that studied oxyfuel combustion in a lime kiln, which is located in a kraft pulp mill. However, some results can be rationally compared to other studies in the area. These comparisons are shortly presented here to validate the model created in this thesis.

Emissions

Kuparinen et al. (2019) studied a kraft pulp mill, which had a lime kiln using natural gas as the fuel. From their results of a Northern Europe softwood kraft pulp mill, it can be calculated that the lime kiln produced 0.92 tonnes of CO_2 per tonne of reburned lime. This is 25 % less than with the comparable case in this model (case TC-NG). However, the model by Kuparinen et al. (2019) also uses approximately 30 % less energy to produce a ton of reburned lime. By taking the energy consumption differences into consideration, it can be said that CO_2 emission levels are relatively similar between their work and the model created here.

The share of CO_2 due to fuel combustion varies between 39–57 % in the TC model (when hydrogen combustion is not included). The smallest share of fuel-based CO_2 emissions is for natural gas, and the highest for producer gas. This same share was 34 % based on the data from the US in 1995 (Miner & Upton 2002), and 36–45 % in the study by Kuparinen et al. (2019). Both studies based the values of fuel-based CO_2 mostly on natural gas combustion. Therefore, it can be said that the share of CO_2 due to natural gas combustion in this thesis is comparable to these two studies examined here. CO_2 emission data from lime kilns is not widely available for renewable fuels, so the model results for renewable fuels cannot be compared here.

In terms of other emissions, it was already mentioned in Chapter 4.1 that the emissions of NO_x, SO_2, TRS and PM gathered from the model are not comparable to real lime kilns. The emission concentrations of NO_x and TRS are lower than with real lime kilns, while SO_2 and PM emissions are unnaturally high. So if emphasis would want to be concentrated on these other emissions, the model would need to be improved drastically.

Energy consumption

A similar model to the one created here was created by Lundqvist (2009) in his master's thesis concerning mass and energy balances of a lime kiln. Therefore, the energy consumptions can be compared between these two models. For simplicity's sake, the model created by Lundqvist (2009) will be referred to as M1 and the model created in this thesis as M2.

The largest differences in the energy balances are the share of outgoing energy for calcination and flue gases. In model M1, only 15 % of energy is lost with the flue gases. This is very low compared to the amount of energy lost with the flue gases in model M2 (approximately 40 % with the TC model). This can be explained by the differences in flue gas temperatures. Model M1 has assigned the flue gas temperature to be 200 °C, while the average flue gas temperature is around 475 °C for model M2. Therefore, a lot more heat is lost with the flue gases in model M2 because of the high temperature.

The calcination process requires 51 % of energy in model M1 and around 30 % of energy in model M2. The differences in the energy consumption of the calcination process can be related to the way that the energy balance was determined in model M2. Because calcination energy consumption was determined using the other parameters in the energy balance, each of these parameters will affect the final share of energy for calcination. The other shares of energies are affected by the different model settings used in model M1 and M2. If the model settings would be set identical between the models, the energy balance gained from the models would most probably be more alike.

The lime kiln energy usage can also be compared to the lime kiln survey results by Francey et al. (2011). In the survey it was stated that lime kilns require 5–8 GJ of energy per ton of lime produced (GJ/CaO t). Lime kiln heat rates calculated with the case analysis results can be seen in Table 9. The heat rates are calculated only with the heat input from the fuel similarly like it is stated in the survey. With the TC model, only hydrogen achieves the average survey value for lime kilns. By using oxyfuel combustion approximately all fuels have a heat rate of under 8 GJ/CaO t. On average, the lime kiln model seems to use more energy than the survey indicates as the average value. However, the calcination zone temperature and heat losses were set quite high in the model. Therefore, the difference in lime kiln heat rates between this thesis and the survey does not seem that unreasonable.

Table 9: The lime kiln heat rates (GJ/CaO t) in different cases.

Case	TC-NG	TC-HY	TC-LI	TC-PG	TC-WR	OC-NG	OC-HY	OC-LI	OC-PG	OC-WR
GJ/CaO t	8.8	7.9	9.5	9.8	10.4	7.0	6.8	7.6	8.2	8.1

FGR split fraction

Although Eriksson et al. (2014) did not study a lime kiln in a kraft pulp mill, their results on the effect of FGR split fraction in oxyfuel combustion can be compared to the results studied in Chapter 4.2.1. The effect of FGR on decreasing the combustion temperature are similar between the models. In both models, each increasing percentage of the FGR split fraction decreases the combustion temperature by 18 °C. This similarity between the models can be seen in Figure 28 as well.

The FGR split fraction sensitivity analysis in Chapter 4.2.1 also concluded that the energy efficiency of the lime kiln is decreased when the level of FGR was increased. Similar results were observed by Granados et al. (2014) in their study of oxyfuel combustion in a rotary cement kiln. In this study, the lowest FGR split fraction they studied proved to be most energy efficient compared to other split fractions. However, Granados et al. (2014) also note that combustion temperatures at lower levels of FGR are not applicable for the materials in the kiln.

