

Mass and energy balances over the lime kiln in a kraft pulp mill

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Abstract

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This report describes the construction of a model that calculates mass- and energy balances over the lime kiln in a kraft pulp mill. The model was implemented in FORTRAN to serve as the lime kiln block in the WinGEMS simulation software. The mass balance is based on a number of user specified parameters as well as chemical relations found in the literature. A general method to approach the different concentrations and mass flows when constructing a WinGEMS block is also included in the report. In the energy balance the fuel consumption of the lime kiln is calculated. The model is equipped to handle up to three different fuels at a time which compositions and heating values may either be specified by the user or calculated by the model. Methods to approximate heating values and adiabatic flame temperatures are presented. The fuel consumption is calculated analytically by establishing an energy balance over the kiln where the energy for calcination, drying as well as the heat energy of the in- and outgoing streams is accounted for. To calculate the heat energy of the different streams, polynomials were used to describe the temperature dependent heat capacities of the different components. The polynomials were fitted to thermodynamic data from the literature. Examples on how the heat rate of the kiln is affected when changing different parameters are shown. Two kinds of simulations were also performed with the lime kiln model. In the first simulation the possible effects of increased intake of non-process elements with the use of bio fuels are studied. In the second simulation the amounts of energy that may be retrieved from the flue gases when combining a more efficient lime mud filter with an external dryer is studied.

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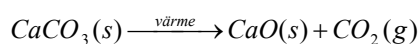
Preface

This Master thesis was carried out at STFI-Packforsk in Stockholm. I would like to express my gratitude towards the people who have helped me with this work. Special thanks to Rickard Wadsborn who has been my main source of support and guidance in the daily work with the lime kiln model. I also wish to thank Niclas Berglin and Hans Theliander at STFI-Packforsk as well as Bengt Carlsson at Uppsala University.

Sammanfattning

Syften med examensarbetet är att skapa en mesaugn som beräknar mass- och energibalanser över processen. Modellen ska kunna integreras i simuleringar av stora fabrikssystem i programvaran WinGEMS. Förutom att leverera rimliga beräkningar är därför användbarhet och driftsäkerhet viktiga faktorer i arbetet med modellens utformning.

Mesaugnen används inom sulfatprocessen, vilken är den vanligaste processen för tillverkning av kemisk pappersmassa. I sulfatprocessen kokas veden i en kemikalieblandning vilket lösgör fibrerna från ligninet och gör dem till pappersmassa. De använda kemikalierna tillsammans med ligninet förs sedan genom en återvinningscykel för att återskapa kokkemikalierna samt utvinna energin i ligninet. Mesaugnen är en del av denna återvinningscykel och har till uppgift att omvandla mesa (CaCO_3) till bränt kalk (CaO) genom kalcinering:



En mesaugn är normalt en liggande cylinder som roterar längs sin egen axel och vars lutning får det fasta materialet att röra sig framåt i ugnen. Fuktig mesa förs in i den högre änden varpå materialet på sin väg genom ugnen torkas, värms upp, kalcineras och sintrar (bildar större partiklar). Värme tillförs ugnen från en brännare placerad i ugnens motsatta ände. Energi överförs från förbränningsgaserna till det fasta materialet medan de rör sig i motsatt riktning gentemot varandra. Mesaugnen kan därmed liknas vid en motströms direktkontaktvärmeväxlare.

De flesta av dagens mesaugnar använder naturgas eller eldningsolja som bränsle. Moderna brännare ger dock möjlighet till stor flexibilitet och de flesta sorters bränslen kan användas. De biobränslen som är intressantast är dels restprodukter från processen t.ex. metanol och tallolja eller billigare fasta bränslen som bark eller träpulver.

Modellens materialbalanser utgår till stor del från ett antal parametrar som specificeras av användaren. Bland annat så är det möjligt att specificera hur stor del av kalciumkarbonatet som omvandlas till kalciumoxid (kalcineringsgrad) och hur stor del av kalket som blir överbränt. Antagelser om natrium- och svavelföreningarnas beteende inuti mesaugnen har gjorts efter litteraturstudier. När det gäller emissionerna av svaveldioxid så har litteraturstudier av experiment med förbränning av svavelhaltiga gaser använts för att kunna kvantifiera emissionerna som en funktion av mängd ingående svavel i ugnen.

Mesaugnsmodellen beräknar en bränsleförbrukning utifrån den ingående mesaströmmen samt specifikationer från användaren. Upp till tre olika bränslen kan användas, varav ett alltid måste vara ospecificerat i massflöde, eftersom detta beräknas av modellen. Vad gäller bränslesammansättningen så kan användaren antingen specificera denna själv eller använda standardsammansättningar för olika bränslen. Värmevärdet kan också antingen specificeras eller approximeras av modellen utifrån sammansättning och bränslespecifikation. Modellen beräknar även

den adiabatiska flamtemperaturen, som är ett teoretiskt mått på lågans temperatur för ett specifikt bränsle.

Energiförbrukningen beräknas analytiskt av modellen efter en värmebalans som utgår från att den energi som kommer ut från ugnen är lika stor som den som kommer in. En referenstemperatur på 25°C har antagits vid beräkningarna. De stora energiposterna är den för kalcinering och torkning men en del energi är även kvar i utgående rökgaser och det fasta materialet i form av värme. Värmeenergin har beräknats med hjälp av värmekapacitetspolynom som har anpassats till data för värmekapaciteter vid olika temperaturintervall.

För att kunna få fram ett uttryck som gör det möjligt att beräkna bränsleförbrukningen analytiskt är det nödvändigt att separera på de delar av rökgaserna som är beroende av bränslet och de delar som inte är det. Energin från det eller de bränslen vars massflöde var specificerats måste även dras bort från den totala energiförbrukningen för att beräkna det ospecificerade bränsleflödet.

Två olika simuleringsförsök har även genomförts med mesaugnsmodellen. I det första försöket undersöktes vad det ökade intaget av t.ex. kisel och fosfor med biobränslen skulle kunna ha för effekt på processen. När koncentrationen av dessa blir för höga bildar de kalciumföreningar vilket dels minskar mängden fritt CaO som kan bildas och dels utgör ballast i processen. För att förhindra en ackumulering av dessa ämnen kan mer mesa behöva dumpas och ersättas med inköpt kalk. Simuleringarna visar att detta kan bli ett problem om bark med hög fosforhalt används som bränsle. Ekonomiska överslagsberäkningar visar dock att kostnaden för ökat kalkinköp förmodligen kan uppvägas av lägre bränslekostnader.

Det andra simuleringsförsöket undersöker möjligheterna att utvinna energi ur mesaugnens rökgaser om torrhalten på mesan ökar samt en extern tork används. Endast en ökning av mesans torrhalt ger inga större energivinster eftersom det genererar varmare rökgaser. Om någon form av värmeväxlare kunde installeras mellan mesaugnen och den externa torken skulle dock högvärdig energi kunna användas för ångproduktion medan den lågvärdiga energin användes för torkning. Simuleringarna visar t.ex. att ca 24 % av energin kan återvinnas om torrhalten höjs från 70 % till 85 % samtidigt som rökgastemperaturen efter torkningen sänks från 250°C till 150°C. Detta motsvarar ca 256 MJ/ton massa eller 35,6 GWh per år för en fabrik som tillverkar 500 000 ton massa årligen.

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1. Introduction

Kraft pulping is a process where cooking chemicals are used to delignify the wood and create pulp. Spent cooking chemicals are sent through a recovery cycle so that they may be reused. A part of this cycle is the limekiln that converts CaCO_3 to CaO by burning it under a flame. As the last big consumer of fossil fuel in many kraft mills, increasing energy prices may however bring a new dawn for the lime reburning process. To improve kiln performance as well as converting to non-fossil fuels knowledge about the fundamental mass- and energy balances is crucial.

The purpose of this thesis is to create a model of the lime kiln that performs mass- and energy balances over the process. This model is to be integrated in the WinGEMS software that is used to simulate mill systems in the pulping industry. There is an existing lime kiln block in WinGEMS but since has proven inadequate and in need of replacement. Since the model should be used in the every day work at STFI-Packforsk, usability and robust operating are important factors in the development of the model.

The model is implemented in FORTRAN. This report describes the assumptions and theories that constitute the model. Since the FORTRAN code is not included a lot of the work put in to create a working model is not visible in the report. Instead the model itself is in many ways the most important result of this thesis. The intent is that the reader will get a good picture of how the model works by reading this report.

Two different simulations were also conducted using the lime kiln model. The possible effects of using bio fuels in the lime kiln were studied in the first simulations. An increased input of non-process elements through the ash may cause problems with accumulation in the lime cycle. Five different fuels were tested in a reference mill system to study the effects on the lime cycle and the product lime. An economic evaluation was also done to investigate the possible economic impacts of an increased input of ash.

The potential to recover energy from the hot lime kiln flue gases using better lime mud filters and an external flash dryer was studied in the second set of simulations. By using this constellation the high-value energy of the flue gases could be used for steam generation instead of being used for drying. The purpose of these simulations was to study the energy balances of the process and draw some general conclusions about the amounts of energy that could potentially be recovered and the temperature intervals at which this recovery could be done.

2. Theory

2.1 Kraft cooking and the recovery cycle

In chemical pulping cooking chemicals are used to remove the lignin from the wood and thereby releasing the fibers. This is substantially different from the mechanical pulping where the fibers are laid bare through grinding of the wood. Mechanical pulping will therefore use a larger portion of the wood material but will require a lot of energy to run the process. In the chemical pulping on the other hand the lignin is combusted generating large amounts of energy (Theliander 2004) and (Grace et al. 1985).

The chemical pulping process commonly used in the world is kraft cooking. This is an alkaline process where white liquor (NaHS and NaOH) is used to delignify the wood. This is done in digesters that are either continuous or batch-wise. Used cooking chemicals along with the lignin from the wood will leave the digester as black liquor. The black liquor will then go through a recovery cycle that has two main purposes:

1. Recover the cooking chemicals
2. Utilize the energy from the lignin

Figure 1 shows a simplified flow sheet to illustrate the different steps of the Kraft recovery cycle.

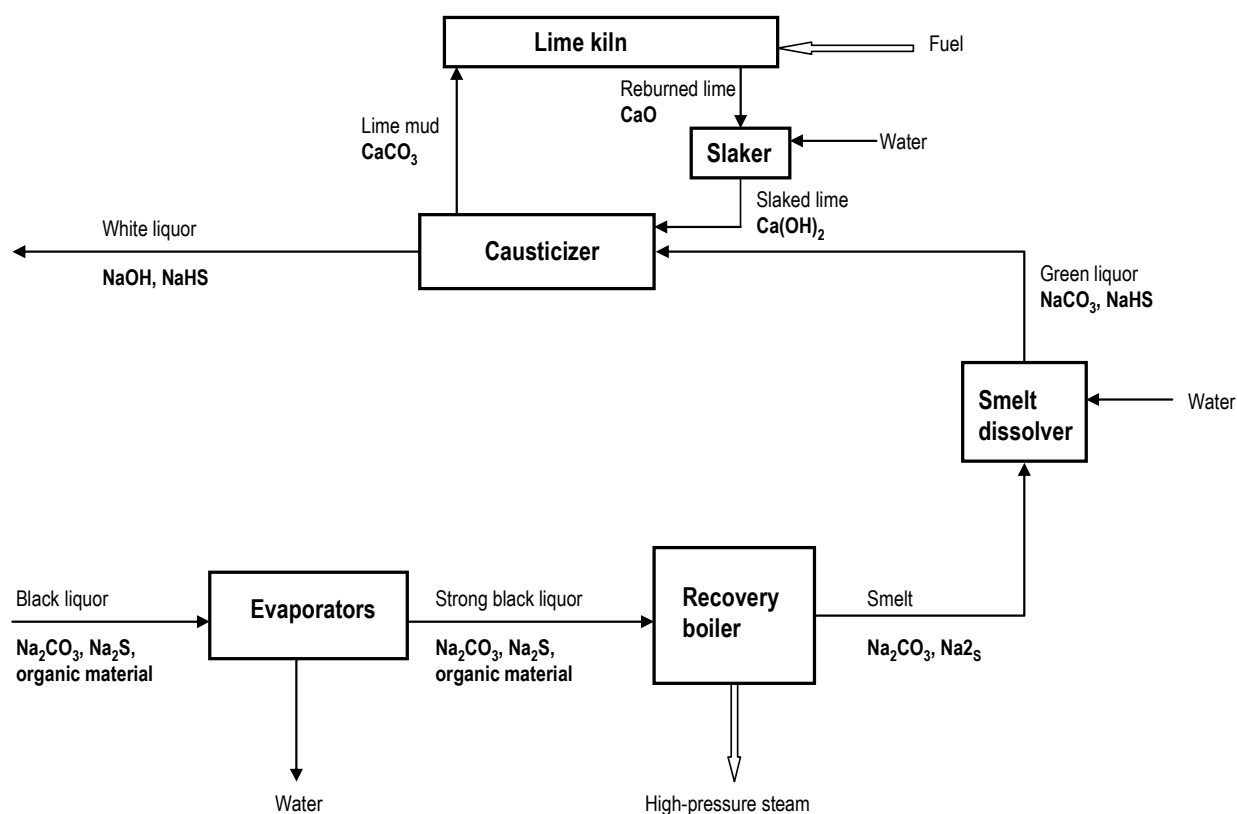


Figure 1. Flow sheet of the recovery cycle.

The black liquor leaving the digester will consist of water, organic material as well as the used cooking chemicals sodium carbonate and sodium sulfide. Although there is a lot of energy in the black liquor the low dry content of 15-20 % makes it impossible to combust before some of the water has been removed. This is done through a series of evaporators until the black liquor has a dry content of 70-80 % and is referred to as strong black liquor (Theliander 2004).

In the recovery boiler the strong black liquor is dried, pyrolysed and finally combusted with air as oxidizer. The large amounts of heat generated in the recovery boiler are used to produce high-pressure steam. The chemicals leave the furnace as a salt smelt that is transported further to the smelt dissolved where they are dissolved to create green liquor (Theliander 2004).

The sodium carbonate is transformed to sodium hydroxide in the causticizer through the following reaction:



This completes the recovery cycle since the cooking chemicals sodium hydroxide and sodium hydrosulfide have both been reformed. To maintain the causticizing reaction however it is necessary to find a way to convert CaCO_3 back to Ca(OH)_2 . In the kraft process this is done through the calcination and slaking reactions. Together with the

causticizing reaction they constitute the lime cycle that aims to maintain the formation of the cooking chemical sodium hydroxide. The lime cycle is illustrated in Figure 2.

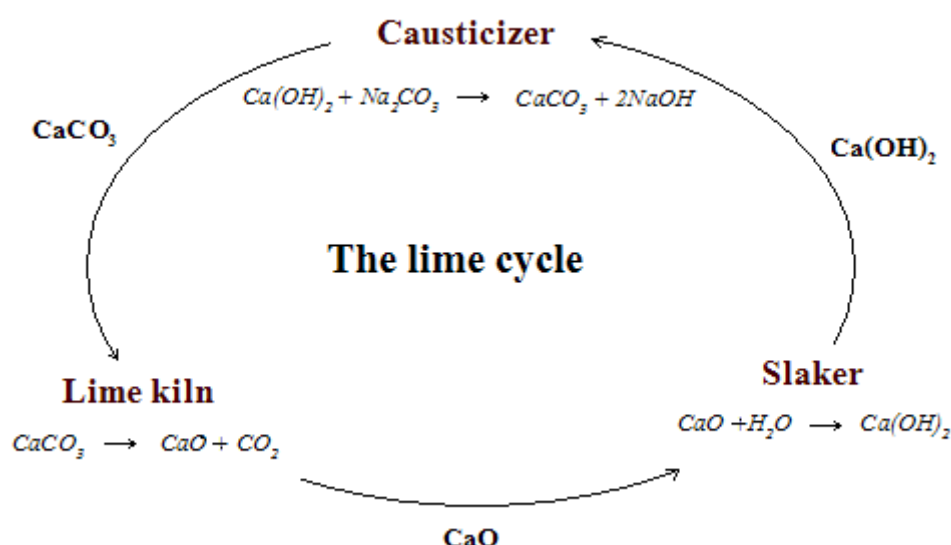


Figure 2. The lime cycle.

When leaving the causticizer the lime mud is separated from the white liquor through filtering and transported to the lime mud wash where it is washed. The lime mud then enters the lime kiln where it undergoes the endothermic calcination reaction:



The carbon dioxide is lost through the flue gases while the reburned lime is transported to the slaker where it is mixed with water:



This reaction completes the lime cycle which includes three different calcium components. The lime cycle is a solid-phase process in contrary to the rest of the recovery cycle which mostly handles liquids (Theliander 2004).

2.2 Lime reburning

The purpose of the lime reburning is to convert the $CaCO_3$ produced in the causticizing process to CaO that can be reused in the slaker. This is done by heating the $CaCO_3$ until reaction 2 occurs. The most common way to do this is by using a rotary lime kiln, which is basically a large steel tube that is slightly tilted, typically between 1.5 and 3.5 ° (Grace et al. 1989). Wet lime mud enters the kiln at the high end (feed end) and is transported towards the low end (discharge end) due to the rotation and inclination of the kiln. On its way through the kiln, lime mud is heated by hot flue gases that move counter-current compared to the solids. Heat is supplied from

a burner located at the discharge end. The process can be divided into the following steps, each representing a specific section of the lime kiln (Theliander 2004).

1. Drying of the lime mud. (The drying zone is usually equipped with a chain system to enhance the heat transport from the hot flue gas to the lime mud.)
2. Heating the lime mud to calcination temperature (about 850 °C).
3. Calcination of CaCO_3 according to (2). The solids will remain at calcination temperature until all CO_2 has been driven off.
4. Sintering of the lime. When the lime powder is heated further the small particles agglomerates, forming larger particles.

The positioning of the different zones inside the kiln is very important for the quality of the lime. If the sintering zone is too long there is a risk of overburning the lime, reducing the amount of available CaO . However, not enough sintering will cause the lime to leave the kiln as dust particles. This causes problems with dusting and makes the reburned lime less separable. Consequently, a trade-off has to be made to attain a product that is reactive in the causticizing process as well as manageable (Tran 2000).

Another difficulty of the calcination process is that the lime product should have a low CaCO_3 content without being overburnt, causing the lime to be less reactive in the slaker. A good general guideline for most lime kilns is that a residual carbonate between 1 % and 2 % result in good lime quality with little overburning (Grace et al. 1989). The fraction of active CaO in the reburned lime is expressed by the lime reactivity, which typically ranges from 85-95 %. In addition to showing the quality of the product, lime reactivity is used to indicate the accumulation of inert materials in the lime cycle (Tran 2000).

The flue gas leaving the feed end of the kiln will consist of combustion products, carbon dioxide from the calcination and water evaporated from the wet mud. Flue gas flow is mainly controlled through the induced draft fan located at the feed end (Hough 1985). This fan is often one of the limiting factors in the kiln capacity (Grace et al. 1989).

Air for the combustion is supplied by primary and secondary air at the firing end of the kiln. This makes it possible to control the flame pattern of the burner. The burner should produce a long soft flame so that the release of heat is spread out over a large area of the kiln. A shorter flame has a higher temperature which makes the heat transfer more efficient but may result in overburned lime and cause damage to the refractory of the kiln (Hough 1985).

To maintain the structural integrity of the kiln, it is important to have a refractory that is able to withstand heat and chemical attack. Because of the change in temperature, different refractory materials are usually used along the length of the kiln. Common are silica and aluminum compounds with the aluminum content being higher in the hot zones of the kiln for heat resistance purposes (Grace et al. 1989).

2.2.1 Dusting

As the lime mud moves through the kiln, part the solids will form dust particles. One obvious risk with dusting is loss of mass, considering that the dust flow out of the feed end typically amounts to 5 to 20 % of the dry lime mud. Most of the dust is returned to the kiln through precipitators and scrubbers. However, if a wet scrubber is used, the recycled dust will bring additional water to the feed, reducing kiln capacity. Modern cyclone type dust collectors may instead return the dust to the kiln dry, thereby avoiding this problem and increase energy efficiency (Manning et al. 2007).

2.2.2 Ring formation

A problem in lime kiln operations is the formation of rings on the inside of the kiln. These rings obstruct the movement of lime mud and may in severe cases result in kiln shutdown for ring removal. There are several types of rings but the most troublesome are mid-kiln rings that are formed in the middle of the kiln (Tran 2000).

What causes the ring formation is not fully understood, although there is believed to be a connection to the levels of alkali and sulfur in the lime cycle. Sodium compounds have relatively low melting temperatures which makes the lime mud more prone to stick to the refractory lining. In laboratory works where the sodium (Na_2CO_3) content of lime mud was varied, this correlation could be shown. Pure CaCO_3 lead to no accumulation of lime mud whereas at 5 wt% Na_2CO_3 , the tube was heavily coated with deposits. Once lime mud has adhered to the kiln wall, the hardening of the rings is mainly due to recarbonation. In this process, CaO is converted back to CaCO_3 which strengthens the structure of the ring. Recarbonation is favored by low temperatures and high concentrations of CO_2 . Ring hardening through the forming of CaSO_4 also occurs but this is less common due to the relatively low concentration of SO_2 (Tran et al. 1992).

2.2.3 Energy efficiency

The energy entering the lime kiln can go three directions (Grace et al. 1989):

1. Into the lime solids.
2. Out through the shell of the kiln.
3. Out through the back end with the flue gas.

The energy put into the solids is used for heating, drying and calcination of the lime mud. The energy required for calcination will be relatively constant and hard to affect whereas the energy for drying will depend on the moisture content of the lime mud. An efficient separation of lime mud from white liquor resulting in high dry content of the feed is therefore crucial for the energy efficiency of the lime kiln.

Energy used to heat the lime mud may be retained to some extent using tube coolers. Hot lime will drop through holes at the discharge end of the kiln, into the tube coolers where it will preheat the combustion air to 260-370 °C. The lime will thereby leave the kiln with a temperature of 200-300 °C instead of ~1100 °C, reducing the amount of energy that has to be provided to the process (Hough 1985).

The amount of energy leaving out the shell will depend on the proportions, temperature profile and insulation of the kiln. For energy efficiency, insulation is the most obvious tool for minimizing this kind of heat loss. Heat resistant high aluminum bricks are however poor insulators. This problem may be solved by using a refractory lining with double bricks. Insulating bricks are placed between the steel shell and the aluminum bricks, thereby reducing the heat losses without losing the resistive properties of the refractory (Grace et al. 1989). In a lime kiln, heat losses from the shell are usually 10-15 % of the energy input (Norbom 1985).

The drying zone of the lime kiln is usually equipped with a chain system to promote heat transfer from the flue gas to the solids. As the kiln rotates, the warm chains dip into the wet solids that will stick to the chain and thereby exposing a large surface area to the flue gases. These kind of low temperature heat exchangers are very efficient and may lower the temperature of exit gas in kilns from ~650 °C to less than 200 °C (Hough 1985).

The energy efficiency of a lime kiln may be described by the heat rate. The heat rate is amount of energy that is consumed to create a certain amount of reburned lime. Usually this is expressed as MJ/ton CaO. For most lime kilns, the heat rate is between 6 and 9 MJ/ton CaO (Norbom 1985).

2.2.4 Flash drying

In a conventional lime reburning process the lime mud is dried, heated, calcinated and sintered inside the rotary kiln. It is however possible to separate the drying process and perform this in an external flash dryer. Feeding dry lime mud to the lime kiln will substantially increase the exit gas temperature of the kiln. The hot exit gases (typically 540-680 °C) are then used to dry the lime mud in the flash dryer (Hough 1985).

In principle, flash drying is just a way to move the drying process out of the lime kiln and into an external dryer. The overall heat balance over the process is therefore not necessarily affected. The capacity of the lime kiln will however increase, since a larger part of the kiln may be used for calcination (Hough 1985). Using flash dryers may also make it easier to retrieve energy from the exit gases of the kiln. This is further discussed in chapter 8.

2.2.5 Fuels

The fuels most widely used in lime kilns are fuel oil and natural gas. In many kilns a variety of fuels may be used in the same burner which increases the flexibility and makes it possible to use whatever fuel is available to the mill. The use of bio fuels is increasing as the price for crude oil rise as well as the need for environmental policies. Bio fuels available to the mill either as a by-product or as an existing raw material may be of most interest. Tall oil and methanol, both by-products from the Kraft process are liquid fuels that may be used without too much modification of the process. Different kinds of solid bio fuels like bark or lignin on the other hand requires preparation before being fed to the burner. There are basically two ways of preparing the solid fuels used in mills today (Wadsborn et al. 2007):

1. The solids are dried and then grinded to a fine powder that is fed to the burner.
2. The solids are dried and then gasified into a gas mixture that is fed to the burner.

In the Swedish mills using solid fuels in the lime kiln, the process of preparing the fuel is usually more challenging than the actual combustion. Malfunctions will cause the line of preparation to be inactive during some periods during which time other fuels must be used instead. A back-up system is therefore required to secure supply of fuel to the kiln. In the Swedish mills there seems to be more problems regarding the gasifying process with an availability of 65-75 % compared to 80-90 % for the wood powder process (Wadsborn et al. 2007).

There is another factor in which the two preparation processes differ from each other. When using wood powder as a fuel all of the ash will end up in the reburned lime whereas in the gasifying preparation a portion of the ash will be purged from the process through the gasification. Since the accumulation of silicon, phosphorous and other non-process elements may cause problems, especially when using bio fuels, there are advantages with the gasification process in this perspective.

2.2.6 Fuel parameters

The combustion properties of the fuel have a major impact on the performance of the kiln. When using natural gas for example, the exit gas temperature will always be at least 50 degrees higher than when using fuel oil under otherwise identical conditions (Grace et al. 1989). The main reason for this is that fuel oil burns with a hotter flame than natural gas. Most of the heat transfer in the kiln is through radiation, a process that depends on the fourth power of the temperature. High combustion temperatures will therefore lead to efficient heat transfer with low exit gas temperatures and heat rates as a result.

According to simulations the two fuel parameters that predominantly determine the performance of the kiln are the adiabatic flame temperature and the flame length (Adams & Svedin 2008). When studying the simulated exit gas temperatures and heat rates for different fuels it was seen that there was an almost perfect correlation with these two parameters (Adams & Svedin 2008). The adiabatic flame temperature was the most important parameter. It gives an indication on the combustion temperature of a given fuel and is more thoroughly described in chapter 6.2.6.

The flame length also had a significant importance for kiln performance. It is known that a short hot flame will give better kiln performance than a long less hot flame (Gorog & Adams 1986). Solid fuels will usually create longer flames than liquid or gaseous fuels since the particles are larger and the combustion will therefore be less instant.

The most obvious effect of poor kiln performance is a larger fuel consumption. Another effect is that the amount of required combustion air increases, which increases the load on the induced draft fan. This is often described as a problem by mills that wish to switch to bio fuels, since the ID fan is usually one of the limiting factors on kiln capacity. Converting to an alternative fuel with a lower adiabatic flame

temperature and a longer flame than fuel oil or natural gas will presumably lower the kiln performance with increased gas flow and possibly a need to invest in a new fan equipment as a result (Grace et al. 1989).

It is quite common to burn non-condensable gases (NCG) in the lime kiln. These are sulfur rich gases that are by-products from the digester and evaporator plants. Burning NCG in a kiln without optimizing the combustion may cause lower heat transfer resulting in kiln instability and increased fuel consumption. The combustion of NCG may also enhance ring formation in the lime kiln by destabilizing the burner flame (Tran et al. 1992).

2.2.7 Formation of NO_x

There are two major pathways through which nitrogen oxides are formed in a lime kiln. Thermal NO_x is formed through a reaction between the nitrogen and oxygen in the air and is strongly temperature dependent. Fuel NO_x is a result of oxidization of nitrogen in the fuel and may occur at much lower temperatures than thermal NO_x. The NO_x emission from a specific lime kiln is therefore expected to depend on both fuel properties and combustion conditions. Kilns where thermal NO_x is the main production route will have a stronger temperature-NO_x emission correlation while kilns that produce a lot of fuel NO_x will depend more on the nitrogen content of the fuel (Löfblad et al. 1993).

2.3 Non-process elements in the lime cycle

Non-process elements (NPE) are elements that do not have any active part in the process. It is important to control the input of NPE since they tend to accumulate in the different cycles, leading to operating problems as well as dead load. Since different elements are active in different parts of the kraft process, an element may be considered an NPE in one place but not in another. Sulfur is for example an active substance in the digester but an NPE in the lime cycle. Calcium on the other hand plays an important role in the lime cycle while considered an NPE in most other parts of the kraft process.

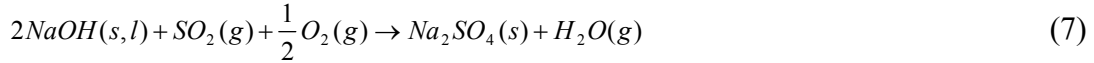
In the following section the behavior of the most important non-process elements of the lime cycle is presented.

2.3.1 Sulfur

Sulfur may enter the lime cycle either by the fuel at the discharge end or from the lime mud at the feed end. At combustion, the sulfur of the fuel will primarily be oxidized to sulfur oxides:



The sulfur oxides may either flow out of the kiln with the flue gas or react further with product lime or sodium hydroxide (Tran 2000).



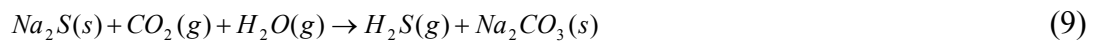
The formation of calcium sulfate in particular is an important reaction that has proven very efficient in the means of cleaning the flue gas from sulfur emissions. However, in experiments where combustion of high sulfur non condensable gases was introduced into the kiln, the sulfur removal efficiency (part of the sulfur oxides that are converted to calcium sulfate) dropped from 98 % to 89 %. Consequently, the SO₂ concentration in the flue gases increased from 25 ppm to 519 ppm. In the study it was implied that as the sulfur input to the kiln reaches a critical level, the sulfur removal efficiency drops significantly resulting in an abrupt increase in SO₂ emissions. The critical sulfur level will vary between kilns but in the kiln studied in these experiments it appeared to be around 40 kg/h (Tran et al. 2004).

In local reducing conditions caused by poor burner conditions, sulfur and hydrogen may react to form H₂S. Hydrogen sulfide is the main component of malodorous TRS (total reduced sulfur) and should be minimized. Since there is an excess of oxygen and a temperature higher than 1000 °C in the hot end of the kiln, H₂S will rapidly be oxidized to SO₂ (Tran 2000):



By proper burner design, the formation of hydrogen sulfide at the hot end of the kiln is normally avoided (Järvensivu et al. 1998). It may therefore be assumed that the sulfur content of the fuel should have no major impact on the H₂S concentration in the outgoing flue gas. In the experiment with combustion of NCG, no significant increase in the TRS concentration of the flue gas was witnessed as a result of increased sulfur content in the fuel (Tran et al. 2004).

The sulfides in the lime mud, mainly sodium sulfide, derive from the white liquor. Upon entering the kiln, they may react with the carbon dioxide and water of the flue gas.



Hydrogen sulfide is created in this way mainly in the drying and heating zones whereas in warmer parts of the kiln hydrogen sulfide will be directly oxidized according to (8) (Järvensivu et al. 1998). This reaction however, is largely temperature dependant and occurs only slowly at low temperatures. Laboratory studies where N₂ gas containing 1000 ppm of H₂S was fully mixed with various concentrations of oxygen showed that at temperatures above 550 °C oxidation of H₂S was completed in less than a second. At 350 °C though, little oxidation was observed even with a 5 % concentration of O₂ (Tran 2000). Most of the H₂S created in the feed end will therefore not be oxidized but transported out of the kiln through the flue gas.

Typically 40-60 % of the lime mud sodium sulfide content forms hydrogen sulfide (Lidén & Sjödin 1992) and (Järvensivu et al. 1998).

Consequently, unless the concentration is very high, almost all of the sulfur in the fuel will end up as CaSO_4 (and to some extent Na_2SO_4). If the sulfur content of the fuel is very high, for example while burning NCG, the SO_2 level may rise. The sulfur content of the fuel will not have any major impact on the emission of H_2S from the lime kiln, unless the burner conditions are poor. H_2S created in the feed end however, will not be exposed to high enough temperatures to oxidize. 40-60 % of the sulfides in the wet lime mud may form H_2S .

2.3.2 Sodium

There are basically three types of sodium compounds in lime mud:

- Water-soluble sodium
- Water-insoluble sodium
- Guarded sodium

Water-soluble sodium derives from the white liquor residual in the lime mud. The main components are the cooking chemicals NaOH and Na_2S but small amounts of Na_2CO_3 , Na_2SO_4 and NaCl are also present. Most NaOH will react rapidly with the carbon dioxide in the flue gas (Tran 2000).



Some of the sodium hydroxide will also react with sulfur dioxide and oxygen to create sodium sulfate according to (7).

The sodium sulfide will form sodium carbonate according to (9). If there is still sodium sulfide left in the higher temperature zones, it will be oxidized:



Hence, as the water-soluble sodium moves through the kiln, it will gradually become a mixture of Na_2CO_3 and Na_2SO_4 that will melt at around 800°C (Tran 2000).

Water-insoluble sodium is chemically bound in silicates and therefore does not dissolve easily in water. It is mainly formed in reactions between water-soluble sodium and silica or silicate minerals in the mud or refractory bricks of the lime kiln. Water-insoluble sodium compounds are expected to be relatively inert inside the kiln (Tran 2000).

The guarded sodium is water-insoluble in room temperature but becomes water-soluble at high temperatures. When entering the hot parts of the kiln the guarded sodium will therefore acquire the same properties as the water-soluble sodium. In contrary to the latter though, the guarded sodium can not be minimized through washing of the lime mud which makes it difficult to control (Dorris 2003).

Although the formation of guarded sodium is not fully understood, laboratory studies have suggested that it is formed during the causticizing process. Sodium ions together with calcium ions react with carbonate ions in the green liquor to form a structure where the sodium ions are “guarded” in the lattice of the CaCO_3 crystal structure. Sodium is expelled from the lattice structure and released as Na_2CO_3 at temperatures below the decomposition temperature of CaCO_3 (Mao et al. 2004).

Sodium usually has the highest concentration of the NPE in the lime cycle. It is also of interest because the low melting point of sodium compounds that enhance sintering and may contribute to ring formation. Sodium also has a tendency to accumulate inside the lime kiln. This is due to an internal cycle where sodium is vaporized in the hot part of the kiln and then transported to the feed end where it is condensed (Dorris 2003). Sodium also has a tendency to enrich in the dust fraction. This is shown by the fact that the sodium content in the lime mud dust is usually two or three times higher than in the feed mud (Tran 2000).

2.3.3 Silicon

Silicon enters the pulp process through wood material, make-up chemicals, process water and biofuels when used in the lime kiln. The silicon content in wood materials varies from 0.01-0.05% in Scandinavian wood to 5-7 % in rice straw. The use of annual plants greatly increases the input of silicon with the risk of enrichment in the lime cycle. Pulp mills that use rice or wheat straw therefore seldom reuse the lime used in the causticization. The major outputs of silicon from the pulp process are pulp, green liquor sludge and lime grits formed in the lime kiln. However, less silicon will be purged from the soda cycle due to increased process closure which may lead to enrichment in the lime cycle (Theliander 1996).

The silica in green liquor will react with calcium oxide to form calcium silicate, CaSiO_3 that causes several problems in the lime cycle. It has been suggested that the formation of calcium silicate hydrates makes the lime mud harder to dewater resulting in a lower dry content of the feed into the lime kiln (Ribeiro et al. 2007). The presence of silicon in the lime cycle also affects the lime reburning process. It is known that each 1 wt % of silicon reduces lime availability by around 6 wt%. This is a result of the formation of calcium silicates (Ulmgren 1997). Laboratory studies have shown that the lime reactivity drops significantly with increased silica concentration. It was observed that calcium carbonate available for decomposition was reduced from 98 % to 69 % when silica increased from 0 to 5.5 % (Mathur et al. 1999).

2.3.4 Phosphorus

Most of the phosphorus entering the pulp process will accumulate in the lime cycle due to its higher solubility in green liquor than in white liquor (Ulmgren & Rådeström 1997). To keep the phosphorus at an acceptable level it is usually necessary to keep the lime cycle partly open, not reusing all of the reburned lime (Lindblom & Theliander 1999).

Phosphorous is present in the lime mud mainly as calcium hydroxiapatite, $\text{Ca}_5\text{OH}(\text{PO}_4)_3$. Most of the calcium hydroxiapatite will then react to form tricalcium phosphate, $(\text{Ca}_3(\text{PO}_4)_2)$, inside the lime kiln. A lime with 1 wt% phosphorus will

therefore contain 5 wt% tricalcium phosphate. This causes problems with high dead-loads as well as low lime reactivity since three calcium ions will be tied to every two phosphate ions (Taylor & Bossons 2006).

The fuel is an important input of phosphorous to the lime kiln. In one mill mass balance it was discovered that 21 % of the phosphorous entering the lime cycle originated from the fuel oil (McGuffie & Taylor 2007). This figure is expected to rise further if phosphorous rich bio fuels are used in the lime kiln.

2.3.5 Aluminum

In resemblance to silicon, aluminum enters the process through the wood and may accumulate in the lime cycle resulting in dead-load as well as reduced dry content of the lime mud. It is also known that the formation of aluminum silicates cause glass like scaling in the evaporator plant that is very difficult to remove (Theliander 1996).

Lime grits and dust particles from the lime kiln are generally considered to be important outputs of aluminum from the pulping process. However, mass balances have also shown that both the lime grits and the precipitator catch have an aluminum content roughly the same as the lime mud (McGuffie & Taylor 2007).

2.3.6 Magnesium

Magnesium resembles calcium in its chemical reactions. The magnesium carbonate of the lime mud is calcinated in the kiln forming magnesium oxide that may react with water in the slaker to form magnesium hydroxide. Magnesium will however not causticize sodium carbonate but will instead remain in the lime mud as magnesium hydroxide. Because of its small particle size, $Mg(OH)_2$ lowers the filterability of the lime mud, thus reducing the dry content of the lime kiln feed (Gullichsen & Fogelholm 1999).

It has also been shown that there is a correlation between the magnesium content and the aluminum content in the reburned lime. By forming magnesium aluminum compounds, magnesium is therefore an important factor in accumulating aluminum in the lime (Theliander 1996).

2.3.7 Iron, manganese and copper

These elements do not usually cause problems in the lime cycle, although they have been known to promote dusting in the kiln (Warnqvist 1998). In the lime mud, the metals probably occur as hydroxides that lowers the dry dry content of lime mud (Gullichsen & Fogelholm 1999).

2.3.8 Potassium

Potassium is expected to parallel the chemistry and concentrations of sodium in the recovery cycle. It may therefore be involved in ring formation, but will normally not cause problems in the lime cycle (Warnqvist 1998). Increased intake of potassium with for example bio fuels may however cause problems in the recovery boiler.

2.4 Previous work within lime kiln modelling

Several works within the field of lime kiln modelling are found in the literature. Most of these models are designed to solve a specific task. Examples are thermal models to predict the temperature profile along the kiln (Eriksson et al. 1991) as well as dynamic models developed to enable automatic control of the process (Karhela et al. 1998). These models are fundamentally different from this lime kiln model and therefore not particularly useful as a direct source of information.

3. The simulation software

3.1 WinGEMS

WinGEMS is a software that can be used to simulate processes in the pulping industry. A system in WinGEMS is constructed through a number of blocks each representing a process unit in the mill that is to be simulated. The recovery boiler and the lime kiln are example of such process units. A block usually has one or more adjustable parameters that are available so that the block may be adjusted to resemble a unit in a specific mill. The blocks are connected through streams that represent flow of material between the different modules. These streams are more carefully explained in the next chapter.