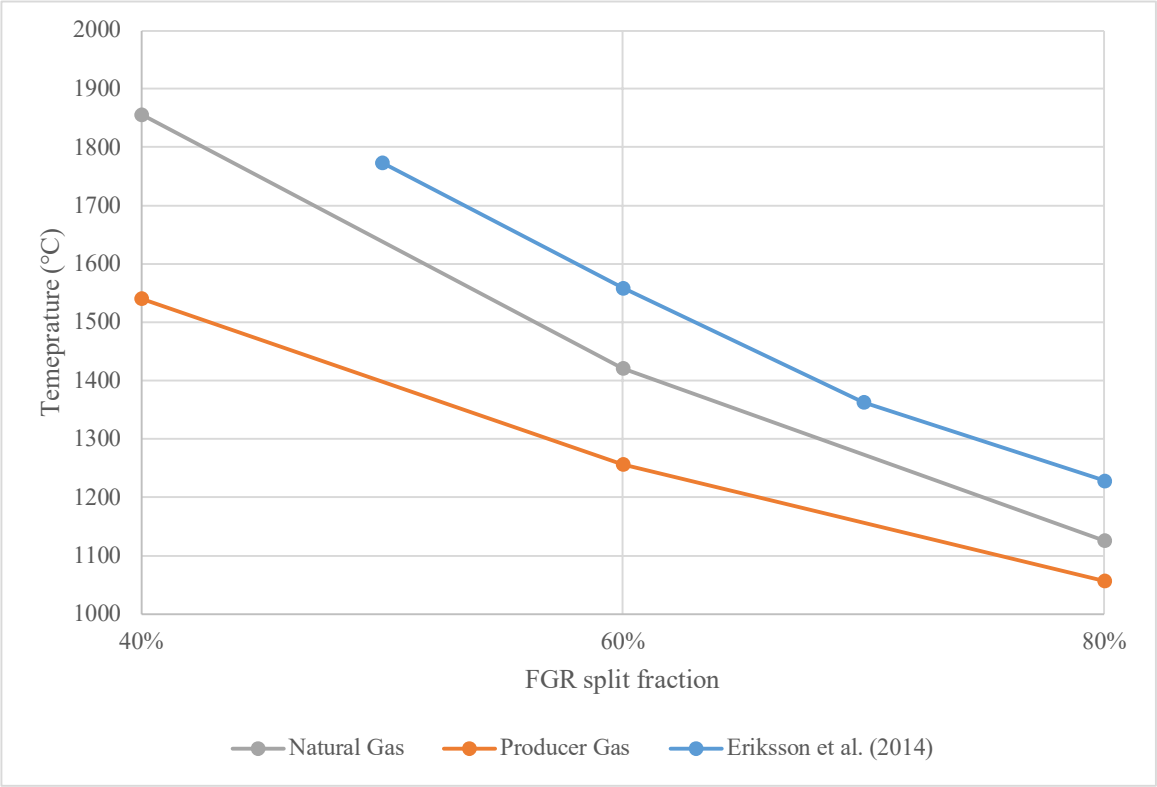


Figure 28: Comparing the results from Chapter 4.2.1 to the results by Eriksson et al. (2014).

Effect of fuel mass flow rate on calcination

Chapter 4.2.2 focused on the sensitivity analysis of the fuel mass flow rate. The results showed that while there is still $CaCO_3$ to be converted into CaO in lime mud, the calcination zone temperature stays constant. The same type of result can be seen the study of a lime kiln by Syamsudin and Susanto (2016). From their results it can be seen that the calcination temperature for natural gas was just under 800 °C. This is a very similar result that was observed for lignin in Chapter 4.2.2. Lignin is a good comparison fuel for natural gas, because both fuels have similar CO_2 concentrations in combustion gases.

One difference between the results shown in Chapter 4.2.2 and the study by Syamsudin and Susanto (2016) is the point where the calcination zone temperature starts to increase. In Chapter 4.2.2 it was observed that this point it almost exactly where the residual $CaCO_3$ content is 0 wt-%. However, the results by Syamsudin and Susanto (2016) show that the residual $CaCO_3$ is still at 10 wt-% when the calcination zone temperature starts to increase. This difference in the calcination reaction can be due to differences in the way the models have been constructed. Because Syamsudin and Susanto (2016) do not provide an in-depth explanation of the model they have used in the study, any model differences cannot be compared straightforwardly.

5 Discussion

Oxyfuel combustion and renewable fuels were studied using the Aspen Plus model in Chapter 4. Theoretically, the lime kiln could be carbon negative if renewable fuels, oxyfuel combustion and CCS would be integrated into the process (Kuparinen et al. 2019). If biomass-based fuels are used at the kiln, then the process of BECCS would be implemented for the lime kiln. According to the model, approximately 1.5 tonnes of CO_2 per tonne of lime product were produced by the biomass-based fuels in oxyfuel combustion. With an average lime production of 320 t/d (Francey et al. 2011) and CO_2 capture rate of 96 % (Yadav & Mondal 2021), the CO_2 emissions of an average kraft pulp mill could be decreased with BECCS by over 168 000 tonnes per year.

Oxyfuel combustion cannot be implemented into the lime kiln without some downsides. Converting into oxyfuel combustion requires new equipment, such as an ASU and a FGR system (Eriksson et al. 2014). Producing pure oxygen by air separation is also a very energy intensive process. Some estimates say that producing 95 % pure oxygen requires around 0.23 kWh of electricity per a kilogram of oxygen gas (Yadav & Mondal 2021). Using this energy cost of air separation, it can be calculated that the oxyfuel combustion cases in this thesis would need surplus electricity between 34–43 MWh for air separation. This amount of energy is equivalent to averagely 6 % of the total heat input brought by the fuel into the lime kiln. If CO_2 capture from flue gases would be implemented with oxyfuel combustion, this would require even more energy.