When a system of blocks and streams has been created the simulation may start. This is done by assigning a start-up stream from which the simulation begins. The software will then calculate the rest of the streams sequential until back at the start-up stream which completes the first iteration. It will then repeat the same procedure over and over again until all streams converge, meaning that the difference between two iterations must not be larger than a specified value. When this is achieved, the simulation stops and the system is in a steady-state.

Although there are a number of premade blocks in WinGEMS it is also possible to create own blocks. In these block one can incorporate information that might not exist in the original block which makes the simulations more accurate. A self-made block consists of the following files:

1. One DLL-file
2. One WGB-file
3. Possibly a help-file

The DLL-file is constructed through a FORTRAN compiler. This is the foundation of the block and the place where all the calculations are made. The WGB-file is created in a text editor and is the link between the WinGEMS interface and the DLL-file. It is in the WGB-file that the different adjustable parameters are declared as well as warnings that should appear to the WinGEMS user at certain situations.

Figure 3 shows the basic in- and outgoing streams of the lime kiln block.

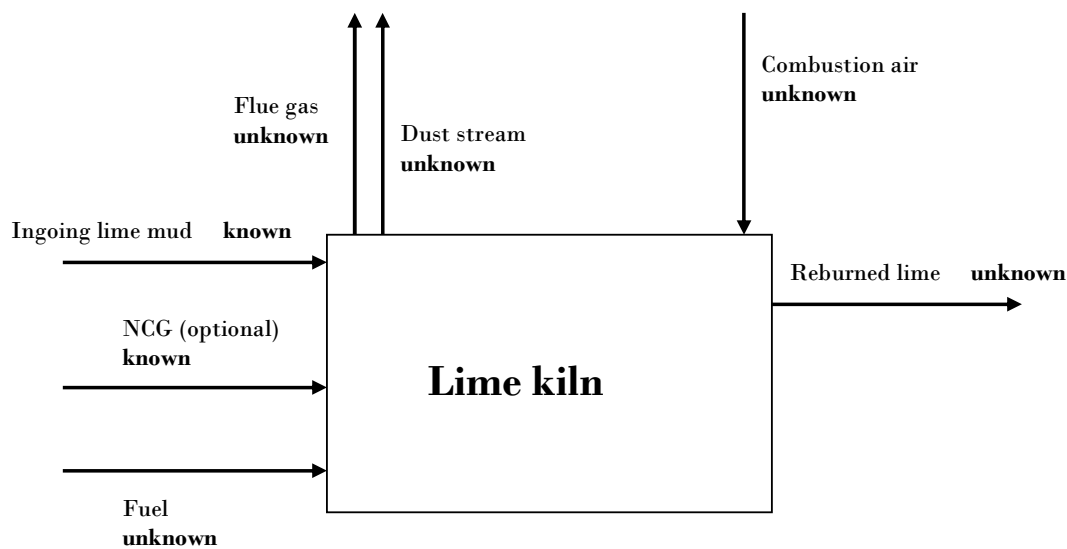


Figure 3: In- and outgoing streams of the lime kiln.

As seen in Figure 3 only the lime mud stream and the non condensable gases (if any) are known to the block. The task for the block is to calculate the size and composition of the rest of the streams given the known streams and a number of user specified parameters. In this figure there is only one fuel stream which is somewhat of a simplification. In the complete model several fuels may be used. This is explained further in section 5.3.

3.2 Stream structures

In WinGEMS the mass flows are represented by streams of different types. Every stream has a stream structure that contains information about the stream. Usually the stream structure will consist of mass flow (in ton/hr), temperature (in °C) and concentrations of the different components in the stream.

WinGEMS use different stream types to represent different flows. The stream types used in the lime kiln model are:

1. Special gas streams
2. Liquor streams
3. Generic streams

3.2.1 Special gas stream

The special gas stream type has a fixed stream structure consisting of 11 parameters that can not be changed by the user:

1. Mass flow of gas (ton/hr)
2. Temperature of gas (°C)
3. Concentration of Na_2SO_4 (kg/ton gas)
4. Concentration of NaCl (kg/ton gas)
5. Concentration of Na_2CO_3 (kg/ton gas)

6. Concentration of SO₂ (kg/ton gas)
7. Concentration of CO₂ (kg/ton gas)
8. Concentration of HCl (kg/ton gas)
9. Concentration of H₂O (kg/ton gas)
10. Concentration of O₂ (kg/ton gas)
11. Concentration of N₂ (kg/ton gas)

For the lime kiln, where the special gas is used to represent the combustion air and the exit gas of the kiln, the compounds of interest are H₂O, CO₂, SO₂, N₂ and O₂.

The mass flow of a specific compound in ton/hr is calculated as:

$$m_{component} = \frac{m_{gas} \cdot C_{component}}{1000} \quad (12)$$

where m_{gas} is the mass flow of gas in ton/hr and $C_{component}$ is the concentration of the component in kg/ton gas. When the mass flow of gas and component is known, the concentration is calculated as:

$$C_{component} = 1000 \cdot \frac{m_{component}}{m_{gas}} \quad (13)$$

3.2.2 Liquor stream

Liquor streams are used to describe liquids of different composition. A liquor stream will basically consist of three different kinds of components: Water, suspended solids and dissolved solids. The stream structure is not fixed as in the special gas, but can be modified by the WinGEMS user. However, the stream structure will consist of the following component divisions.

1. Standard variables
 - Mass flow of liquor (ton/hr)
 - Temperature of liquor (°C)
 - Suspended solids (fraction)
2. Suspended solid components
 - Fraction of total suspended solids (frac)
3. Dissolved solid components
 - Concentration (kg/ton liquor)

Mass flow of liquor is the combined flow of water and dissolved solids. Suspended solids describes the mass flow of suspended solids in proportion to the liquor flow and is defined as:

$$SS = \frac{m_{SS}}{m_{Liquor}} \quad (14)$$

where m_{SS} is the mass flow of suspended solids in ton/hr and m_{Liquor} is the mass flow of liquor in ton/hr.

By this definition SS may be higher than one (and will often be so in the lime cycle). The total mass of suspended solids (m_{SS}) is calculated through multiplying m_{Liquor} with SS .

Since the liquor stream consist of water, suspended solids and dissolved solids, which is equivalent to liquor and suspended solids, the total mass flow of the stream in ton/hr is calculated as:

$$m_{Total} = m_{Liquor} \cdot (1 + SS) \quad (15)$$

Whereas the total amount of suspended solids is available through the standard variables one will need to look in the second component division to see what suspended solid components are present in the stream. The concentration of different suspended solid components (for example $CaCO_3$ or CaO) is expressed as fractions of total amount of suspended solids. This means that the fractions in the second component division should sum up to one.

The mass flow of a specific suspended solid component in ton/hr is calculated as:

$$m_{SS\ component} = m_{Liquor} \cdot SS \cdot \eta_{SS\ component} \quad (16)$$

where $\eta_{SS\ component}$ is the component fraction of total suspended solids.

In analogy, the fraction of suspended solids, $\eta_{component}$ for a certain component may be calculated as:

$$\eta_{component} = \frac{m_{SS\ component}}{m_{Liquor} \cdot SS} \quad (17)$$

The third component division will hold information about the different dissolved solid components. These are expressed through concentrations (kg of component per ton of liquor). Since the liquor flow consist of both water and dissolved solids the concentrations in the third components division will not sum up to 1000 unless there is no water present in the stream.

The mass flow of a specific dissolved solid component in ton/hr is received through the following calculation:

$$m_{DS\ component} = \frac{m_{Liquor} \cdot C_{DS\ component}}{1000} \quad (18)$$

where $C_{DS\ component}$ is the concentration of the dissolved solid component in kg/ton liquor.

In the same way, the concentration of a dissolved solid component in kg/ton liquor is calculated from the mass of dissolved solid component and the mass flow of liquor as:

$$C_{DS \text{ component}} = 1000 \cdot \frac{m_{DS \text{ component}}}{m_{Liquor}} \quad (19)$$

To get a better understanding of the liquor stream type, the reader is advised to look in Appendix 2 where it is illustrated with an example.

In the lime kiln model, the liquor stream is used to describe the lime mud, the reburned lime, the exit dust and the non condensable gases.

3.2.3 Generic streams

The generic streams do not have any predefined stream structure at all. What the different components in a generic stream represent is decided by the constructor of the block. Since these components will not have any units visible in the WinGEMS interface it is very important to describe to the user what they actually represent. Generic streams are only used when no other stream type may be used to describe the streams. In the lime kiln model generic streams are used for the fuel streams. The stream structure of the fuel streams is:

1. Mass flow of fuel (ton/hr)
2. Weight fraction of carbon in fuel
3. Weight fraction of hydrogen in fuel
4. Weight fraction of oxygen in fuel
5. Weight fraction of sulfur in fuel
6. Weight fraction of ash in fuel
7. Lower heating value of fuel (MJ/kg fuel)
8. Adiabatic flame temperature of fuel (°C)

4. Mass balances

4.1 Generally

4.1.1 Handling stream structures

One objective of the lime kiln model is to establish a mass balance over the kiln. Provided with an ingoing stream of lime mud and a number of parameters set by the user, the model is required to calculate the mass flow, temperature and composition of the rest of the in- and outgoing streams. WinGEMS uses the liquor stream type to represent the lime mud and reburned lime flows. The stream structure of the liquor stream will consist of standard variables, suspended solids and dissolved solids as described in section 3.2.

Inside the block, the model has access to the stream structure through a vector of length n , where n is the number of components in the stream structure (for example 11 in a special gas stream). This vector holds all the information that the model needs about the stream. However, the information about the different components is available as fractions and concentrations. In order to perform the mass balance, the model will need to transform this information into absolute mass flows of each component. The way to do this is rather straightforward which was shown in (11), (16) and (18). This step is called *step A* in Figure 4.

These calculations were systemized using algorithms in Fortran and the mass flows of each component stored in another vector also of length n . Once the mass flows of all components in the ingoing lime mud are available it is possible for the model to calculate the mass flows in the outgoing streams. When this has been done, however, the model needs to convert the mass flows back to the fractions and concentrations defined in the stream structure. How to do this was shown in (12), (17) and (19). This step is referred to as *step C* in Figure 4.

The process of transforming the information between concentrations and mass flows is illustrated in Figure 4.

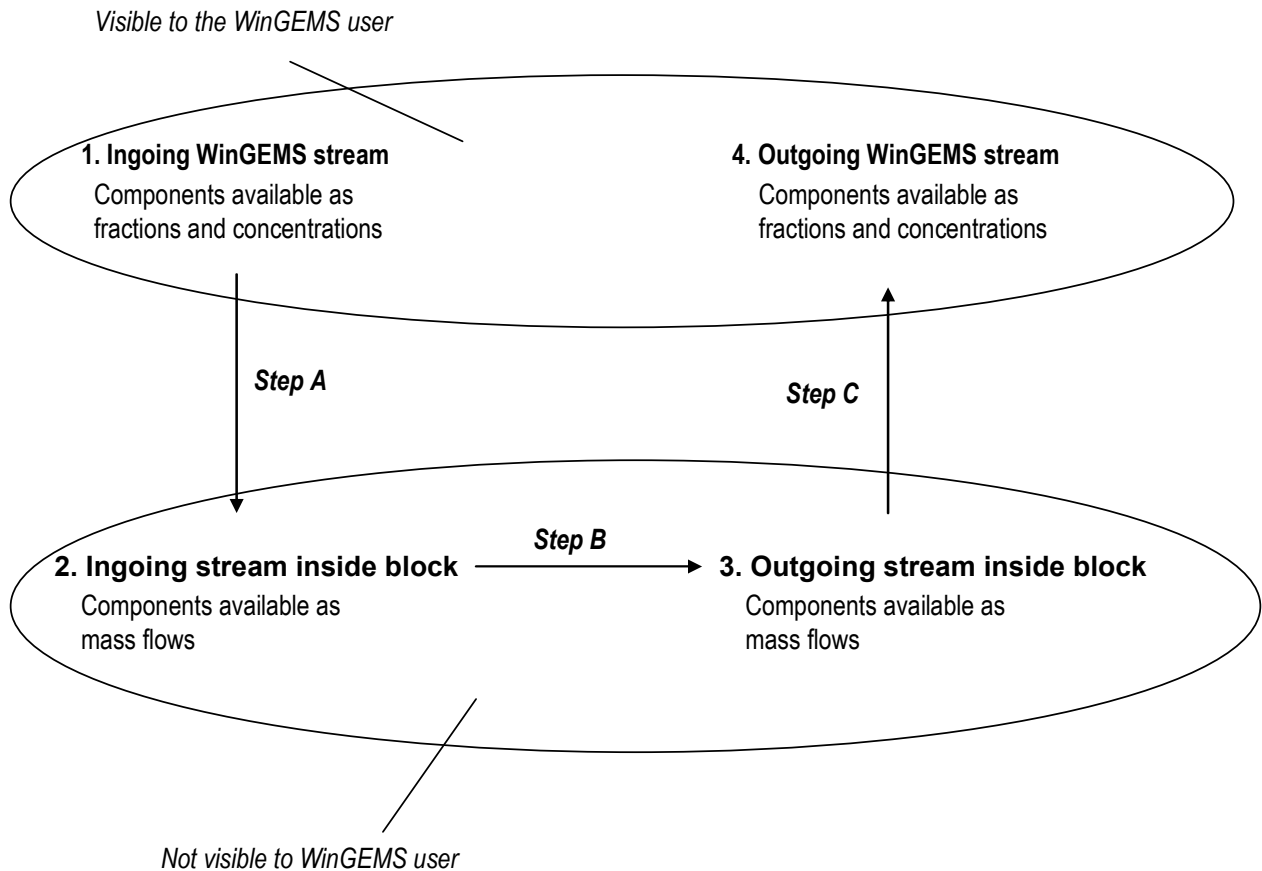


Figure 4. The process of calculating the outgoing streams.

Note that the term *outgoing* in Figure 4 refers to the fact that the stream is calculated by the model. Streams like the combustion air, which is an ingoing stream in the actual process is still considered an outgoing stream according to this definition since it is calculated by the model and sent back to WinGEMS.

The only purpose of step A and C is to transform the stream information between two different formats. In WinGEMS the stream composition is available as concentrations and fractions according to the stream structure. Inside the model on the other hand, all the components are available as mass flows. These mass flows are for the model only and are not visible to the WinGEMS user.

In *step B* the outgoing stream is related to the ingoing stream. This is where the physical and chemical relations built into the model as well as parameters specified by the user are utilized to calculate the different components of the unknown streams shown in Figure 3. For example, this is where the amount of combustion air that is required for to burn the fuel is calculated as well as the mass flow of reburned lime.

The mass- and energy balances include numerous parameters that the user may specify. In this report these parameters are named *P1*, *P2*, *P3* etc. To make it easier for the reader, a compilation of all parameters is available in Appendix 3.

4.1.2 Keeping track of the mass balances

During the construction of the lime kiln model it was critical to keep track of the mass balances to ensure that the amount of material leaving the kiln was equal to that entering. Since this is not done automatically by WinGEMS it had to be done separately in Microsoft Excel. This was done through a function in WinGEMS that transfers the result of a simulation (the stream data) to an Excel worksheet. The worksheet was set up so that the amount of every element entering and leaving the kiln was calculated automatically. In this way it was easy to check so that the balance of every element was correct.

4.3 Restrictions

It was decided early in this work that the emissions of NO_x and reduced sulfur (H₂S) should not be included in this model. The reason is that it is considered too difficult to make any good predictions regarding these emissions.

4.4 Calcination

The main reaction of the lime kiln is the calcination where calcium carbonate is decomposed into calcium oxide and carbon dioxide. The fraction of the ingoing calcium carbonate that is transformed to calcium oxide in the model is regulated through block parameter P1 and is therefore decided by the user. The mass flow of calcium oxide in the reburned lime in ton/hr is calculated as:

$$m_{CaO,RL} = m_{CaCO_3,LM} \cdot P1 \cdot \frac{M_{CaO}}{M_{CaCO_3}} \quad (20)$$

where $m_{CaCO_3,LM}$ is the mass flow of calcium carbonate in the lime mud in ton/hr and M represents the molar mass of the different components in g/mol. In the same way, the mass flow of residual calcium carbonate in the reburned lime in ton/hr is calculated as:

$$m_{CaCO_3,RL} = m_{CaCO_3,LM} \cdot (1 - P1) \quad (21)$$

The carbon dioxide lost to the flue gases through the calcination in ton/hr is calculated as:

$$m_{CO_2,calc} = m_{CaCO_3,LM} \cdot \frac{M_{CO_2}}{M_{CaCO_3}} \quad (22)$$

4.5 Dusting

Some of the ingoing lime mud will leave the kiln as dust particles. The dusting will depend on the composition and dry content of the ingoing lime mud as well as the structure of the lime kiln itself. It is therefore not possible to predict the amount of dust simply by studying the data available in computer simulations of the lime cycle. Instead, the model lets the user specify the fraction of ingoing lime mud that leaves the kiln as dust. This is done by two parameters in the lime kiln block:

P6. Fraction of the ingoing solids that leave the kiln as dust

P7. Fraction of the ingoing sodium that leave the kiln as dust

The dust solids will have the same composition as the ingoing lime mud. It is thereby assumed that the dust is generated before the lime mud reaches the calcination zone of the kiln. The second parameter is included in the model to enable the sodium to enrich in the dust fraction. Sodium is present in the kiln in several compounds but it is assumed that the evaporated sodium is sodium carbonate.

4.6 Overburnt lime

Some of the lime in the kiln will be overburnt forming inert material that can not be used for causticizing. The fraction of ingoing calcium that is overburnt is specified through parameter *P5* and the inert lime is stored in the suspended solid stream component Ca_{inert} .

4.7 Sulfur capture

Most of the fuel that enters the kiln will be absorbed by the calcium oxide and the sodium hydroxide according to (6) and (7). Few studies have been made to quantify this sulfur capture. The only one found in the literature is one where the concentration of sulfur dioxide was studied when high sulfur non-condensable gases were burned in the kiln as opposed to a low sulfur fuel (Tran et al. 2004). The result is shown in Table 1 and Figure 5.

Table 1. Sulfur removal efficiency and SO₂-concentration in flue gas for different sulfur inputs. (Tran et al. 2004).

Total sulfur input <i>Kg/h</i>	Sulfur removal efficiency <i>%</i>	Concentration of SO ₂ in flue gas <i>Ppm</i>
54.2	98.1	25
157.2	88.2	519

The kiln in the study had a lime mud flow of approximately 15.75 tons per hour. It would be expected for the kiln size to be an important parameter for the sulfure capture. If two kilns of different size would be subject to the same sulfur input, it is likely that the bigger kiln would have higher sulfur removal efficiency than the smaller kiln. For the results in Table 1 to be used in lime kilns of various sizes, the sulfur input would have to be related to the size or capacity of the kiln. This was done using the term *relative sulfur input* that was defined as the sulfur input in kg per kg of lime mud entering the kiln.

Table 1 is illustrated in Figure 5.