Some processes at the mill could be combined to make producing pure oxygen for oxyfuel combustion less costly. Producing hydrogen through water electrolysis produces oxygen as a byproduct, which then could be combusted in the kiln with hydrogen. Although water electrolysis is also energy intensive, combining it with oxyfuel combustion could bring potentially good improvements to system efficiency. Kuparinen et al. (2019) also mention that kraft pulp mills usually have equipment onsite, which can produce pure oxygen. This could make equipment investment costs decrease significantly.

The renewable fuels studied in this thesis using the model were hydrogen, lignin, producer gas and pulverized wood residues. Table 10 presents some of the main operating parameters that were gained from the TC model for all studied fuels. The combustion temperature for lignin proved to be similar to natural gas. Producer gas and pulverized wood residues had lower combustion temperatures due to higher flue gas mass flow rates. The combustion temperature with hydrogen was relatively high. This could become problematic with some lime kilns refractory materials, which cannot withstand too high operating temperatures (Gorog et al. 2015). On the other hand, the high flue gas mass flow rate of producer gas can bring problems related flue gas capacity and dusting (Hart 2020).

Hydrogen produced much less CO_2 per tonne of reburned lime than other renewable fuels. All of the CO_2 from using hydrogen comes from the calcination reaction. The biomass-based renewable fuels produce approximately 25 % more CO_2 than natural gas during the process. However, all of this CO_2 comes from biomass and as such can be thought be less impactful than the CO_2 from natural gas. Only hydrogen proved to use less fuel heat input than natural gas. Other renewable fuels have higher heat inputs due to the increase in flue gas mass flow rates. For pulverized wood residues, there is a 18 % increase in fuel heat input compared to natural gas. Producer gas would also have a higher fuel heat input if heat losses would be calculated more accurately in the model.

In terms of impurities in reburned lime, there is not major variance in the results. Only lignin and pulverized wood residues have slightly more impurities because of the ash in the fuels. This variance of impurities should not bring problems to the lime reburning process, but a more detailed analysis could be done with more accurate fuel and lime mud composition data to determine the amount of make-up lime needed.

Table 10: Selected operating parameters observed for the fuels in the TC model.

	Natural gas	**Hydrogen**	**Lignin**	**Producer gas**	**Pulverized wood residues**
Combustion temperature	1730 °C	1930 °C	1740 °C	1620 °C	1660 °C
Flue gas mass flow rate	1540 t/d	1230 t/d	1572 t/d	1756 t/d	1681 t/d
Total CO_2 t / CaO t	1.22	0.75	1.57	1.75	1.67
Fuel heat input	32.8 MW	29.2 MW	35.0 MW	36.5 MW	38.6 MW
Impurities in lime	4.46 wt-%	4.46 wt-%	4.69 wt-%	4.46 wt-%	5.07 wt-%

Table 11 presents financial and logistical aspects for the studied renewable fuels. The advantage of each fuel is that all of them can be produced at the kraft pulp mill. The production of hydrogen and lignin can also be beneficial for the mill in other processes. Water electrolysis produces oxygen and low-grade waste heat: both of which can be used at the mill for various purposes. Lignin separation from black liquor can help to increase pulp production, but also decreases the electricity production available from the recovery boiler. (Kuparinen & Vakkilainen 2017)

Hydrogen production through water electrolysis can prove to be too expensive to implement at the mill. The investment cost of an electrolyzer is high and it needs large amounts of electricity to provide enough hydrogen for the lime kiln. The electricity can be gained from the surplus electricity generated by the recovery boiler, but it might be more economically feasible to sell the electricity to the grid. The investment and running costs might prove to be too high at the moment to use water electrolysis at the mill, but these prices might decline in the future. (Hart 2020)

Implementing the LignoBoost process to use lignin as a fuel comes also with a high investment cost, but relatively low running costs. Power consumption needed for lignin production is low, and CO_2 for the process can be obtained from the lime kiln flue gases. (Tomani et al. 2011) The biggest disadvantage with using lignin as a fuel might be the value of lignin for production of more value-added products. In many cases it might be more economically reasonable to sell lignin to other companies instead of combusting it in the lime kiln. (Bajwa et al. 2019)

Using different wood residues to pulverize them or to make producer gas can be reasonable if the wood residues can be gained from near the mill and at a cheap price. The investment costs of both processes are relatively low compared to lignin or hydrogen production. Production of producer gas requires low power consumption and is already implemented at multiple mills. Pulverizing wood residues requires more power and problems may arise during the grinding process. Pulverized wood residues can also bring more impurities into the lime cycle, what would increase costs related to make-up lime. (Kuparinen & Vakkilainen 2017) Taking these aspects into consideration, preparing producer gas from wood residues can be more economically feasible compared to pulverizing the wood residues for fuel use.

Table 11: Advantages and disadvantages of studied renewable fuels on financial and logistical aspects.