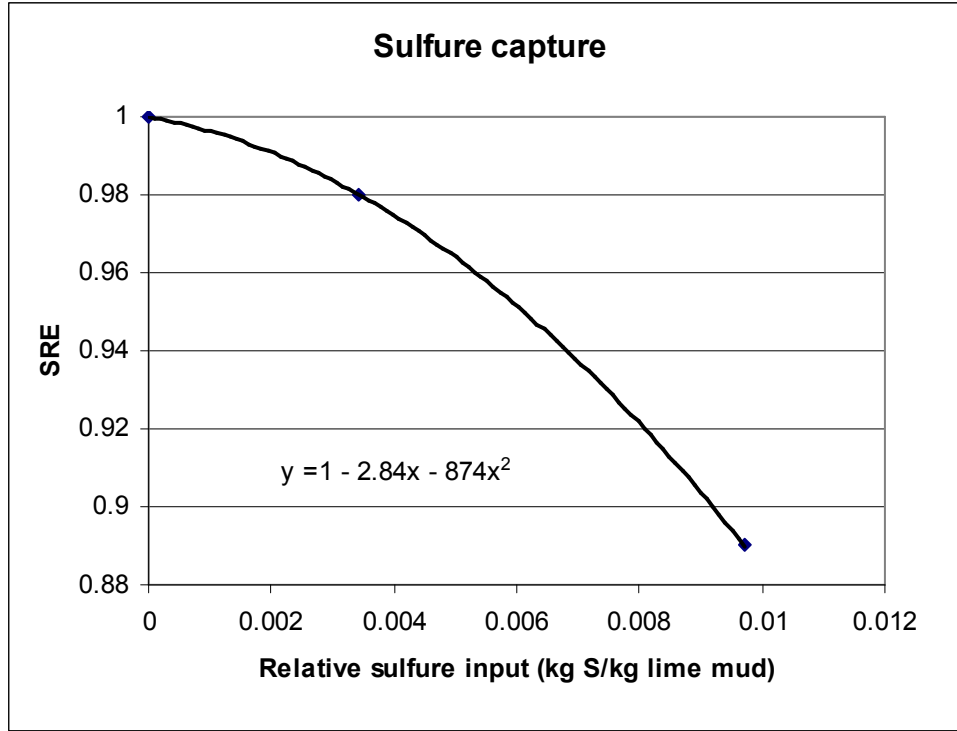


Figure 5. Sulfur removal efficiency as a function of relative sulfur input (Tran et al. 2004).

Also shown in Figure 5 is the second degree polynomial that was fitted to the data. This polynomial is shown in (23).

$$SRE = 1 - 2.84 \cdot \frac{m_S}{m_{LM}} - 874 \cdot \left(\frac{m_S}{m_{LM}} \right)^2 \quad (23)$$

where m_S is the input of sulfur in kg/h and m_{LM} is the input of lime mud in kg/h.

The accuracy of this sulfur capture model may be questioned since it is based on only two data points. To make it more precise further studies regarding the correlation between the sulfur input and the SO_2 emissions are needed.

Nonetheless, the result of the sulfur removal efficiency according to (23) is that low sulfur contents in the fuel will result in almost no sulfur dioxide emissions whereas high sulfur contents will give substantial emissions. Table 2 and Figure 6 show how the SO_2 concentration in the flue gas varies with different sulfur contents of the fuel according to this sulfur capture model. In this simulation the heating value of the fuel is 41 MJ/kg and there are no sulfides in the lime mud.

Table 2. Concentration of SO₂ in exit gas for fuel oils with different sulfur contents.

wt_S	Conc SO₂ in exit gas
%	Ppm
0.1	0.007
0.5	0.18
1	0.79
3	9.65
5	33.7
10	201

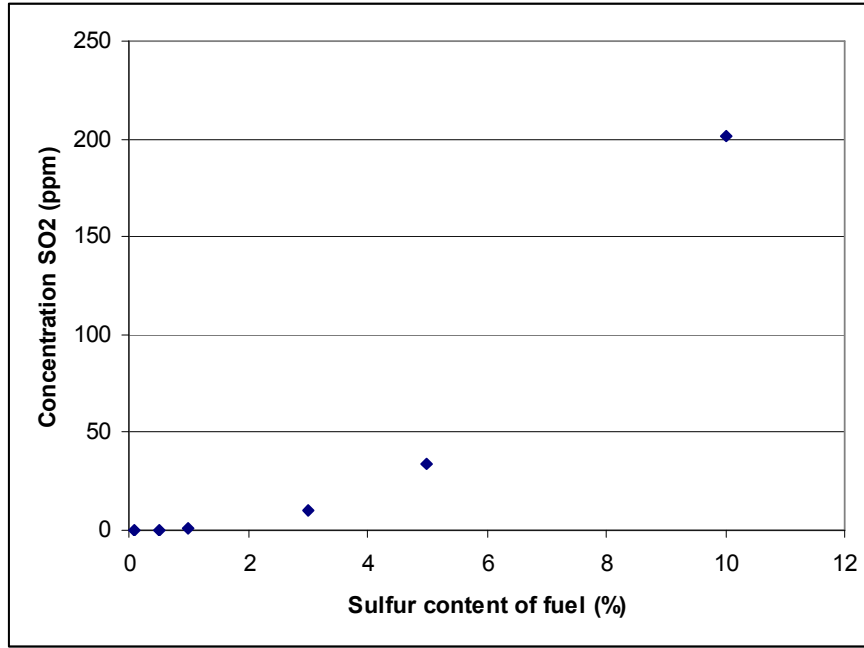


Figure 6. Concentration of SO₂ in exit gas for fuel oils with different sulfur contents.

The sodium may be captured by either CaO or NaOH according to reactions (6) and (7). The distribution of the sulfur capture between these two reactions is not well documented in the literature. However, it is obvious that the calcium reaction should dominate due to the fact that there is a lot more calcium in the kiln than there is sodium.

To examine this further, the equilibrium constants of the two reactions at three different temperatures was calculated. The equilibrium constant, that describes the relation between the amount of product and reactant, relates to Gibbs energy according to (Atkins 1994):

$$\ln K = \frac{-\Delta_r G}{RT} \quad (24)$$

where R is 8.314 kJ/K mol, T is the temperature in K and $\Delta_r G$ is the Gibbs free energy of the reaction in kJ/mol. The latter is calculated from the standard Gibbs energy of formation $\Delta_f G$ according to (Atkins 1994):

$$\Delta_r G = \sum_{\text{products}} \Delta_f G - \sum_{\text{reactants}} \Delta_f G \quad (25)$$

The calculated equilibrium constant for the two sulfur capture reactions at different temperatures are shown in Table 3.

Table 3. Equilibrium constants for the two sulfure capture reactions at different temperatures.

	Calcium capture (6)	Sodium capture (7)
<i>T(K)</i>	<i>Log K</i>	<i>log K</i>
298.15	-	76.89
500	-	42.82
1200	7.53	12.54
1500	3.42	8.354

According to these results both reactions have high equilibrium constants in the temperature intervals relevant to the lime kiln. The two low temperatures may represent the cool parts of the kiln while the two high temperatures are equivalent to those of the calcination and sintering zones of the lime kiln. The equilibrium constant for the calcium reaction was not calculated for the lower temperatures since there will be almost no calcium oxide present below the calcination temperature (850 °C).

It is clear that the sodium capture is more spontaneous than the calcium capture. However the difference is not very large and both reactions may be considered thermodynamically favorable even at calcination and sintering temperatures.

Another factor that has to be considered is that there is a fundamental difference between the sodium hydroxide and the calcium oxide in the lime kiln process. The sodium hydroxide is a reactant of the process that is present in the lime mud but will gradually be consumed, mainly by the creation of sodium carbonate according to (10). The calcium oxide on the other hand is not present in the lime mud but will be produced inside the lime kiln. This means that the amount of calcium oxide will increase as the solids move through the kiln as oppose to the amount of sodium hydroxide that will decrease.

At the hot end of the kiln there will only be very small amounts of sodium hydroxide left in the lime mud whereas there will be large quantities of calcium oxide present. It is in this part of the kiln that the combustion of fuel takes place with the resulting formation of sulfur dioxide. Consequently there will be high quantities of both sulfur dioxide and calcium oxide in the hot zone which will strongly favor this reaction. The sodium on the other hand will only be available in large amounts in the cold zone where there will not be much sulfur dioxide left to absorb. This is illustrated in Figure 7.

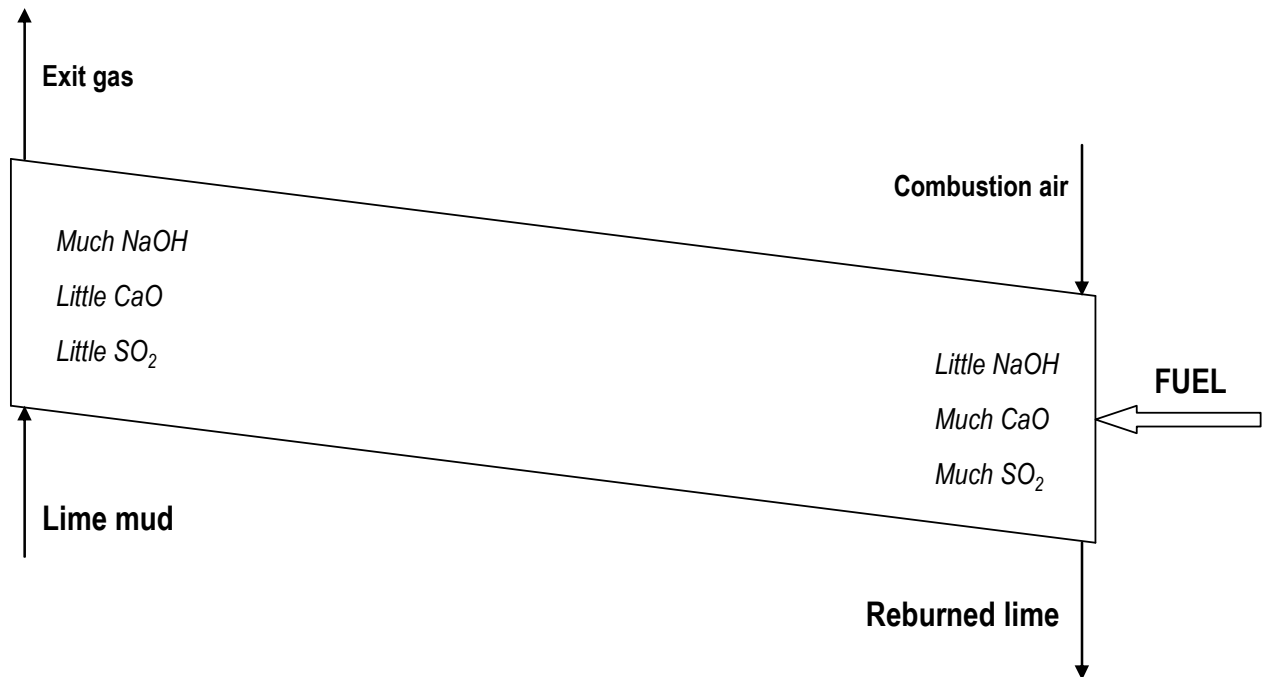


Figure 7. NaOH, CaO and SO₂ at both ends of the lime kiln.

It is also obvious that there will be many times more calcium than sodium present inside the lime kiln. These facts indicate that the calcium reaction will dominate and that the sodium reaction will be of much less importance. The latter is therefore ignored in the model and it is assumed that all sulfur is captured through the calcium reaction.

4.7 Sodium compounds

As mentioned in chapter 3.3.2 there are three different kinds of sodium compounds in the lime mud: water soluble sodium, water insoluble sodium and guarded sodium. The water insoluble sodium will be considered inert inside the kiln. Guarded sodium is not included in the stream structure of WinGEMS and will therefore not be included in the model. This means that only the water soluble compounds are taken into account in this model.

The compounds of main interest are sodium hydroxide and sodium sulfide. Sodium hydroxide may react either with sulfur dioxide and create sodium sulfate (reaction 6) or with carbon dioxide to create sodium carbonate (reaction 10). In the previous section it was decided that the former should be neglected which means that all sodium hydroxide is assumed to react according to (6).

The sodium sulfide may either react with oxygen to form sodium sulfate according to (11) or react with carbon dioxide and water to form hydrogen sulfide according to (9). Since emissions of hydrogen sulfides are not included in this model it is assumed that all of this is oxidized further to sulfur dioxide according to (8). Combining (8) and (9) gives the overall reaction:



According to chapter 3.3.1 40-60 % of the sulfides in the lime mud typically forms hydrogen sulfides. In this model it is therefore assumed that 50 % of the sulfides react according to (26) and the other 50 % will form sodium sulfate according to (11).

5. Energy balances

5.1 Generally

Energy entering the kiln will be consumed by heating, drying and calcination of the lime mud as well as radiation-, convection- and flue gas losses. In order to calculate the fuel consumption of the lime kiln it is necessary to quantify these different energies as well as specify the properties of the fuels. This is done in the following chapter.

5.2 Heat capacities

The heat capacity C_p in kJ/kg K is defined as the energy in kJ required raising the temperature of one kilogram of a material one kelvin Celsius at constant pressure (Atkins 1994).

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (27)$$

This parameter will usually vary with temperature. To calculate the energy needed to raise a certain amount of material from one temperature to another, it is therefore necessary to quantify this temperature dependence. This is usually done through regression, where the heat capacity is described through a polynomial. In this model, the following polynomial was used:

$$C_p(T) = a_0 + a_1T + a_2T^2 + a_3T^{-1} + a_4T^{-2} \quad (28)$$

where $C_p(T)$ is the heat capacity in kJ/kg K and T is the temperature in K.

The polynomial model (28) was fitted to heat capacity data (Barin 1989) in the temperature interval 298.15 K to 2 500 K using the least squares method. This gave the coefficients given in Table 4.

Table 4. Heat capacity coefficients according to (27) for different compounds.

	a_0	$a_1 \cdot 10^5$	$a_2 \cdot 10^8$	a_3	a_4
CO_2	1.466	5.56	1.47	-309.1	35 560
O_2	1.340	-6.56	2.08	-242.6	36 476
N_2	1.041	23.99	-4.91	-85.9	19 606
$H_2O(l)$	4.03	487.0	0	0	0
$H_2O(g)$	1.084	125.9	-21.00	175.1	-14 500
SO_2	1.109	-6.97	1.16	-226.7	26 115
$CaCO_3$	1.009	25.36	0.64	-4.7	-20 965
CaO	0.949	3.71	1.01	-27.0	-10 574

Integrating (27) the change in enthalpy for a component with heat capacity C_p when the temperature is raised from T_1 to T_2 is calculated as:

$$H(T) = \int_{T_1}^{T_2} C_p dT \quad (29)$$

When combining (28) and (29) the change in enthalpy in kJ/kg when a substance is raised from the temperature T_1 to T_2 may be calculated as:

$$\Delta H = \left(a_0(T_1 - T_2) + \frac{a_1}{2}(T_1^2 - T_2^2) + \frac{a_2}{3}(T_1^3 - T_2^3) + a_3(\ln(T_1) - \ln(T_2)) - a_4(T_1^{-1} - T_2^{-1}) \right) \quad (30)$$

The change in energy in kJ is obtained by multiplying the enthalpy in kJ/kg with the mass of the particular component in kg.

5.3 Fuels

A variety of fuels are used in lime kilns and it is common for several different fuels to be used in the same kiln. For the model to resemble real cases it is therefore required to have some flexibility regarding the fuel input. This flexibility should involve both fuel parameters, like heating value and composition, and the number of fuels used in a simulation.

The fuel details are specified in parameters $P9$ to $P22$. A minimum of one and a maximum of three different fuels may be used in the same simulation. Since the fuel consumption is calculated in the model, the mass flow of one fuel must always be unspecified. This fuel is called *external fuel* and should be thought of as a fuel with an unlimited supply. In most cases the external fuel will be a purchased fuel such as fuel oil or natural gas. Details on the external fuel are specified in parameters $P9$ to $P12$.

In addition to the external fuel, one or two *internal fuels* may be used. The difference between the external and the internal fuel is that the supply of the latter must be specified. This will often represent a byproduct like tall oil or methanol or a raw material that due to availability may be limited in supply. If internal fuels are being used they will naturally supply energy to the kiln thereby decreasing the consumption of external fuel. This is further explained in section 6.3. Details on the internal fuels are specified through parameters $P13$ to $P22$.

Some mills will combust non condensable gases in the lime kilns. In this model, NCG may be used but it is not specified through block parameters but through an input liquor stream according to Figure 3. It is assumed that the non condensable gases consist of only H_2S .

5.3.1 Fuel types

The following fuels are available for the user to choose between. This choice is made through parameter $P9$ for the external fuel and parameters $P13$ and $P18$ for the first and second internal fuel respectively.

1. Natural gas (methane)
2. Fuel oil

3. Tall oil
4. Lignin
5. Methanol
6. Wood powder
7. Bark

5.3.2 Fuel composition

The fuel in the lime kiln model is assumed to consist of carbon, hydrogen, oxygen, sulfur and ash. The ash itself will be made up by numerous compounds, some of which may influence the lime cycle. For usability reasons however, they are not included in the fuel composition of the model. These compounds may be included in a simulation but must be done so by a separate input stream. This is more carefully explained in section 7.

Different plants and situations calls for flexibility regarding the composition of the fuel. In some cases, the user may have a complete elementary analysis of the fuel whereas in other situations the user is content with using default compositions. The following three options are therefore available to the user. This option is made in parameter *P10* for the external fuel and parameters *P14* and *P19* for the first and second internal fuel respectively.

1. Use default compositions
2. Specify composition
3. Specify sulfur content. Use default composition for carbon, hydrogen, oxygen and ash.

In all three alternatives it is the dry composition of the fuel that is used. The moisture content of the fuels is specified separately. Table 5 shows the default compositions used in the model. These are also visible to the user when deciding what composition to use.

Table 5. Default compositions used in the model for different fuels.

Fuel	$wt_{C,dry}^{def}$	$wt_{H,dry}^{def}$	$wt_{O,dry}^{def}$	$wt_{S,dry}^{def}$	$wt_{ash,dry}^{def}$
Natural gas	0.748	0.252	0	0	0
Fuel oil	0.876	0.120	0	0.004	0
Tall oil	0.794	0.100	0.106	0	0
Lignin	0.652	0.058	0.269	0.02	0.001
Methanol	0.375	0.126	0.499	0	0
Wood powder	0.495	0.063	0.435	0	0.007
Bark	0.512	0.060	0.398	0	0.030

If the second alternative is chosen, the user specifies the composition in the fuel stream. Here, it is only the relation between the contents that is important, since these will be normalized by the model so that the sum is equal to one. It is therefore indifferent whether the contents are specified in fractions or in percent.

In the third alternative, only the sulfur content is specified in the fuel stream. The content of carbon, hydrogen, oxygen and ash are then calculated from the default compositions as:

$$wt_{C,dry} = wt_{C,dry}^{def} \cdot \frac{1 - wt_{S,dry}^{spec}}{1 - wt_{S,dry}^{def}} \quad (30)$$

$$wt_{H,dry} = wt_{H,dry}^{def} \cdot \frac{1 - wt_{S,dry}^{spec}}{1 - wt_{S,dry}^{def}} \quad (31)$$

$$wt_{O,dry} = wt_{O,dry}^{def} \cdot \frac{1 - wt_{S,dry}^{spec}}{1 - wt_{S,dry}^{def}} \quad (32)$$

$$wt_{ash,dry} = wt_{ash,dry}^{def} \cdot \frac{1 - wt_{S,dry}^{spec}}{1 - wt_{S,dry}^{def}} \quad (33)$$

where $wt_{S,dry}^{spec}$ is the sulfur content specified by the user

When the dry composition of the fuel has been determined it is adjusted to the specified moisture content of the fuel, wt_{moist} :

$$wt_C = wt_{C,dry} \cdot (1 - wt_{moist}) \quad (35)$$

$$wt_H = wt_{H,dry} \cdot (1 - wt_{moist}) \quad (36)$$

$$wt_O = wt_{O,dry} \cdot (1 - wt_{moist}) \quad (37)$$

$$wt_S = wt_{S,dry} \cdot (1 - wt_{moist}) \quad (38)$$

$$wt_{ash} = wt_{ash,dry} \cdot (1 - wt_{moist}) \quad (39)$$

where wt_{moist} is specified in parameter *P11* for the external fuel and parameters *P15* and *P20* for the first and second internal fuel respectively.

5.3.3 Combustion products

In this model the fuels are assumed to undergo complete combustion forming carbon dioxide, sulfur dioxide and water according to (49)-(51). The combustion products will also consist of nitrogen and oxygen given that an excess of air is being used. The fraction of excess air is specified in parameter *P2*. When air is used as an oxidizer, the mass of combustion products in kg/ kg burnt fuel may then be calculated as:

$$m_{CO_2} = wt_C \cdot \frac{M_{CO_2}}{M_C} \quad (40)$$

$$m_{H_2O} = \frac{1}{2} wt_H \cdot \frac{M_{H_2O}}{M_{H_2}} \quad (41)$$

$$m_{SO_2} = wt_S \cdot \frac{M_{SO_2}}{M_S} \quad (42)$$

$$m_{O_2} = \left(wt_C \cdot \frac{M_{O_2}}{M_C} + \frac{1}{2} wt_H \cdot \frac{M_{O_2}}{M_{H_2}} + wt_S \cdot \frac{M_{O_2}}{M_S} - wt_O \right) \cdot P2 \quad (43)$$

$$m_{N_2} = \left(wt_C \cdot \frac{M_{O_2}}{M_C} + \frac{1}{2} wt_H \cdot \frac{M_{O_2}}{M_{H_2}} + wt_S \cdot \frac{M_{O_2}}{M_S} - wt_O \right) \cdot \frac{79}{21} \cdot \frac{M_{N_2}}{M_{O_2}} \cdot (1 + P2) \quad (44)$$

where M is the molar mass of each component in g/mol.

The non condensable gases (hydrogen sulfide) will react according to (8) which gives the following combustion products in kg:

$$m_{H_2O} = m_{H_2S} \cdot \frac{M_{H_2O}}{M_{H_2S}} \quad (45)$$

$$m_{SO_2} = m_{H_2S} \cdot \frac{M_{SO_2}}{M_{H_2S}} \quad (46)$$

$$m_{O_2} = \frac{3}{2} m_{H_2S} \cdot \frac{M_{O_2}}{M_{H_2S}} \cdot P2 \quad (47)$$

$$m_{N_2} = \frac{3}{2} m_{H_2S} \cdot \frac{M_{O_2}}{M_{H_2S}} \cdot \frac{79}{21} \cdot \frac{M_{N_2}}{M_{O_2}} \cdot (1 + P2) \quad (48)$$

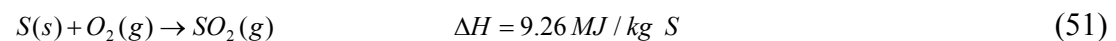
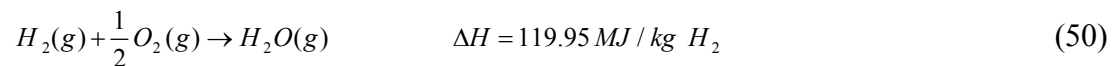
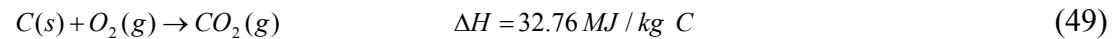
where m_{H_2S} is the mass of NCG in kg.

5.3.4 Heating values

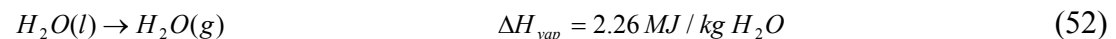
In order to calculate the fuel consumption one must know the amount of energy released from a specific fuel upon combustion. Since the water from the combustion will leave the lime kiln as water vapor, it is the lower heating value that is of interest.

In the lime kiln block, the users may either specify the heating value of the fuel or let the model approximate it. This choice is made through parameter $P12$ for the external fuel and parameters $P17$ and $P22$ for the first and second internal fuel respectively.

The approximation of the lower heating value is based on the composition and the type of the fuel. It is assumed that the carbon, hydrogen and sulfur of the fuel will create carbon dioxide, water and sulfur dioxide according to the reactions below (Barin 1989):



The water in the fuel will be vaporized:



The lower heating value in MJ/kg may then be approximated as:

$$LHV = 32.76 \cdot wt_C + 119.95 \cdot wt_H + 9.26 \cdot wt_S - 2.26 \cdot wt_{moist} - H_{f,fuel} \cdot (1 - wt_{moist}) \quad (53)$$

where $H_{f,fuel}$ (MJ/kg) is a parameter to compensate for the fact that the carbon, hydrogen and sulfur is not present in their elementary form, but bound in the structure of the fuel. Combustion of the fuel will therefore not release as much energy as if the equivalent mass of carbon, hydrogen gas and sulfur would be combusted. For pure substances, like methanol, this parameter will be equal to the enthalpy of formation ΔH_f in MJ/kg fuel. For other fuels, like wood powder or lignin, $H_{f,fuel}$ had to be estimated so that the heating values calculated by the model correlate to the heating values reported in the literature.

Table 6 shows $H_{f,fuel}$ used for the different fuels as well as the resulting lower heating values when using the default compositions according to Table 5.

Table 6. Approximated $H_{f,fuel}$ and LHV of different fuels.

Fuel	$H_{f,fuel}$ MJ/kg	LHV MJ/kg
Natural gas	4.67	50
Fuel oil	1.5	41.6
Tall oil	1.5	36.5
Lignin	3	25.5
Methanol	7.44	20
Wood powder	5	18.8
Bark	5	19

It should be emphasized that heating values calculated by the model through (53) are only approximations. If the user of the model has confirmed data on the heating value of the fuel, this should of course be used. The choice of letting the model approximate the heating value is to be used when the user does not have information about the heating value. In these cases, it is probably more reliable to let the model approximate one than for the user to simply take a guess.

5.3.5 Sulfur capture

Almost all of the sulfur dioxide is captured by the calcium oxide according to (6). This reaction is exothermic with a reaction enthalpy of -501.7 kJ/mole (Barin 1989) meaning that 15.65 MJ of energy is released for every kilogram of sulfur that is captured. As long as the sulfur content of the fuel is moderate this will have little effect on the energy balance of the kiln. With high sulfur fuels however, the energy generated from the sulfur capture may be high enough to be taken into account. At these circumstances almost all the sulfur that enters the kiln originates from the fuel. If the assumption is made that all of this sulfur is captured (a simplification that can be made with only minor inaccuracies) then the energy from this reaction may be included in the heating value of the fuel. This modified lower heating value LHV' is calculated as:

$$LHV' = 32.76 \cdot wt_C + 119.95 \cdot wt_H + 24,91 \cdot wt_S - 2.26 \cdot wt_{moist} - H_{f, fuel} \cdot (1 - wt_{moist}) \quad (54)$$

If the lower heating value LHV is specified by the user, the modified lower heating value LHV' is calculated as:

$$LHV' = LHV + 15.65 \cdot wt_S \quad (55)$$

Table 7 shows the modified lower heating value LHV' for different sulfur contents when the ordinary lower heating value LHV was specified to 41.50 MJ/kg. The relative difference, $\frac{LHV' - LHV}{LHV}$ is also shown in the right column.

Table 7. Modified lower heating values for fuel oils with different sulfur contents. In this modified heating value, the energy from the capture of the fuel sulfur has been included.

Sulfur content (%)	LHV'	Relative difference
	MJ/kg	%
0.4	41.56	0.15
1	41.67	0.38
3	41.97	1.13
5	42.28	1.89

From Table 7 it is clear that the energy from the sulfur capture will only have any real impact on the energy balance when the sulfur content of the fuel is high. However, this modified lower heating value is used in the energy balance described in chapter 5.3. The heating value sent back to the WinGEMS user through the fuel stream structure on the other hand, is the conventional lower heating value calculated according to (53).

The non condensable gases will be combusted according to (8) generating 15.20 MJ of energy per kg of H_2S (Barin 1989). Assuming that all sulfur dioxide will be captured according to (6), this will produce an additional 14.72 MJ of energy. The modified lower heating value of the NCG is therefore, in analogy with (50), 29.92 MJ/kg H_2S .

5.3.6 Adiabatic flame temperature

In the combustion process, the chemical energy of the fuel is transformed into heat. If the simplification is made that all of this heat is used to raise the temperature of the combustion products, the adiabatic flame temperature (AFT) of the fuel may be calculated. In the ideal combustion of a hydrocarbon in air, the combustion will consist of carbon dioxide, water, nitrogen, oxygen and possibly sulfur dioxide. The adiabatic flame temperature may then be calculated as:

$$AFT = T_{ref} + \frac{LHV}{\int_{T_{ref}}^{AFT} (m_{CO_2} C_{P, CO_2} + m_{H_2O} C_{P, H_2O} + m_{N_2} C_{P, N_2} + m_{O_2} C_{P, O_2} + m_{SO_2} C_{P, SO_2}) dT} \quad (56)$$

where T_{ref} is the starting temperature of fuel and combustion air in K, LHV is the lower heating value of the fuel in kJ/kg, m is the mass of each combustion product in kg and C_P are the heat capacities of each component in kJ/kg K according to (28) and Table 4.

For a fuel with the weight composition wt_C , wt_H , wt_O and wt_S that is combusted in air with the excess air fraction $P2$, the mass of combustion products per kg fuel is calculated according to (40)-(44).

Given that the heat capacities of the combustion products are known, it is possible to calculate AFT according to (55). To solve this equation analytically may be difficult however, since the heat capacities are described by third degree polynomials. Instead, this calculation was made numerically in the lime kiln model using the following procedure. The reference temperature was set to room temperature, 25 °C.

1. The mass of the combustion products are calculated according to (40)-(44)
2. AFT is assigned an initial value of 1 800 °C.
3. The energy E needed to raise the temperature of the combustion products from T_{ref} to AFT (the denominator in equation 55) is calculated.
4. The error of AFT, ΔT is approximated as: $\Delta T = \frac{LHV - E}{LHV} \cdot (AFT - T_{ref})$
5. ΔT is evaluated. If it is lower than 0.1 °C, AFT is considered accurate enough and the calculation is finished. This means that the energy in the fuel and the energy required raising the temperature of the combustion products from T_{ref} to the calculated AFT are practically the same. If ΔT on the other hand is higher than 0.1, a new AFT is assigned according to: $AFT = AFT + \Delta T$ and the algorithm jumps back to step 3.

Table 8 shows calculated adiabatic flame temperatures for a number of fuels with default composition according to Table 5 and the lower heating values according to Table 6. Calculations were made with no excess air.

Table 8. Adiabatic flame temperatures calculated by the model for different fuels.

	C %	H %	O %	S %	Ash %	LHV MJ/kg	AFT °C
Natural gas	74.8	25.2	0	0	0	50.0	2053
Fuel oil	87.6	12.0	0	0.4	0	41.6	2139
Tall oil	79.4	10.0	10.6	0	0	36.5	2176
Lignin	65.2	5.8	26.9	2.0	0.1	25.5	2147
Methanol	37.5	12.6	49.9	0	0	20.0	1957
Wood powder	49.5	6.3	43.5	0	0.7	18.8	2085
Bark	51.2	6.0	39.8	0	3.0	19.0	2056

As seen in Table 8 there is no real correlation between the heating value and the adiabatic flame temperature. Both the tall oil and the lignin will for instance burn with a hotter flame than the natural gas even though their heating values are much lower than the latter. There are however strong correlations between the adiabatic flame temperature and the fuel composition.

The carbon content of the fuel has a positive correlation with the AFT. Although the carbon will not release huge amounts of energy when combusted, the low heat capacity of the combustion product (carbon dioxide) will result in a high flame temperature.

It may be surprising that high hydrogen content will cause a low flame temperature since the combustion of hydrogen releases a lot of heat. On the other hand it will also create water vapor, a substance with a heat capacity more than twice that of carbon dioxide or nitrogen. The combustion of hydrogen also consumes a lot more oxygen per mass unit than the combustion of carbon which will increase the amount of nitrogen that has to be heated in the flame. Consequently the fact that the hydrogen increases the heating value of the fuel does not compensate for the increase in mass and heat capacity of the combustion products.

The oxygen content has the weakest correlation with the flame temperature according to these results. Oxygen is not combusted and high oxygen content will therefore decrease the heating value of the fuel. On the other hand oxygen is used as an oxidizer in the combustion which decreases the amount of combustion air and consequently the amount of nitrogen in the combustion products.

The adiabatic flame temperature represents the maximum flame temperature of a given fuel under certain conditions. The actual flame temperature is usually much lower than the adiabatic flame temperature due to losses and non-ideal combustion. Therefore the adiabatic flame temperature does not reveal the actual temperature of the combustion. However, it is still useful in order to predict how the flame temperature in a furnace varies with different fuels. Under similar conditions, a fuel with an AFT of 2 100°C creates a hotter flame than a fuel with an AFT of 1 900°C.

After being calculated, AFT is sent back to the user through the fuel stream structure. Knowing the adiabatic flame temperature may help to predict the performance of the kiln when switching between different fuels. In section 3.2.6 it was described that there is a strong correlation between the temperature of the flame and for example the exit gas temperature. By looking at the adiabatic flame temperature that the model returns it is therefore possible for the user to adjust the exit gas temperature in order to make the simulation more precise.

5.3 Calculating the energy demand of the lime kiln

The energy that enters the lime kiln is used to dry, heat and calcinate the lime mud. Some of the energy will also be lost in the flue gases and by radiation and convection through the kiln shell. In order to predict the fuel consumption in the lime kiln it is necessary to approximate the energy going into each of these processes. In the lime kiln model, this is done through an energy balance. A simple approach to such a balance is to make the assumption that all the energy that enters the kiln must also somehow leave it. The sum of the energy contents in the ingoing streams must therefore be equal to the energy in the outgoing streams, including the radiation and convection losses.

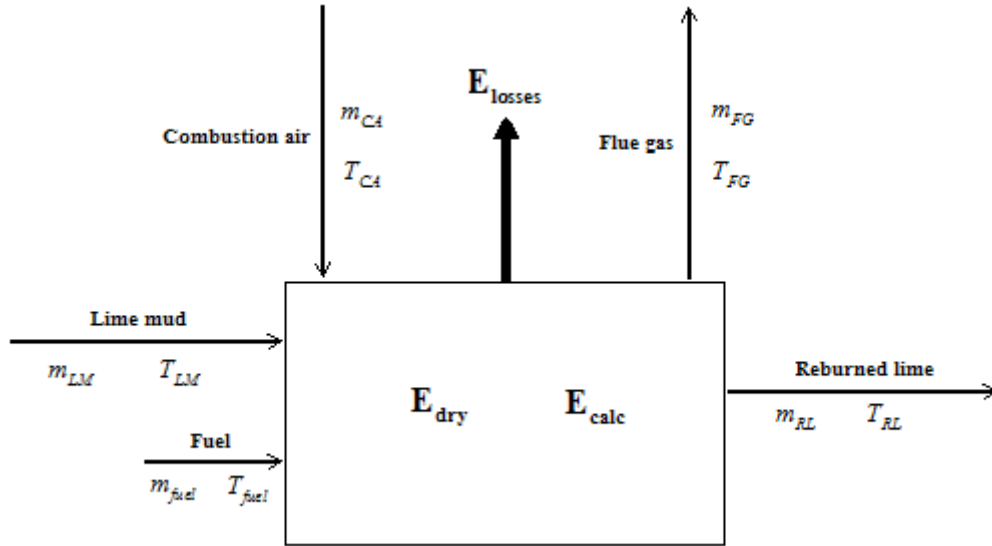


Figure 8. The energy balance of the lime kiln.

The energy for calcination in kJ/hr is calculated as:

$$E_{calc} = m_{CaCO_3,LM} \cdot Pl \cdot H_{calc} \quad (57)$$

where $m_{CaCO_3,LM}$ is the mass flow of calcium carbonate into the kiln in kg/hr, Pl is the calcination degree, the fraction of the calcium carbonate that is calcinated, and H_{calc} is the enthalpy for the calcination of $CaCO_3$, 1786 kJ/kg $CaCO_3$ at 25 °C (Barin, 1989).

The energy for drying the lime mud in kJ/hr is calculated as:

$$E_{dry} = m_{H_2O,LM} \cdot H_{vap} \quad (58)$$

where $m_{H_2O,LM}$ is the mass flow of water in the lime mud in kg/hr and H_{vap} is the heat of vaporization for water, 2260 kJ/kg H_2O at 25°C (Barin 1989).

In addition to the energy for calcination and drying, the heat energy of the outgoing and ingoing streams must be estimated. The heat energy in a stream component in kJ/hr in relation to a reference temperature T_{ref} is calculated as:

$$E = m \int_{T_{ref}}^T C_p(T) dT \quad (59)$$

where m is the mass flow of the component in kg/hr, C_p is the heat capacity of the component in kJ/kg K and T is the stream temperature in K.

By performing this calculation for each stream component and summarizing, the total amount of heat energy in the stream is obtained. As a reference temperature, 25 °C

was chosen, since this is the set temperature for the combustion air and fuel in the model, which minimizes the amount of calculation work.

In the energy balance of this model the lime mud is simplified into consisting of only two components, water and calcium carbonate. All the solids in the lime mud are therefore treated as calcium carbonate. In reality, other solid compounds like calcium sulfate, calcium phosphate and inert calcium will also be present. However, since the fractions of these components are relatively small (around 10%) and their heat capacities are comparable with that of calcium carbonate, this assumption is considered to be accurate enough. The energy content of the lime mud in kJ/hr may consequently be approximated as:

$$E_{LM} = m_{H_2O,LM} \cdot \int_{298.15}^{T_{LM}} C_{P,H_2O(l)}(T) dT + m_{SS,LM} \cdot \int_{298.15}^{T_{LM}} C_{P,CaCO_3}(T) dT \quad (60)$$

where $m_{H_2O,LM}$ and $m_{SS,LM}$ are the mass flows of water and suspended solids in the lime mud in kg/hr and C_p are the heat capacities in kJ/kg according to (27) and Table 4. T_{LM} is the temperature of the ingoing lime mud in K.

With the same reasoning, all of the reburned lime is treated as calcium oxide. The energy in the reburned lime in kJ/hr is calculated as:

$$E_{RL} = m_{RL} \cdot \int_{298.15}^{T_{RL}} C_{P,CaO} dT \quad (61)$$

where m_{RL} is the mass flow of solids in the reburned lime in kg/hr and $C_{P,CaO}$ is the heat capacity of CaO in kJ/kg K according to (27) and Table 4. T_{RL} is the temperature of the reburned lime in K which is specified through parameter $P3$.

The flue gases will consist of carbon dioxide, water vapor and sulfur dioxide from the combustion of the fuels, oxygen and nitrogen from the combustion air, water vapor from the lime mud and fuel and carbon dioxide from the calcination. Almost all of the sulfur dioxide will be captured in the solids and the small amount that is still in the flue gas may be disregarded from an energy point of view.

If the energy content of the flue gas was known, the consumption of external fuel in kg/hr could be calculated as:

$$m_{fuel,ext} = \frac{E_{calc} + E_{dry} + E_{FG} + E_{RL} + E_{losses} - E_{LM} - E_{fuel,int} - E_{NCG}}{LHV_{fuel,ext}} \quad (62)$$

where E_{FG} is the heat energy in the flue gas in kJ/hr, E_{losses} is the heat lost from radiation and convection, $E_{fuel,int}$ and E_{NCG} are the energies supplied in from internal fuel (one or two) and NCG in kJ/kg and $LHV_{fuel,ext}$ is the heating value of the external fuel in kJ/kg. However, this expression can not be used since E_{FG} will depend on the amount of combustion products and therefore on $m_{fuel,ext}$. Due to this cross-

dependence, it is necessary either to separate the flue gas into components that originates from the fuel and components that are fuel independent or to solve the energy balance with a numerical approach. In this model, the first alternative was chosen to enable the fuel consumption to be calculated analytically, thereby minimizing the amount of calculations.

Assume that three fuels are being used, one internal fuel and non condensable gases both with specified mass flows and one external fuel whose mass flow is to be calculated. The flue gas may then be separated into five different components.

1. Evaporated water from the lime mud
2. Carbon dioxide from the calcination reaction
3. Combustion products and moisture of internal fuel
4. Combustion products of NCG
5. Combustion products and moisture of external fuel

Out of these five components, the first four will not depend on the external fuel whereas the mass and thereby the heat energy of the last component will be proportional to the mass flow of external fuel.