	Advantages	Disadvantages
Hydrogen	• Can be produced onsite from water [a] • Byproducts from fuel production can be used at the mill [b]	• High power consumption [b] • High investment cost [a]
Lignin	• Can be produced onsite from black liquor [a] • Fuel production can increase potential for pulp production [a] • Low power consumption [a]	• High investment cost [a] • More value-added products can be produced from lignin [c] • Power output from recovery boiler is decreased [a]
Producer gas	• Can be produced onsite from a variety of biomass feedstock [d] • Low power consumption [a]	• Need for large amounts of biomass feedstock [d]
Pulverized wood residues	• Can be produced onsite from biomass [a]	• Need for large amounts of biomass feedstock [a] • Potential problems in biomass pretreatment [a]

Note. The information in the data is from different sources labelled with letters a–d. Sources are as follows: [a] Kuparinen and Vakkilainen (2017); [b] Hart (2020); [c] Bajwa et al. (2019); [d] Taillon et al. (2018).

6 Conclusions

The main objective of this thesis was to construct a model of a lime kiln, which can simulate the use of different renewable fuels in the process. The results in Chapter 4 showed that with four different renewable fuels, the model produced results that were comparable to real lime kilns by most aspects. The renewable fuels also acted relatively similar to natural gas, which was used as a baseline comparison fuel in the analysis. Therefore, it can be said that all of the analyzed renewable fuels could work theoretically in lime kilns.

The model accurately predicts process variables, such as fuel and oxidizer mass flow rates, temperatures at specified locations and CO_2 emissions. These and other variables are comparable to other models created in literature and real lime kiln data. One aspect, which the model does not accurately predict, is NO_X, SO_2, TRS and PM emissions. The values observed for these emissions were not similar to real lime kiln data. The model would need to be improved if these emissions would want to be analyzed more accurately. For example, a kinetically controlled model would be required for proper nitrogen chemistry.

The second objective of the thesis was to study oxyfuel combustion in a lime kiln. No other works were found in literature where oxyfuel combustion was modelled for a lime kiln located in a kraft pulp mill. The results showed that oxyfuel combustion can decrease fuel usage by approximately 19 % compared to a traditional combustion process. In terms of lime kiln energy efficiency, a 10 % increase was found when switching to oxyfuel combustion. In addition to improvements in energy consumption, the changes in flue gas composition makes it possible to capture CO_2 more efficiently. Oxyfuel combustion comes with high investment and running costs, which can make oxyfuel combustion not economically feasible to implement into the lime kiln at the moment.

The third objective of the thesis was to compare renewable fuels on financial aspects. This comparison was made broadly for the studied renewable fuels: hydrogen, lignin, producer gas, and pulverized wood residues. Hydrogen production at a kraft pulp mill produces useful byproducts, but the costs related to water electrolysis are relatively high. Lignin can be efficiently separated from black liquor to be combusted at the lime kiln. However, lignin can be also used to create more valuable products, what would make using it as a fuel wasteful in terms of profits. Producer gas and pulverized wood residues can be both produced from a variety of biomass, but transportation of large amounts of biomass from outside of the mill can prove to be challenging.

Taking into consideration both the results from the model and the financial realities of each renewable fuel, producer gas seems to be the best alternative studied in this thesis. Although producer gas increases the required fuel heat input in the lime kiln, the economics and logistics of producer gas can be very relatively advantageous if there is cheap biomass available for the kraft pulp mill. Therefore, it is no surprise so many lime kilns throughout the world have turned to using producer gas as an alternative lime kiln fuel.

Although the lime kiln model built for this thesis proved to relatively comparable to other models and real lime kiln data, it had multiple restrictions. All of these restrictions of the model could be included to the model to create a more in-depth lime kiln model in the future. Some improvements would be adding lime mud dusting processes, better chemistry for emission calculations and improvements to

the thermodynamics of the model. In addition to these improvements, more renewable fuels could be easily studied using the model.

The analysis in this thesis used data from various sources. This makes the results relatively indefinite that do not represent any individual lime kiln. Using data from a specific real lime kiln could be used to compare results between the model and a real lime kiln. This way any changes in lime kiln operation could be first simulated using this model before implementation at the real lime kiln. By adding other processes to the model, the usability of the model could be increased. These other processes could be processes related to the lime kiln, such as flue gas cleaning or CCS, or other kraft pulp mill processes. This way a detailed full-scale model of a kraft pulp mill could be constructed.

According to the model results, oxyfuel combustion and renewable fuels can be effectively used at the lime kiln to decrease emissions in the pulp and paper industry. However, the financial aspects of oxyfuel combustion and renewable fuels were not studied in detail. More research should be directed towards applying oxyfuel combustion in a kraft pulp mill setting. This would include studying all costs related to oxyfuel combustion, such as investment costs and electricity demand of the auxiliary equipment. Any fuel should also be studied extensively for each kraft pulp mill because costs related to fuels are always dependent on multiple factors, such as the location of the pulp mill and pulp production capacity. A much more in-depth techno-economic analysis of fuel alternatives should be done before the final fuel choice.

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Appendix A: Composition of fuels and lime mud in the model

Hydrogen

The hydrogen stream, which is used as a fuel in the lime kiln, is assumed to be composed of purely hydrogen molecules. This hydrogen is produced by water electrolysis onsite or transported to the pulp mill via a hydrogen gas grid.

Lignin

The ultimate analysis and proximate analysis of lignin are shown Tables A1 and A2. The values in the tables are based on the values presented by Suopajärvi et al. (2017). The values are for kraft lignin, which is the lignin type obtained from the kraft pulping process. Lignin is dried before combustion in the lime kiln, so the moisture content is assumed to be relatively low. The ultimate analysis is on dry basis.