The heat content of the evaporated water in the flue gas in kJ/hr is calculated as:

$$E_{H_2O\,evap} = m_{H_2O,LM} \cdot \left(\int_{298.15}^{373.15} C_{P,H_2O(l)} dT + \int_{373.15}^{T_{FG}} C_{P,H_2O(g)} dT \right) \quad (63)$$

where $m_{H_2O,LM}$ is the mass flow of water in the lime mud in kg/hr (same as in equation 60). T_{FG} is the temperature of the flue gas in K, specified through parameter $P4$.

In a similar way the heat energy of the carbon dioxide from the calcination in kJ/hr is calculated:

$$E_{CO_2\,calc} = m_{CO_2\,calc} \cdot \int_{298.15}^{T_{FG}} C_{P,CO_2} dT \quad (64)$$

where $m_{CO_2\,calc}$ is the mass flow of calcinated carbon dioxide in kg/hr calculated in (23).

When treating the combustion products it is convenient to introduce a variable that represents the heat energy in the products created in the combustion of one kilogram of fuel. For the internal and external fuels, this variable H_{CP} in kJ/kg fuel is calculated as:

$$H_{CP, fuel} = m_{CO_2,CP} \cdot \int_{298.15}^{T_{FG}} C_{P,CO_2} dT + m_{H_2O,CP} \cdot \int_{298.15}^{T_{FG}} C_{P,H_2O(g)} dT + \\ + m_{O_2,CP} \cdot \int_{298.15}^{T_{FG}} C_{P,O_2} dT + m_{N_2,CP} \cdot \int_{298.15}^{T_{FG}} C_{P,N_2} dT + wt_{moist} \cdot \left(\int_{298.15}^{373.15} C_{P,H_2O(l)} dT + \int_{373.15}^{T_{FG}} C_{P,H_2O(g)} dT \right) \quad (65)$$

Notice that m in this equation represents the mass of each combustion product that is

created per mass unit of fuel in kg/kg fuel according to equations (40)-(44). wt_{moist} is the moisture content of the fuel, specified through parameter $P11$ for the external fuel and parameters $P15$ and $P20$ for the first and second internal fuel respectively.

Since this energy balance assumes that all sulfur dioxide is captured the combustion products of the non condensable gases will consist of only water. The energy of the combustion products is therefore calculated as:

$$H_{CP, NCG} = m_{H_2O, CP} \cdot \int_{298.15}^{T_{FG}} C_{P, H_2O(g)} dT + m_{O_2, CP} \cdot \int_{298.15}^{T_{FG}} C_{P, O_2} dT + m_{N_2, CP} \cdot \int_{298.15}^{T_{FG}} C_{P, N_2} dT \quad (66)$$

where m represents the combustion products per kg of NCG according to (45), (47) and (48).

Since the combustion air and the fuel have a temperature of 25 °C, they will not hold any heat energy according to the definition in (59).

The heat losses from the shell of the lime kiln are specified by the user as a fraction of the total energy consumption. When calculating however, it is more convenient to use a variable that describes the heat losses in relation to the total energy consumption with the heat losses excluded. This variable is then multiplied with the calculated energy consumption (heat losses excluded) to receive the heat losses. If the parameter specified by the user is called μ_{losses} , this new variable μ'_{losses} is calculated as:

$$\mu'_{losses} = \frac{\mu_{losses}}{1 - \mu_{losses}} \quad (67)$$

An expression for the calculation of the external fuel consumption may now be assembled:

$$m_{fuel, ext} = \frac{(E_{calc} + E_{dry} + E_{RL} - E_{LM} + E_{CO_2 calc} + E_{H_2O evap}) \cdot (1 + \mu'_{losses})}{LHV_{fuel, ext} - H_{CP, ext} \cdot (1 + \mu'_{losses})} - \frac{\sum_{i=1}^2 (m_{fuel, int i} \cdot (LHV_{fuel, int i} - H_{CP, int i} \cdot (1 + \mu'_{losses}))) + m_{NCG} \cdot (LHV_{NCG} - H_{CP, NCG} \cdot (1 + \mu'_{losses}))}{LHV_{fuel, ext} - H_{CP, ext} \cdot (1 + \mu'_{losses})} \quad (68)$$

where E_{calc} is calculated as in (57), E_{dry} as in (57), E_{RL} as in (61), E_{LM} as in (60), $E_{H_2O evap}$ as in (63), $E_{CO_2 calc}$ as in (64), $H_{CP int i}$ and $H_{CP ext}$ as in (65), $H_{CP, NCG}$ as in (66), μ'_{losses} as in (67). LHV_{NCG} is 29.92 MJ/kg, $LHV_{fuel, ext}$ and $LHV_{fuel, int i}$ are either calculated according to (54) or specified through parameter $P12$, $P17$ and $P22$ and then modified according to (55). $m_{fuel, int i}$ is the flow of internal fuel (one or two) that is specified in parameter $P18$ and $P23$ for the first and second internal fuel respectively.

A complete derivation of (68) is found in Appendix 1.

A potential problem that the model needs to handle is the situation where the user specifies mass flows of internal fuel that are greater than the total energy demand of the lime kiln. This would cause the consumption of external fuel calculated in (68) to be negative, which is of course unacceptable. This is solved by a simple routine that checks if this is the case. If so, the model sends out a warning to the user and performs the calculation again, this time with the internal fuels excluded

5.5 Evaluating the energy balance

To illustrate the size of the different components in the energy balance a reference simulation was carried out. The input data for this simulation is shown in Table 9.

Table 9. Input parameters of the reference simulation.

Dry content of lime mud	75%
Temperature of lime mud	60°C
Temperature of flue gases	200°C
Temperature of reburned lime	200°C
Shell heat losses	12%
Excess air	10%

Table 10 shows the result of the simulation. E_{FG} represents the total energy of the flue gases which is $E_{FG,CO_2calc} + E_{FG,H_2O\,evap}$ and $\sum m_{fuel} \cdot H_{CP}$ combined.

Table 10. The energy balance of the reference simulation.

	Energy <i>MJ/ADt</i>	Heat rate <i>MJ/kg CaO</i>	Fraction of total consumption
Energy for calcination	786	3.18	51%
Energy for drying	350	1.41	23%
Energy in flue gases	237	0.96	15%
Heat in lime mud	-54	-0.22	-4%
Heat in reburned lime	39	0.16	3%
Shell heat losses	185	0.75	12%
Total	1543	6.4	100%

Following the reference case, further simulations were carried out to study the effect of changing the different input parameters of the simulation. All the input parameters in Table 9 except the lime mud temperature were varied one at a time. The resulting energy consumptions and heat rates are shown in Table 11-15.

Table 11. Energy consumption with different dry contents of the lime mud (75% in reference case).

Dry content	80%	70%	65%
<i>Energy consumption (kJ)</i>	1409.4	1673.6	1836.3
<i>Heat rate (kJ/kg lime)</i>	5.70	6.77	7.42
<i>Change compared to reference scenario</i>	-8.0%	9.1%	19.7%

The dry content of the lime mud is one of the most important parameters in the energy balance of the kiln. Lowering the dry content from 75% to 65% will increase the amount of water entering the kiln with more than 60%. All this water will need to be heated and vaporized, increasing the energy consumption with nearly 20%. The dry content of the lime mud is determined by both lime mud quality and the properties of the mud filter.

Table 12. Energy consumption with different flue gas temperatures (200°C in reference case).

Flue gas temperature	150°C	250°C	300°C
<i>Energy consumption (kJ)</i>	1461.5	1609.4	1692.1
<i>Heat rate (kJ/kg lime)</i>	5.91	6.51	6.85
<i>Change compared to reference scenario</i>	-4.6%	5.0%	10.4%

As shown in Table 12 the flue gas temperature is also important to the overall energy balance of the kiln. Every 10 degrees increase from the reference temperature will add approximately one percent to the energy consumption of the kiln. Important factors for the flue gas temperature are fuel parameters (especially AFT) and the dry content of the lime mud.

Table 13. Energy consumption with different lime temperatures (200°C in reference case).

Reburned lime temperature	300°C	500°C	900°C
<i>Energy consumption (kJ)</i>	1562.4	1624.4	1753.7
<i>Heat rate (kJ/kg lime)</i>	6.32	6.57	7.10
<i>Change compared to reference scenario</i>	1.9%	6.0%	14.4%

The heat left in the reburned lime at 200°C represents only about 2.5% of the total energy consumption of the kiln according to Table 9. However, the energy in the lime product at temperatures around 1000°C will contribute significantly to the heat balance of the kiln. This indicates the importance of using coolers in lime kiln, lowering the temperature of the reburned lime.

Table 14. Energy consumption with different shell heat losses (12% in reference case).

Shell heat losses	10%	15%	20%
<i>Energy consumption (kJ)</i>	1495.5	1592.3	1702.5
<i>Heat rate (kJ/kg lime)</i>	6.05	6.44	6.89
<i>Change compared to reference scenario</i>	-2.4%	3.9%	11.1%

In this case, the shell heat losses are expressed as a fraction of total energy consumption. By this definition it is obvious that raising the losses from 12% to 20% will affect the kiln energy consumption significantly. The heat losses will be determined by kiln geometry, refractory properties as well as the ambient temperature.

Table 15. Energy consumption with different fractions of excess air (10% in reference case).

Excess air	5%	15%	20%
<i>Energy consumption (kJ)</i>	1526.9	1538.5	1544.4
<i>Heat rate (kJ/kg lime)</i>	6.18	6.23	6.25
<i>Change compared to reference scenario</i>	-0.4%	0.4%	0.8%

Increasing the fraction of excess air will increase the mass flow of predominantly nitrogen in the flue gases of the kiln. As seen in Table 15 though, the excess air has no large effect on the kiln energy balance. The excess air is however an important parameter from an operating point of view. Increasing the flow of flue gas will increase the load on the ID fan which may constrict the capacity of the lime kiln.

In these simulations the different parameters were changed separately. This was done to study the effect of each of these input parameters on the overall energy balance of the lime kiln. In real operating conditions however many of the parameters will be interacting, meaning that it is impossible to change one without affecting others.

According to Table 11 for example, it is possible to save a lot of energy by raising the dry content of the lime mud. In a real kiln however this would result in a higher flue gas temperature which counters this fuel saving effect. In a similar way, it is conceivable that there is a correlation between shell heat losses and lime temperature since product coolers that lower the lime temperature also have big heat losses.

6. Creating a robust and user-friendly model

To confirm that the model behaved properly in large simulations it was tested thoroughly in numerous systems and modified to correct any problems. This was important since all mill systems are different from each other and the fact that the model runs robust in one type of simulation is not a guarantee for it to do so in another.

One example of a model modification was handling a non-existing lime mud stream. When simulating a large mill system there will usually be no ingoing lime mud in the first iteration. It was found that if the lime kiln block responded to this with sending out no reburned lime stream then the lime cycle would not start to simulate properly. It was clear that a start-up stream was necessary for the simulation of the lime cycle to begin. This was solved with a simple routine that sent out a warning and a default lime flow when there was no ingoing lime mud.

Another part in this work was to provide the model with a number of warnings that are displayed to the user whenever there is an error or unclarity in the input-data. Examples of this is when the user specifies a heating value of the fuel that differs considerably from the calculated value or when the sulfur content of the fuel is specified in percent instead of as a fraction.

7. Bio fuels in the lime kiln - Potential effects in the lime cycle

7.1 Background

Many mills are looking to replace the fossil fuels used in the lime kilns with bio fuels for economic as well as environmental motives. Due to the nature of the lime reburning process and the lime cycle, bio fuels may however cause problems others than those expected in other types of furnaces. These problems are related to the increased quantity of ash that is introduced to the process with many bio fuels. In most furnaces the main objective is to produce heat and the ash is therefore not a major problem since it does not interfere with the product. In the lime kiln on the other hand the lime will be mixed with the ash left from the combustion. The quality of the product will therefore be directly affected by the ash content of the fuel.

It is mainly the silicon and phosphorous that may cause problems if introduced in the lime cycle in large quantities. The formation of calcium silicate, CaSiO_4 and calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ causes obstruction of the calcium, thereby preventing it from forming calcium oxide. By doing so it will reduce the causticizing capacity as well as contribute to dead load in the lime cycle. When the intake of silicon or phosphorous is high it is usually necessary to purge more lime mud to stop these compounds to accumulate in the lime cycle and thereby decreasing the amount of available lime (Ulmgren 1997).

7.2 Simulations

In these simulations five different bio fuels were tested to approximate the effects of different ash compositions. The fuels are tall oil, wood powder and three different kinds of bark. The ash content of the different fuels is shown in Table 16 (Wadsborn 2008).

Table 16. The concentration of NPE (mg/kg fuel) in the fuels tested (Wadsborn 2008).

Concentration (mg/kg fuel)	<i>Wood</i>				
	<i>powder</i>	<i>Tall oil</i>	<i>Bark 1</i>	<i>Bark 2</i>	<i>Bark 3</i>
<i>Ca</i>	797	6	8000	8740	6350
<i>K</i>	510	36	5100	1860	3180
<i>Mg</i>	133	5	1330	1075	874
<i>Mn</i>	16	1	157	620	343
<i>Al</i>	3	6	31	140	908
<i>Si</i>	7	14	72	48	60
<i>P</i>	31	24	313	661	1260
<i>Cl</i>	5	5.1	51	<50	-
Total ash content, summarized (%)	0.15	0.01	1.51	1.31	1.30

Table 17. The concentration of NPE (kg/ton ash) in the fuels tested.

	Wood Powder	Tall oil	Bark 1	Bark 2	Bark 3
Concentration (kg/ton ash)					
Ca	530.6	61.8	722.1	664.9	489.4
K	339.5	370.8	174.4	141.5	245.1
Mg	88.5	51.5	5.7	81.8	67.4
Mn	10.7	10.3	27.2	47.2	26.4
Al	2.0	61.8	6.8	10.7	70.0
Si	4.7	144.2	3.7	3.7	4.6
P	20.6	247.2	11.8	50.3	97.1
Cl	3.3	52.5	0.0	0.0	0.0
Total ash content (kg/ton fuel)	1.50	0.10	15.05	13.14	12.98

As explained in section 5.2, the ash components are not available in the fuel structure and must therefore be inserted through a separate stream.

The ash stream is a liquor stream consisting of only dissolved solids (no water or suspended solids). The concentration of dissolved solids in the liquor stream is expressed as kg dissolved solid per metric ton liquor which is equal to the concentrations in Table 17. Since there is no water present in the stream, the concentrations will add up to 1000. The liquor flow will be equivalent to the ash flow which is proportional to the amount of fuel burnt in the kiln. It is therefore necessary to relate the liquor flow (ash flow) to the fuel flow. This is done by the WinGEMS “compute” function that allows the user to define a stream component as dependant on another stream component in the process. The liquor flow in ton/hr was related to the fuel flow according to:

$$m_{Liquor} = \frac{m_{fuel} \cdot TAC}{1000} \quad (69)$$

where m_{Liquor} is the liquor flow in ton/hr, m_{fuel} is the fuel flow in ton/hr and TAC is the total ash content in kg ash/ton fuel.

The heating values of the fuels used in the simulations are the default heating values shown in Table 6.

In these simulations a reference mill system was used (FRAM 2005). The process step in the simulation that will determine the formation of calcium silicate and calcium phosphate is the white liquor filter. This is where the lime mud and the white liquor generated in the causticizing reaction are separated from each other. If the concentration of silicon or phosphorous in the liquor entering the filter exceeds the specified solubility limits for either of these components calcium silicate or calcium phosphate is formed. In these simulations the solubility limits for silicon and phosphorous were set to 14 mmol/L and 0.02 mmol/L respectively. These figures are in accordance with those reported in the literature (Ulmgren & Rådeström 1997 & Ulmgren 1997).

Initially a reference scenario was simulated where no ash was introduced to the lime cycle. The fraction of free lime in the reburned lime of the reference scenario was

91.3%. As the intake of NPE increases with the ash this figure is expected to drop since some of the calcium will attach to these components, mainly the silicon and the phosphorous. To maintain the same amount of free lime as in the reference scenario, more lime mud will have to be purged from the process. Doing so will increase the output of NPE which counters the effect of the increased intake through the ash.

The following two scenarios were simulated and compared with the reference scenario:

1. The amount of free lime in the reburned lime was studied for the different bio fuels when the amount of purged lime mud was held constant at the same level as in the reference scenario. In these simulations, the fuel consumption was also compared with that of the reference scenario. Less free lime in the reburned lime will reduce the mass flow of CaO and therefore the causticizing capacity. To compensate this, more lime mud will have to be used which increases the energy consumption, mainly because more water has to be evaporated from the kiln.
2. The amount of purged lime mud was controlled to maintain the same amount of free lime as in the reference scenario (91.3%). This amount may then be compared with the amount purged in the reference scenario.

In both scenarios, the simulations were carried out until all streams converged and steady-state was obtained.

7.3 Results

The first simulations, where the purged lime was held constant, resulted in the following amounts of free lime for different bio fuels.

Table 18. Amount of free lime (%) for different fuels according to simulations.

	Ref	Tall oil	Wood powder	Bark1	Bark2	Bark3
Free CaO (%)	91.3	91.3	91.1	90.9	88.6	86.6

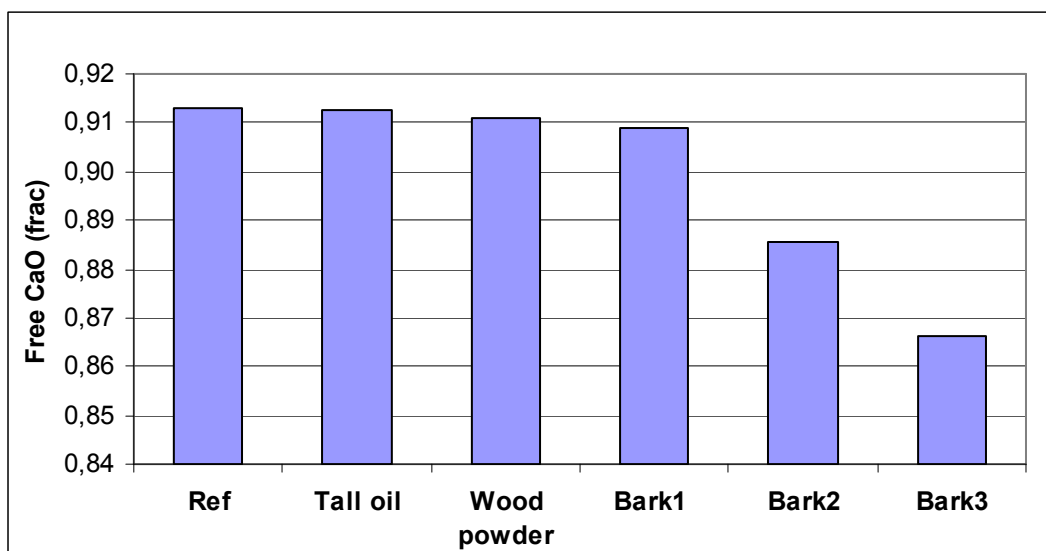


Figure 9. Amount of free lime (%) for different fuels according to simulations-

Figure 9 shows that only the barks have any dramatic effect on the lime reactivity (fraction of free CaO). This particular lime cycle was more sensitive to intakes of phosphorous than of silicon. The bark with the highest phosphorous content therefore created the lowest fractions of free lime.

Table 19 shows the increase in fuel consumption due to the ash content of the different bio fuels. The increase is expressed as percent of the fuel consumption when no ash was introduced to the process.

Table 19. Increased fuel consumption (%) for different fuels according to simulations.

	Ref	Tall oil	Wood Powder	Bark1	Bark2	Bark3
Increased Fuel consumption (%)	-	~0	0.05	0.09	0.59	1.09

In the second simulations the amount of lime mud that has to be purged to maintain the 91.3 % free lime was studied. This as well as the amount of make-up lime that has to be inserted in the lime cycle in kg/ADt (Air dried ton) pulp is shown in the figures below.