Table A1: Ultimate analysis for kraft lignin (Suopajärvi et al. 2017).

Component	Mass fraction (wt-%)
Carbon	65
Oxygen	26.7
Hydrogen	5.6
Sulfur	1.9
Ash	0.7
Nitrogen	0.1

Table A2: Proximate analysis for kraft lignin (Suopajärvi et al. 2017).

Component	Mass fraction (wt-%)
Volatiles	66.4
Fixed carbon	32.9
Moisture	4
Ash	0.7

Lime mud

The lime mud composition shown in Table A3 and chosen for the model is mostly based on the values presented by Tran (2007) as lime mud composition on dry basis. All oxide components do not represent real compounds in lime mud, and they are chosen here to just represent inert impurities. The sodium compounds aim to represent residual white liquor content in lime mud. Moisture content of lime mud is chosen as 25 wt-% based on the average moisture content found from the survey conducted by Francey et al. (2011).

Table A3: The composition of lime mud (Tran 2007).

Component	Mass fraction (wt-%)
$CaCO_3$	71.7
H_2O	25.0
P_2O_5	0.750
MgO	0.750
SO_3	0.675
SiO_2	0.375
NaOH	0.375
Na_2S	0.375

Natural gas

The mole fractions shown in Table A4 are based on the composition of Siberian natural gas in the Natural Gas handbook by the Finnish Gas association (2014). Only significant components of natural gas have been included and the mole fractions have been rounded up to simplify the composition.

Table A4: The composition of natural gas (Finnish Gas Association 2014).

Component	Mole fraction (mol-%)
CH_4	98
N_2	1
C_2H_6	1

Producer gas

Table A5 presents the mole fractions for producer gas. The values in the table are approximated from the values obtained from the article by Manning and Tran (2015). Propane has been left out of the composition due to its small contribution to the total composition. No information is present in the source about what type of biomass has been used to create a producer gas with this composition.

Table A5: The composition of producer gas (Manning, Tran 2015).

Component	Mole fraction (mol-%)
N_2	41
CO	18
CO_2	14
H_2	11
H_2O	10
CH_4	5
C_2H_6	1

Pulverized wood residues

The ultimate analysis and proximate analysis of pulverized wood residues are shown in Tables A6 and A7 respectively. The values in the tables are selected from the values presented by Wilén et al.

(1996). The values chosen for the model are labelled in the source as “Forest residue chips Finnish”. Similarly as with lignin, wood residues are dried before combustion in the lime kiln, so the moisture content is also assumed to be low. The ultimate analysis is on dry basis.

Table A6: Ultimate analysis for pulverized wood residues (Wilén et al. 1996).

Component	**Mass fraction (wt-%)**
Carbon	51.3
Oxygen	40.85
Hydrogen	6.1
Ash	1.33
Nitrogen	0.40
Sulfur	0.02

Table A7: Proximate analysis for pulverized wood residues (Wilén et al. 1996).

Component	**Mass fraction (wt-%)**
Volatiles	79.3
Fixed carbon	19.37
Moisture	4.00
Ash	1.33

Appendix B: Components present in the model

All of the components used in the model are shown in Table B1. Three different component types are used in the lime kiln model: conventional, solid and nonconventional. Conventional components represent compounds, which are fluids and take part equilibrium calculations normally. Similarly, solid components represent compounds, which are in the solid phase all throughout the model. Solid physical properties, such as particle sizes, are not detailed in the model for solid components. Otherwise, default settings are used for both conventional and solid components. Nonconventional components are defined for the biomass-based fuels and for the ash in these fuels. The density and enthalpy property models chosen for nonconventional components are DCOALIGT and HCOALGEN respectively.

Table B1: All of the components present in the Aspen Plus model

Component	**Type**
H_2O	Conventional
CO_2	Conventional
CaO	Solid
$CaCO_3$	Solid
N_2	Conventional
O_2	Conventional
CO	Conventional
CH_4	Conventional
C_2H_6	Conventional
NO	Conventional
NO_2	Conventional
Nonconventional fuel (Lignin/Pulverized wood residues)	Nonconventional
S	Conventional
SO_2	Conventional
SO_2	Conventional
H_2S	Conventional
H_2	Conventional
C	Solid
Ash	Nonconventional
MgO	Solid
SiO_2	Solid
P_2O_5	Solid
NaOH	Conventional
Na_2S	Conventional
Na_2SO_4	Conventional
Na_2CO_3	Conventional