Table 20. Amount of purged lime mud (kg/ADt) and purchased lime (kg/ADt) for different fuels.

	Ref	Tall oil	Wood powder	Bark1	Bark2	Bark3
Purged lime mud (kg/ADt)	17.8	18.1	19.2	21.0	37.3	51.3
Purchased lime (kg/ADt)	9.7	9.9	10.4	11.4	20.5	28.3

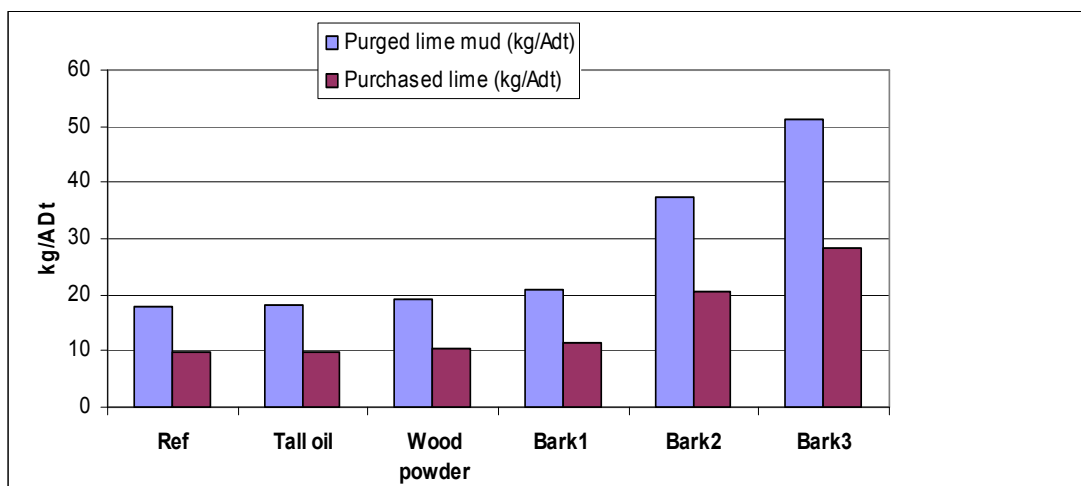


Figure 10. Amount of purged lime mud (kg/ADt) and purchased lime (kg/ADt) for different fuels.

According to these simulations the two most phosphorous rich barks will have big effects on the amount of purged lime mud. If bark number three is used as a fuel it will be necessary to purge almost three times as much lime mud as in the reference scenario. To replace the increase in purged lime mud more lime will also need to be purchased.

The third bark has a very high phosphorous content, roughly four times as high as the first bark and twice as high as the second. Due to the threshold effect in the formation of $\text{Ca}_3(\text{PO}_4)_2$ this makes a big difference in the quality of the lime product.

7.4 Economy

In this section the economic effects of increased lime purging will be examined. As mention in the last chapter, purged lime will need to be replaced by make-up to maintain the balance of the lime cycle. This may be done either by adding lime mud prior to the lime kiln or by adding lime after the lime kiln. Using lime mud as make-up is cheaper but will increase the load over the lime kiln. If the kiln capacity is a constraining factor in the process, using make-up lime may be a better alternative although it is more expensive than the lime mud.

In these calculations it is assumed that lime is used as make-up. The cost of lime is approximately 1.50 SEK/kg (Hjulfors 2008). Table 21 shows the the cost per ADt pulp as well as the yearly cost for a mill that produces 500 000 ADt pulp.

Table 21. Approximate lime cost for different fuels according to simulations

	Ref	Tall oil	Wood powder	Bark1	Bark2	Bark3
Lime cost (SEK/ADt)	14.5	14.8	15.7	17.1	30.7	42.5
Yearly lime cost (MSEK/year)	7.3	7.4	7.9	8.6	15.4	21.3

Bark number three will increase the lime cost with approximately 28 SEK/ADt pulp. For a mill that produces 500 000 ADt pulp yearly this corresponds to an increased cost of 14 million SEK yearly.

Many mills are looking to replace fuel oil or natural gas with bio fuels. One important incitement for this is to lower fuel costs. Since these simulations show that some bio fuels may cause a rise in lime cost it might be interesting to compare this cost with the potential fuel savings when converting from oil to bio fuel. When simulating the reference scenario using fuel oil with a lower heating value of 41 MJ/kg the fuel consumption was 35.1 kg oil per ADt pulp. The price for fuel oil in Sweden is approximately 10 000 SEK per cubic meter or 10 SEK per kg (SPI, 2009) giving a total fuel cost of 350.1 SEK/ADt pulp. This is more than ten times as high as the increase in lime cost when using the most phosphorus rich bark. Decreasing the fuel cost with just ten or twenty percent by using a cheaper fuel like bark or wood powder could therefore be enough to counter the effects of the increased lime mud purge. This indicates that although the increase in lime cost may be substantial it is still considerably smaller than the total fuel cost.

Another problem that many mills report when using bio fuels is that the flame is less stable and may cause more damage to the refractory. If the refractory is damaged the kiln has to be shut down for maintenance which usually stops the production for several days during which bought lime has to be used for causticizing. A fluctuating flame may also increase the formation of rings which makes it necessary to stop the kiln for ring removing.

The assumption is made that the introduction of bio fuels causes the lime kiln to shut down for an extra two weeks every year. According to the reference scenario 250 kg of CaO was needed for every ADt of pulp. For a mill that produces 500 000 ADt pulp per year this will lead to a yearly increase in lime cost of:

$$\text{Increased lime cost} = \frac{14}{365} \cdot 500\,000 \cdot 250 \cdot 1.5 \approx 7\,200\,000 \text{ SEK / year} \quad (70)$$

This may be compared to the 14 million SEK yearly that was the approximated cost for the increased lime mud purge when using bark number three as fuel. According to these calculations the two problems may be economically in the same order of magnitude. It is however hard to draw any more detailed conclusions due to the rather simple nature of the calculations.

8. Recovering energy from the flue gases of the lime kiln

8.1 Background

The amount of water left in the lime mud as it enters the kiln will depend on both the quality of the lime and the filter used in the mud washer. Dry contents are likely to rise as better filter equipments are installed in the mills. Increased dry content will reduce the amount of evaporated water and consequently the energy that has to be put into this process. New filter equipment that increases the dry content from 70 % to 85 % will reduce the water entering the kiln with almost 60 %, a reduction that may be expected to bring big energy savings.

However, increasing the dry content of the lime mud alone will not have a big fuel saving effect. Less water entering the like kiln will decrease the length of the drying zone of the kiln, thereby increasing the flue gas temperature. An increased dry content may therefore not have a major impact on the total energy balance of the kiln. Less energy will obviously be used for drying, but in return a lot more energy will be lost through the flue gases.

To be able to exploit the increased dry content it is therefore necessary to find a way to utilize the increased energy content of the flue gases. In a conventional lime kiln however, the flue gas temperatures will be relatively low representing low-value energy not suitable for steam generation. To make the high-value energy available, the kiln needs to be equipped with an external flash dryer. This equipment is a dryer that uses warm flue gases from the kiln to dry the solids. The lime mud that leaves the flash dryer and enters the kiln will therefore be almost completely dry. Basically this is just a way to separate the drying process from the calcination. Nonetheless, by installing a heat exchanger between the flash dryer and the kiln, the high-value energy of the warm flue gases that leaves the kiln could be accessed. By doing this, the high temperature flue gases could be used for steam generation while the low temperature flue gases are used for drying. A flow sheet of this equipment is shown in Figure 11.

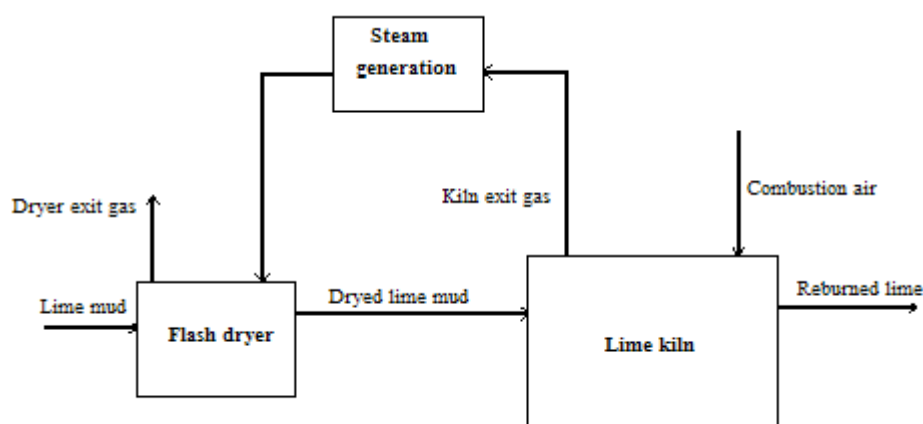


Figure 11. Flow sheet of lime kiln with flash dryer and heat exchanger.

In the steam generation, energy would be recovered from the process thereby lowering the temperature of the gas that enters the flash dryer. The temperature may only decrease to a certain temperature level since there must be enough heat left in the gas to dry the lime mud. To examine these temperature intervals and energies it was convenient to create two new blocks representing the flash dryer and the heat exchanger in Figure 11.

8.2 Flash dryer block

The flash dryer uses hot exit gas from the lime kiln to dry the wet lime mud. Ingoing streams of the block will be a liquor stream representing the lime mud and a special gas stream representing the kiln exit gas. From these two ingoing streams, the block should specify the outgoing streams consisting of dried lime mud (liquor) and dryer exit gas (special gas). The lime mud is heated to 100°C and all the water is assumed to be evaporated. The mass flow of the dried lime mud will be the same as that of the ingoing lime mud apart from the water that is transferred to the outgoing gas.

While the mass balance is solved easily, the energy balance of the flash dryer block needs a bit more work. Figure 12 shows the flash dryer with in- and outgoing streams:

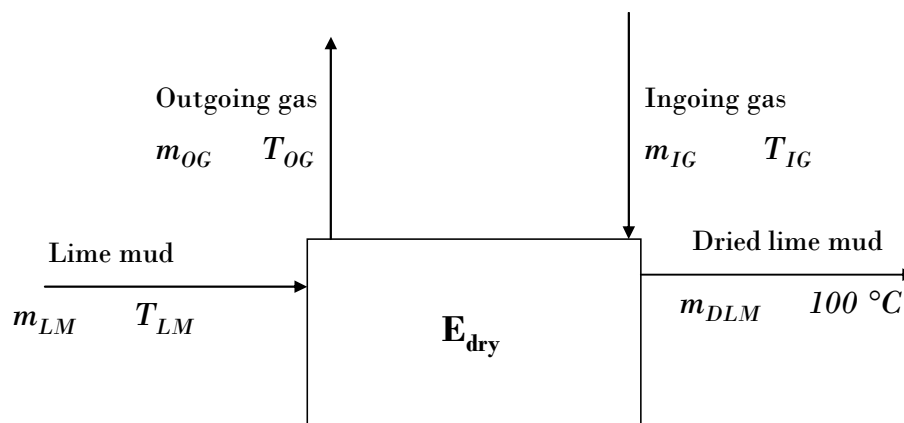


Figure 12. The energy balance of the flash dryer block.

In analogy with the energy balance of the lime kiln, the heat energy in the outgoing streams should be equal to that of the ingoing streams minus the energy for drying, E_{dry} . In this case it is assumed that there are no losses in the flash dryer, so that all the energy lost from the gas is transferred to the solids.

When the mass balance has been solved, the only parameter still unknown in Figure 12 will be the temperature of the outgoing gas, T_{OG} . The purpose of the energy balance will be to determine this temperature. A simple energy balance over the flash dryer will look as follows:

$$\begin{aligned}
 E_{IG} + E_{LM} &= E_{dry} + E_{DLM} + E_{OG} \Rightarrow \\
 \Rightarrow E_{OG} &= E_{IG} + E_{LM} - E_{DLM} - E_{dry}
 \end{aligned}
 \tag{71}$$

where all energies are in kJ/hr. The heat energy in the lime mud, E_{LM} is calculated as in (60) and the energy for drying, E_{dry} as in (58). The heat energy of the dried lime mud is calculated as:

$$E_{DLM} = m_{DLM} \cdot \int_{298.15}^{373.15} C_{P, CaCO_3} dT \quad (72)$$

where m_{DLM} is the dry weight of the lime mud in kg/hr.

Heat energy in the ingoing gas is calculated as:

$$E_{IG} = m_{CO_2, IG} \cdot \int_{298.15}^{T_{IG}} C_{P, CO_2} dT + m_{H_2O, IG} \cdot \int_{298.15}^{T_{IG}} C_{P, H_2O(g)} dT + \\ + m_{O_2, IG} \cdot \int_{298.15}^{T_{IG}} C_{P, O_2} dT + m_{N_2, IG} \cdot \int_{298.15}^{T_{IG}} C_{P, N_2} dT \quad (73)$$

where m are the mass flows of different components of the flue gas in kg/hr and T_{IG} is the temperature of the ingoing gas in K.

The outgoing gas will have the same mass flow as the ingoing gas, except that it also contains the evaporated water from the lime mud. The heat energy of the outgoing gas may therefore be calculated as:

$$E_{OG} = m_{CO_2, IG} \cdot \int_{298.15}^{T_{OG}} C_{P, CO_2} dT + m_{H_2O, IG} \cdot \int_{298.15}^{T_{OG}} C_{P, H_2O(g)} dT + \\ + m_{H_2O, LM} \cdot \left(\int_{298.15}^{373.15} C_{P, H_2O(l)} dT + \int_{373.15}^{T_{OG}} C_{P, H_2O(g)} dT \right) + m_{O_2, IG} \cdot \int_{298.15}^{T_{OG}} C_{P, O_2} dT + m_{N_2, IG} \cdot \int_{298.15}^{T_{OG}} C_{P, N_2} dT \quad (74)$$

where T_{OG} is the temperature of the outgoing gas in K.

This expression may be inserted in the left side of (71). Since all the parameters for the calculations of E_{LM} , E_{DLM} , E_{dry} and E_{IG} are known to the block through the input streams, the right side of (71) may be replaced with a constant. If this constant is kalled k , (71) may be written as:

$$m_{CO_2, IG} \cdot \int_{298.15}^{T_{OG}} C_{P, CO_2} dT + m_{H_2O, IG} \cdot \int_{298.15}^{T_{OG}} C_{P, H_2O(g)} dT + \\ + m_{H_2O, LM} \cdot \left(\int_{298.15}^{373.15} C_{P, H_2O(l)} dT + \int_{373.15}^{T_{OG}} C_{P, H_2O(g)} dT \right) + m_{O_2, IG} \cdot \int_{298.15}^{T_{OG}} C_{P, O_2} dT + m_{N_2, IG} \cdot \int_{298.15}^{T_{OG}} C_{P, N_2} dT = k \quad (75)$$

Through this equation, the unknown variable T_{OG} may be calculated. Given that the heat capacities are described by third degree polynomials, it is suitable to solve this equation numerically. In the flash dryer block this is done through an algorithm

practically identical with the one used in the calculation of the adiabatic flame temperature in chapter 6.2.6.

8.3 Energy recovery block

To examine the amounts of energy that could be recovered from a gas stream, a simple energy recovery block was constructed.

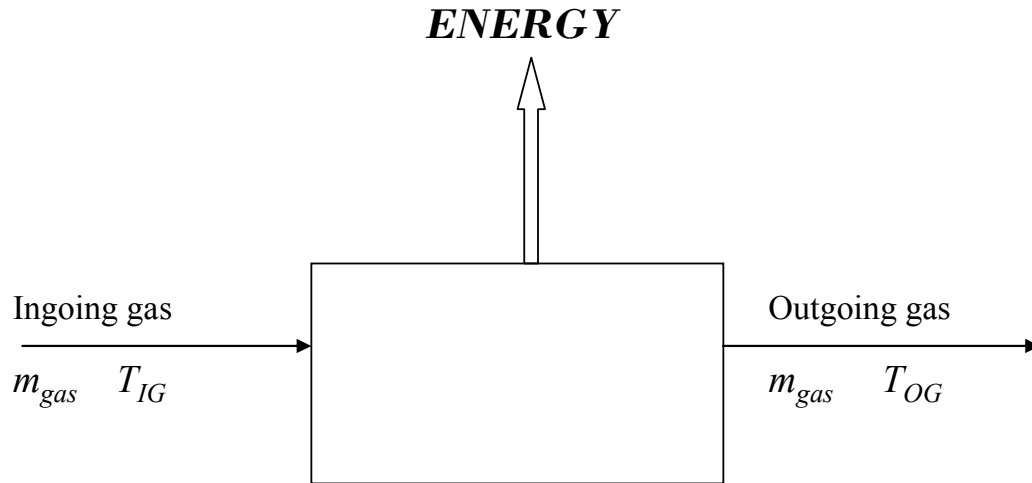


Figure 13. Energy balance over the energy recovery block.

The only function of the block is to lower the temperature of the ingoing stream. The temperature difference is set by the user as an input parameter of the block. Given a mass flow of gas, m_{gas} , with an ingoing temperature T_{IG} that is decreased with a temperature ΔT , the block will return the difference in energy between the ingoing and outgoing gas. This is done through the following calculation:

$$\begin{aligned} \Delta E = & m_{CO_2, gas} \cdot \int_{T_{IG}-\Delta T}^{T_{IG}} C_{P, CO_2} dT + m_{H_2O, gas} \cdot \int_{T_{IG}-\Delta T}^{T_{IG}} C_{P, H_2O(g)} dT + \\ & + m_{O_2, gas} \cdot \int_{T_{IG}-\Delta T}^{T_{IG}} C_{P, O_2} dT + m_{N_2} \cdot \int_{T_{IG}-\Delta T}^{T_{IG}} C_{P, N_2} dT \end{aligned} \quad (76)$$

This energy represents the difference in energy between the streams and may therefore give an indication on the amount of energy available in the hot flue gases of the lime kiln.

8.4 Simulations

The simulations were performed to approximate the amounts of energy that can be recovered from the process when the dry content is raised and/or the exit gas from the flash dryer is lowered.

In the simulations, the blocks were connected as showed previously in Figure 11. Initially a reference case was simulated with a lime mud dry content of 70 % and a temperature of the gas leaving the flash dryer of 250 °C. This was done to represent standard conditions in a lime kiln. The energy recovery block was not used in this reference scenario.

Since the temperature of the gas leaving the flash dryer is calculated in the flash dryer block, it may not be set to a fixed temperature. It is however possible to control this temperature by controlling the temperature of the gas entering the flash dryer. This ingoing gas is the same gas that exits the lime kiln and whose temperature is specified in parameter *P4* of the lime kiln block. Parameter *P4* may therefore be used to regulate the temperature of the gas leaving the flash dryer until the latter reaches a specific value.

In this way the temperature of the lime kiln exit gas was found to be 747 °C. The energy released when the exit gas is cooled from this temperature to 250 °C represents the energy required to evaporate the water in the lime mud when the dry content is 70 %. In the rest of the scenarios, the exit gas temperature of the kiln was fixed to 747 °C. With this parameter fixed, the energy balance and fuel consumption of the lime kiln would remain the same in all scenarios.

In the rest of the simulations, the effects of modifying the dry content and the flash dryer exit gas temperature were studied. With a fixed kiln exit gas temperature of 747 °C, the energy recovery block was activated to regulate the temperature of the gas leaving the flash dryer. As soon as the block is activated, energy will be retrieved from the kiln exit gas and the temperature of the flash dryer exit gas will be lowered. The ΔT input parameter of the energy recovery block may therefore be used to regulate the flash dryer exit temperature. By doing so the amount of energy that could be recovered from the process at different exit temperatures and dry contents was approximated. Also, the approximate temperature interval for the energy recovery was noted. In this interval, the first temperature is the one entering the heat exchanger (will be constant at 747 °C) and the second temperature is that of the gas leaving the heat exchanger (as well as entering the flash dryer).