Appendix C: Additional results from the model

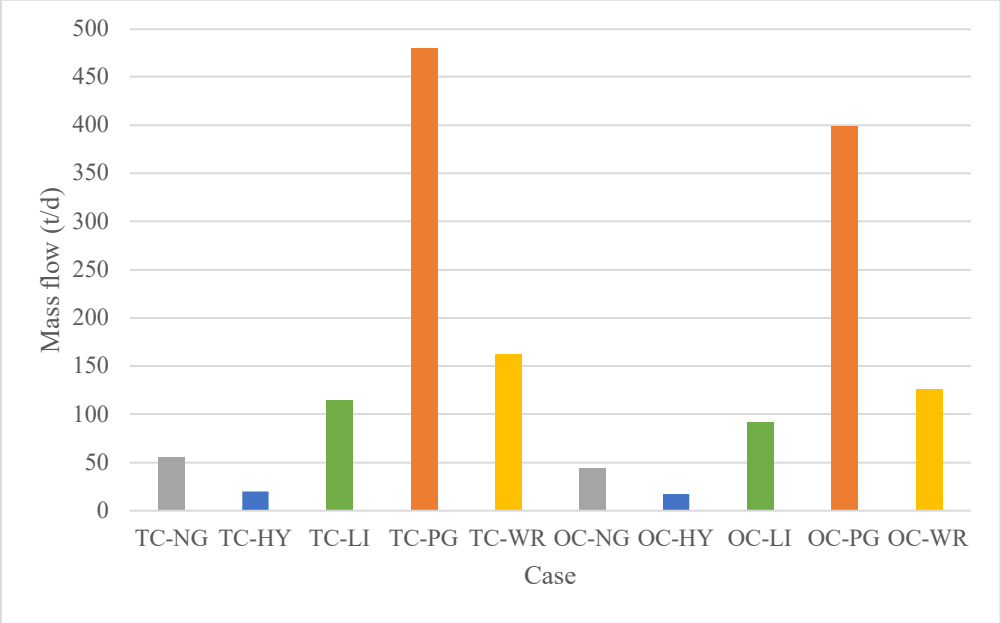

Figure C1: Fuel mass flow rates in different cases.

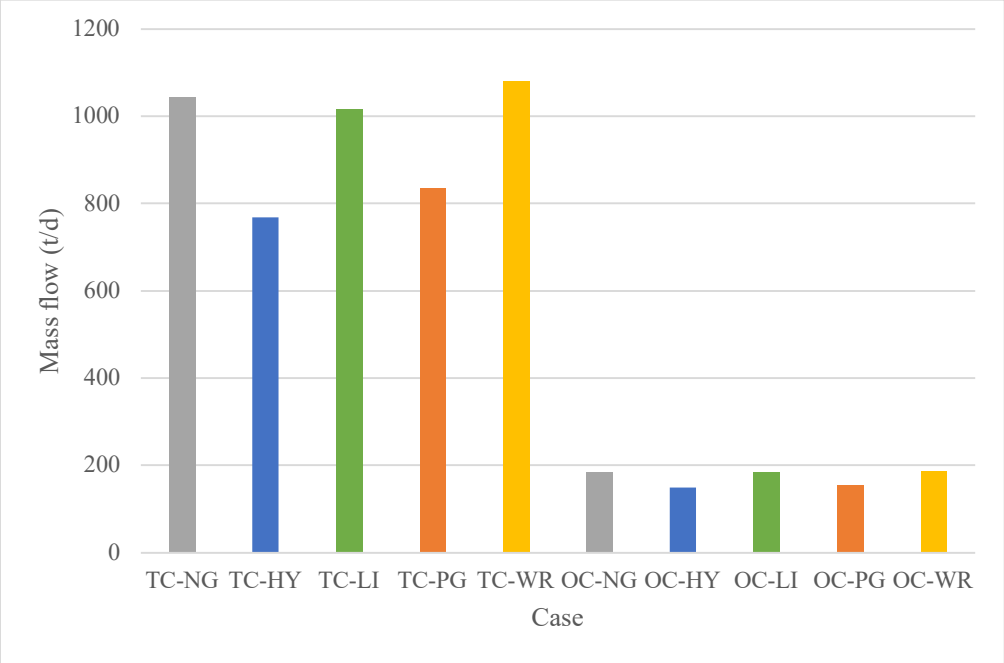

Figure C2: Oxidizer (air in the TC model and pure oxygen in the OC model) mass flow rate in different cases.

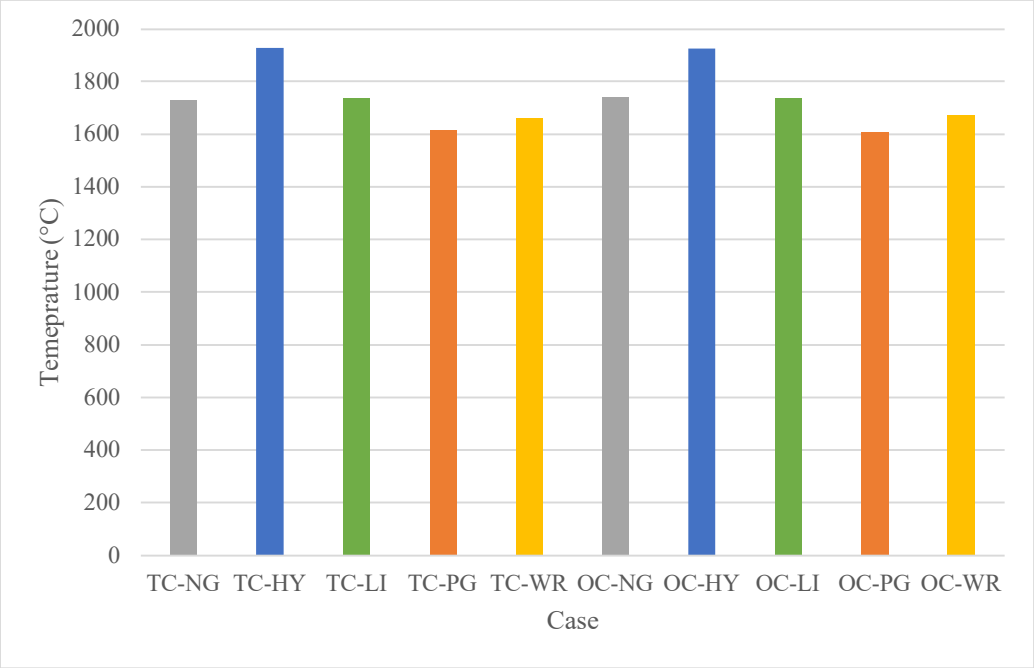

Figure C3: Combustion temperature in different cases.

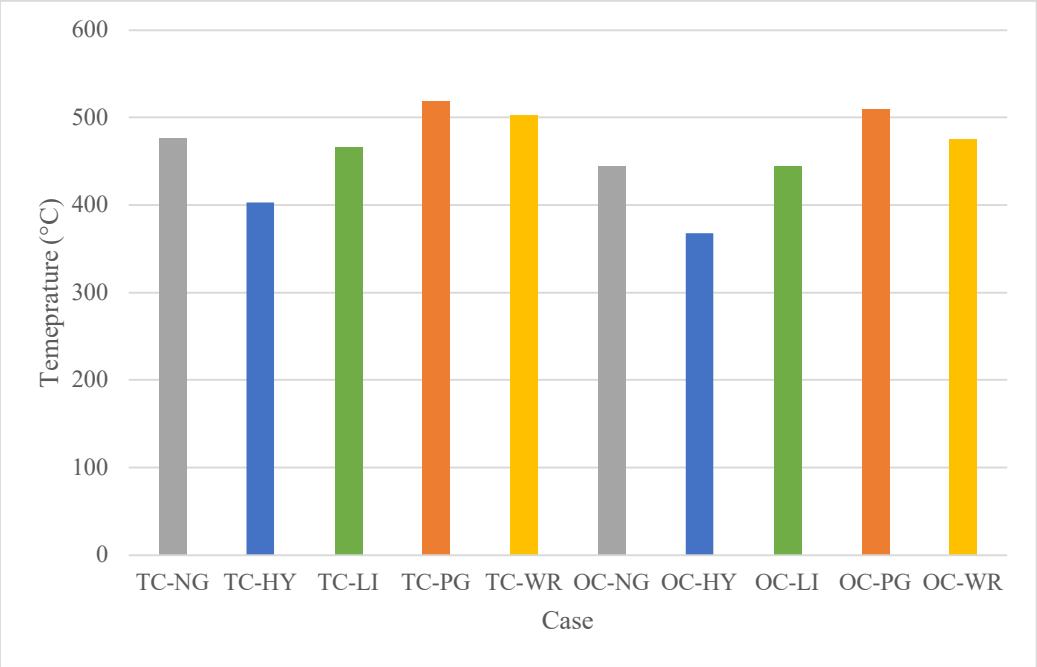

Figure C4: Flue gas temperature in different cases.

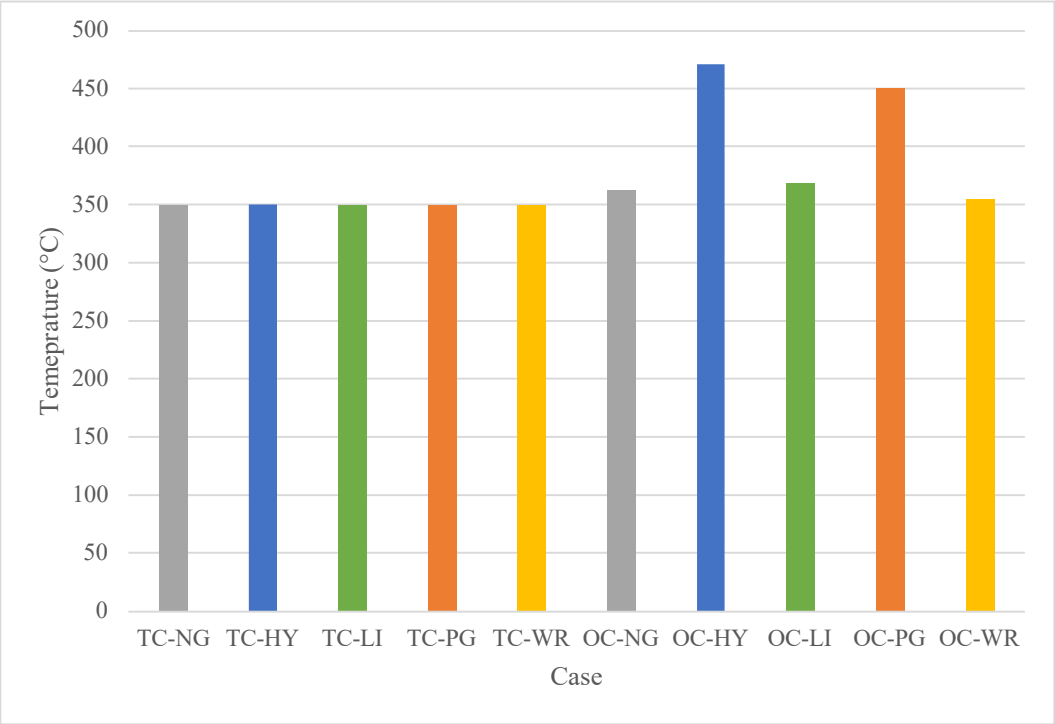

Figure C5: Cooled lime temperature in different cases.

Table C1: The energy balance of the process in different cases. Units in the table are kW.

Case	**TC-NG**	**TC-HY**	**TC-LI**	**TC-PG**	**TC-WR**	**OC-NG**	**OC-HY**	**OC-LI**	**OC-PG**	**OC-WR**
IN										
Fuel	32754	29219	35038	36476	38554	25863	25252	28188	30346	29963
Oxidizer	3584	2640	3497	2869	3711	573	462	568	483	584
Lime mud	5753	5753	5753	5753	5753	5753	5753	5753	5753	5753
OUT										
Calcination	-9595	-10716	-11356	-9596	-12418	-9774	-10517	-11167	-8817	-11864
Drying	-7820	-7820	-7820	-7820	-7820	-7820	-7820	-7820	-7820	-7820
Shell heat losses	-4851	-4210	-5161	-4247	-5639	-3830	-3638	-4153	-3541	-4382
Flue gases	-17686	-12730	-17808	-21298	-19990	-8582	-6939	-9162	-13922	-10067
Reburned lime	-2138	-2138	-2143	-2138	-2152	-2182	-2553	-2207	-2482	-2168
Sum of energy	42090	37613	44288	45098	48018	32189	31467	34509	36582	36300

Table C2: The energy balance from the FGR sensitivity analysis from Chapter 4.2.1. Abbreviations of the fuels are: NG = natural gas & PG = producer gas. Units in the table are kW.

Fuel	**NG**	**NG**	**NG**	**NG**	**NG**	**PG**	**PG**	**PG**	**PG**	**PG**
FGR split	**0 %**	**20 %**	**40 %**	**60 %**	**80 %**	**0 %**	**20 %**	**40 %**	**60 %**	**80 %**
IN										
Fuel	21221	22648	25219	27969	30948	24695	27859	31022	34218	37594
Oxidizer	466	500	558	620	687	389	441	493	545	600
Lime mud	5753	5753	5753	5753	5753	5753	5753	5753	5753	5753
OUT										
Calcination	-11334	-10078	-9812	-9721	-9786	-9840	-9236	-8786	-8399	-8117
Drying	-6350	-7820	-7820	-7820	-7820	-7820	-7820	-7820	-7820	-7820
Shell heat losses	-3143	-3354	-3735	-4142	-4583	-2877	-3246	-3614	-3987	-4380
Flue gases	-4074	-5223	-7933	-10521	-13061	-7512	-11133	-14601	-18037	-21492
Reburned lime	-2539	-2426	-2231	-2138	-2138	-2789	-2619	-2448	-2275	-2138
Sum of energy	27440	28901	31531	34343	37388	30838	34053	37269	40517	43947

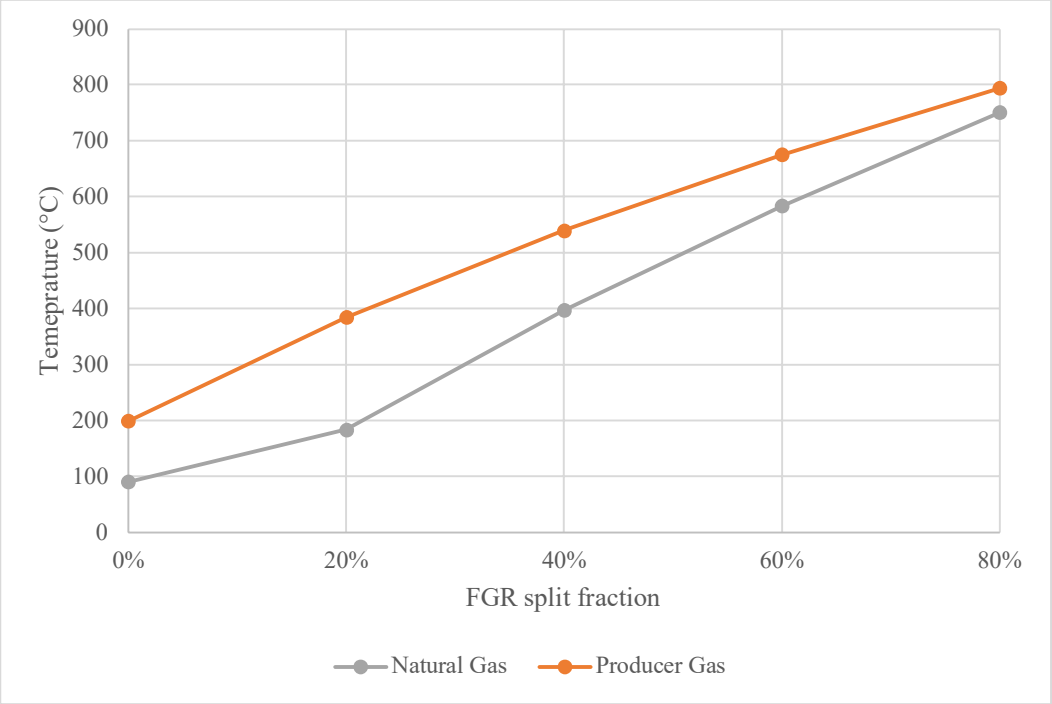

Figure C6: The effect of FGR split fraction on flue gas temperature