Four different flue gas temperatures (250, 200, 150 and 100 °C) were combined with three different dry contents (75, 80 and 85 %). Table 22-25 as well as Figure 14 shows the energy recovered in MJ/ADt as well as in fractions the energy consumption of the kiln. The right columns show the approximate temperature intervals at which energy could be retrieved from the flue gas.

Table 22. Energy recovered for different dry contents when exit gas temperature is 250 °C

	Energy MJ/ADt	Fraction of energy consumption %	Temperature interval for recovery °C
Dry content (%)			
75	70.6	6.7%	747 – 645
80	132.4	12.5%	747 – 552
85	186.9	17.6%	747 – 469

Table 23. Energy recovered for different dry contents when exit gas temperature is 200 °C

	Energy MJ/ADt	Fraction of energy consumption %	Temperature interval for recovery °C
Dry content (%)			
75	109.7	10.4%	747 – 586
80	169.2	16.0%	747 – 496
85	221.7	20.9%	747 – 415

Table 24. Energy recovered for different dry contents when exit gas temperature is 150 °C

	Energy MJ/ADt	Fraction of energy consumption %	Temperature interval for recovery °C
Dry content (%)			
75	148.2	14.0%	747 – 528
80	205.4	19.4%	747 – 441
85	255.9	24.2%	747 – 361

Table 25. Energy recovered for different dry contents when exit gas temperature is 100 °C

	Energy MJ/ADt	Fraction of energy consumption %	Temperature interval for recovery °C
Dry content (%)			
75	186	17.6%	747 – 471
80	241	22.7%	747 – 384
85	289.5	27.3%	747 -307

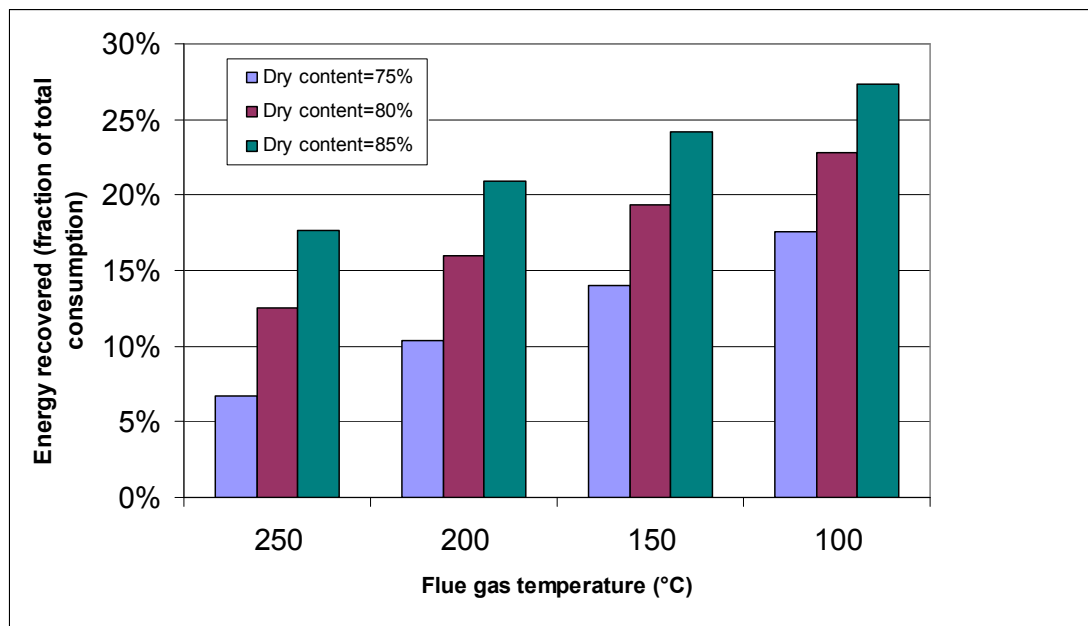


Figure 14. Amount of energy that may be recovered for different dry contents of the lime mud and different flue gas temperatures.

Figure 14 shows that a substantial amount of energy could possibly be retrieved from the process with higher dry contents of the lime mud. With an 85 % dry content, energy corresponding to 17.6 % of the fuel consumption is available for steam generation even if the flue gas temperature is the same as in the reference scenario (250 °C).

The amount of energy that can be recovered will depend strongly on the temperature of the gas leaving the dryer. In a conventional lime kiln, with integrated drying, the exit gas temperature will be determined by operating conditions, mainly fuel parameters and the dry content of the lime mud. In a process with a separate flash dryer and steam generation, as shown in Figure 11, it will however be possible to control the exit gas temperature through the amount of energy recovered from the process. More energy recovered will result in lower temperature of the gas going into the dryer leading to a lower exit gas temperature.

In the reference scenario the exit gas temperature was assumed to be 250 °C at 70 % dry content for standard lime kiln. This is a relatively high temperature and a lot of energy will still be in the gases when released from the kiln. The temperature into the dryer was roughly 750 °C, a very high temperature for drying. It is reasonable to believe that this temperature can be lowered and that some of this energy could instead be used for steam generation.

Four different exit gas temperatures were tried in the simulations. The most extreme case where most energy is recovered is where the dry content is 85 % and the exit temperature 100 °C. In this scenario, the lime mud is dried with gases coming in at about 300 °C and leaving at 100 °C. These temperatures are still reasonable high and certainly high enough to dry a material like wet lime mud. The drying process will however be slower in the temperature interval 300 °C-100 °C than at 750 °C-250 °C.

This question will therefore be a matter of retention times and if the flash dryer will be able to dry the lime mud quickly enough at these lower temperatures.

8.5 Economy

In this section the economic potential of the heat recovery will be examined. The most optimistic scenario in the previous simulations included a dry content of 85 % and a gas temperature of 100 °C leaving the flash dryer. In this scenario the temperature of the gas leaving the lime kiln is lowered from 747.5 °C to 307.1°C which represents a heat recovery of 289.5 MJ/ADt pulp or 27.3 % of the energy supplied by the fuel.

Assuming that this energy may be converted to electricity with 40 % efficiency then 115,8 MJ or 32.2 kWh per ADt pulp could be produced by the lime kiln. For a mill that produces 500 000 ADt pulp per year this means a yearly production of 16 100 000 kWh of power. If one kWh generates 0.50 SEK this means an additional income of around 8 million SEK per year.

9. Discussion

The purpose of this work was to create a model of the lime kiln that calculates mass- and energy balances over the kiln and operates safely in WinGEMS simulations. When starting this work, the assignment was relatively open and there were not many restrictions in what should and should not be included in the model. Consequently there was a lot of freedom for the constructor of the model to focus on the parts of interest. Because of the academic context in which this thesis is performed it was obvious from the beginning that a lot of the focus would be on the fuels and energy balances of the lime kiln. A person with a different academic background would most likely have emphasized other parts of the lime reburning process.

When constructing a model, one may either take a theoretical or an empirical approach. A theoretical model, often called a white-box model, will try to construct the model according to the laws of nature. In an empirical or black-box model on the other hand empiric data is used to adapt the model to the process that is to be simulated. When starting to work with the lime kiln model the intention was to use both these approaches so that the model would be based on both theory and data. As the work progressed however, it became obvious that the data needed for the empirical modeling was in most cases not available. The lime kiln model is therefore almost completely a white-box model.

Another effect of the lack of available data is that validating the model has been difficult. Focus has instead been on constructing a user-friendly model that operates robust. It should however be stated that the model is in need of a thorough validation.

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Appendix 1

The energy that needs to be supplied from the external fuel is equal to the total energy demand of the lime kiln minus the energy content of the internal fuels and the non condensable gases. An energy balance where the energy of the ingoing streams is equal to that of the outgoing streams will look like this:

$$IN = OUT \Rightarrow$$

$$\Rightarrow m_{fuel,ext} \cdot LHV_{fuel,ext} + m_{fuel,int} \cdot LHV_{fuel,int} + m_{NCG} \cdot LHV_{NCG} + E_{LM} (1 + \mu'_{losses}) =$$

$$(E_{calc} + E_{dry} + E_{RL} + E_{FG}) \cdot (1 + \mu'_{losses})$$

In chapter 5.3 the heat energy of the flue gases, E_{FG} , was separated into five different components:

$$E_{FG} = E_{CO_2 calc} + E_{H_2O evap} + m_{fuel,int} \cdot H_{CP int} + m_{NCG} \cdot H_{CP, NCG} + m_{fuel,ext} \cdot H_{CP ext}$$

where H_{CP} was defined as the heat energy in the combustion products per mass unit of fuel. Combining these two equations gives:

$$m_{fuel,ext} \cdot LHV_{fuel,ext} + m_{fuel,int} \cdot LHV_{fuel,int} + m_{NCG} \cdot LHV_{NCG} + E_{LM} (1 + \mu'_{losses}) =$$

$$= (E_{calc} + E_{dry} + E_{RL} + E_{CO_2 calc} + E_{H_2O evap} + m_{fuel,int} \cdot H_{CP int} + m_{NCG} \cdot H_{CP, NCG} + m_{fuel,ext} \cdot H_{CP ext}) \cdot (1 + \mu'_{losses})$$

It is then possible to isolate the variables that are a function of $m_{fuel,ext}$ on the left side of the equation:

$$m_{fuel,ext} \cdot LHV_{fuel,ext} - m_{fuel,ext} \cdot H_{CP ext} \cdot (1 + \mu'_{losses}) =$$

$$= (E_{calc} + E_{dry} + E_{RL} - E_{LM} + E_{CO_2 calc} + E_{H_2O evap} + m_{fuel,int} \cdot H_{CP int} + m_{NCG} \cdot H_{CP, NCG}) \cdot (1 + \mu'_{losses}) -$$

$$- m_{fuel,int} \cdot LHV_{fuel,int} - m_{NCG} \cdot LHV_{NCG} \Rightarrow$$

$$\Rightarrow m_{fuel,ext} \cdot (LHV_{fuel,ext} - H_{CP ext} \cdot (1 + \mu'_{losses})) =$$

$$= (E_{calc} + E_{dry} + E_{RL} - E_{LM} + E_{CO_2 calc} + E_{H_2O evap} + m_{fuel,int} \cdot H_{CP int} + m_{NCG} \cdot H_{CP, NCG}) \cdot (1 + \mu'_{losses}) -$$

$$- m_{fuel,int} \cdot (LHV_{fuel,int} - H_{CP int} \cdot (1 + \mu'_{losses})) - m_{NCG} \cdot (LHV_{NCG} - H_{CP, NCG} \cdot (1 + \mu'_{losses})) \Rightarrow$$

$$\Rightarrow m_{fuel,ext} = \frac{(E_{calc} + E_{dry} + E_{RL} - E_{LM} + E_{CO_2 calc} + E_{H_2O evap}) \cdot (1 + \mu'_{losses}) -$$

$$- m_{fuel,int} \cdot (LHV_{fuel,int} - H_{CP int} \cdot (1 + \mu'_{losses})) - m_{NCG} \cdot (LHV_{NCG} - H_{CP, NCG} \cdot (1 + \mu'_{losses}))}{LHV_{fuel,ext} - H_{CP ext} \cdot (1 + \mu'_{losses})}$$

Appendix 2

Imagine a hypothetical case with a simple 30 °C liquor stream that consists only of water, calcium carbonate, pulp, sodium and hydroxide with the mass flows according to the data below:

Water:	0.8 ton/hr
Calcium carbonate (suspended solid):	2 ton/hr
Pulp (suspended solid):	0.5 ton/hr
Sodium (dissolved solid):	0.1 ton/hr
Hydroxide (dissolved solid):	0.1 ton/hr

This stream would be described in the following way by the WinGems liquor stream type:

Liquor flow	1	ton/hr
Temperature	30	°C
Suspended solids	2.5	Ratio-frac
Calcium carbonate	0.8	frac of suspended solids
Pulp	0.2	frac of suspended solids
Sodium	100	kg/ton liquor
Hydroxide	100	kg/ton liquor

where the colors represent the different component divisions:

Yellow – Standard variables

Blue – Suspended solids

Red – Dissolved solids

Appendix 3

This is a compilation of all the user specified parameters available in the model as they appear to the user. For parameters containing a numbered list, the user has to pick one of the listed alternatives. In all other parameters, the user is free to insert any value as long as it is valid for the parameter unit. A fraction must for example be a value between zero and one.

Kiln parameters

<i>P1</i>	Part of CaCO_3 transformed to CaO (fraction).
<i>P2</i>	Excess air (fraction)
<i>P3</i>	Exit lime temperature ($^{\circ}\text{C}$)
<i>P4</i>	Exit gas temperature ($^{\circ}\text{C}$)
<i>P5</i>	Part of CaO that is overburnt (fraction)
<i>P6</i>	Part of the ingoing solids that leave the kiln as dust (fraction)
<i>P7</i>	Part of the ingoing sodium that ends up in the dust (fraction)
<i>P8</i>	Heat loss from the kiln shell (fraction of total energy)

Details on external fuel

<i>P9</i>	External fuel
	<ul style="list-style-type: none">i. Natural gas [C: 0.749, H: 0.251]ii. Fuel oil [C:0.876, H:0.120, S:0.004]iii. Tall oil [C:0.794, H:0.100, O:0.106]iv. Lignin [C:0.652, H:0.058, O:0.269, S:0.02, Ash:0.01]v. Methanol [C:0.375, H:0.126, O:0.499]vi. Wood powder [C:0.0.495, H:0.063, O:0.435, Ash:0.007]vii. Bark [C:0.512, H:0.060, O:0.398, Ash:0.030]
<i>P10</i>	Dry composition of external fuel
	<ul style="list-style-type: none">i. Use default compositionii. Specify composition in fuel streamiii. Specify sulfur content in fuel stream (weight fraction sulfur), default composition for rest.
<i>P11</i>	Moisture content of external fuel (weight fraction)
<i>P12</i>	Lower heating value of external fuel

- i. Specify lower heating value in fuel stream (MJ/kg)
- ii. Use approximated heating value

Details on first internal fuel

- P13* First internal fuel:
- i. Tall oil [C:0.794, H:0.100, O:0.106]
 - ii. Lignin [C:0.652, H:0.058, O:0.269, S:0.02, Ash:0.01]
 - iii. Methanol [C:0.375, H:0.126, O:0.499]
 - iv. Wood powder [C:0.0.495, H:0.063, O:0.435, Ash:0.007]
 - v. Bark [C:0.512, H:0.060, O:0.398, Ash:0.030]
 - vi. No internal fuel used (Skip parameters 13-21)
- P14* Dry composition of internal fuel
- i. Use default composition
 - ii. Specify composition in fuel stream
 - iii. Specify sulfur content in fuel stream (weight fraction sulfur), default composition for rest
- P15* Moisture content of first internal fuel
- P16* Mass flow of first internal fuel (ton/hr)
- P17* Lower heating value of first internal fuel:
- i. Specify lower heating value in fuel stream (MJ/kg)
 - ii. Use approximated heating value

Details on second internal fuel

- P18* Second internal fuel:
- i. Tall oil [C:0.794, H:0.100, O:0.106]
 - ii. Lignin [C:0.652, H:0.058, O:0.269, S:0.02, Ash:0.01]
 - iii. Methanol [C:0.375, H:0.126, O:0.499]
 - iv. Wood powder [C:0.0.495, H:0.063, O:0.435, Ash:0.007]
 - v. Bark [C:0.512, H:0.060, O:0.398, Ash:0.030]
 - vi. No second internal fuel used (Skip parameters 18-21)
- P19* Dry composition of second internal fuel
- i. Use default composition
 - ii. Specify composition in fuel stream

- iii. Specify sulfur content in fuel stream (weight fraction sulfur), default composition for rest
- P20* Moisture content of second internal fuel
- P21* Mass flow of second internal fuel (ton/hr)
- P22* Lower heating value of second internal fuel:
 - i. Specify lower heating value in fuel stream (MJ/kg)
 - ii. Use approximated heating value

Stream variable specification

- P23* Stream variable number for calcium oxide
- P24* Stream variable number for calcium carbonate
- P25* Stream variable number for calcium sulfate
- P26* Stream variable number for calcium hydroxide
- P27* Stream variable number for hydrosulfide
- P28* Stream variable number for hydroxide
- P29* Stream variable number for carbonate
- P30* Stream variable number for sulfate
- P31* Stream variable number for sodium

P23 to *P31* are available to ensure that the model will function even if the stream structure of the liquor stream is changed.

Appendix 4

The correlation between the composition of the fuel and the adiabatic flame temperatures calculated by the model is shown in the figures below:

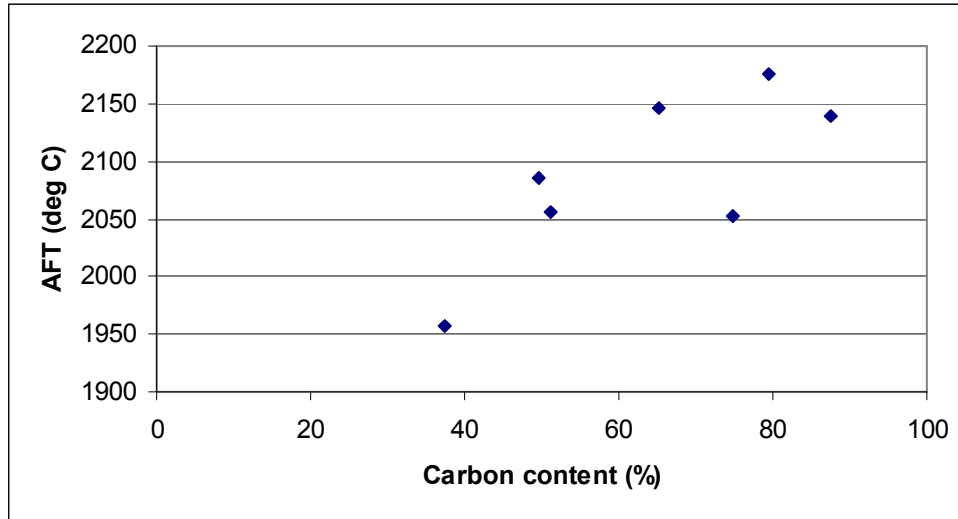


Figure 15. Correlation between adiabatic flame temperature and carbon content for a number of fuels.

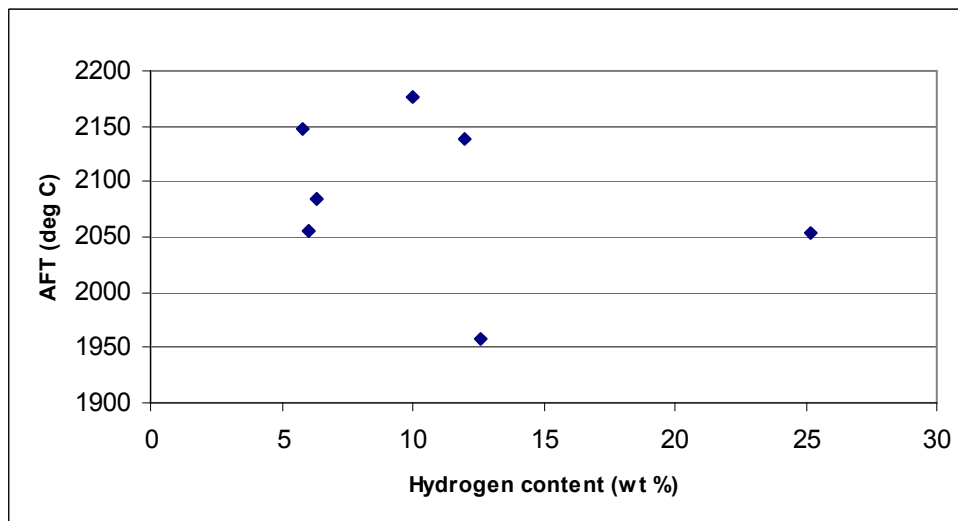


Figure 16. Correlation between adiabatic flame temperature and hydrogen content for a number of fuels.

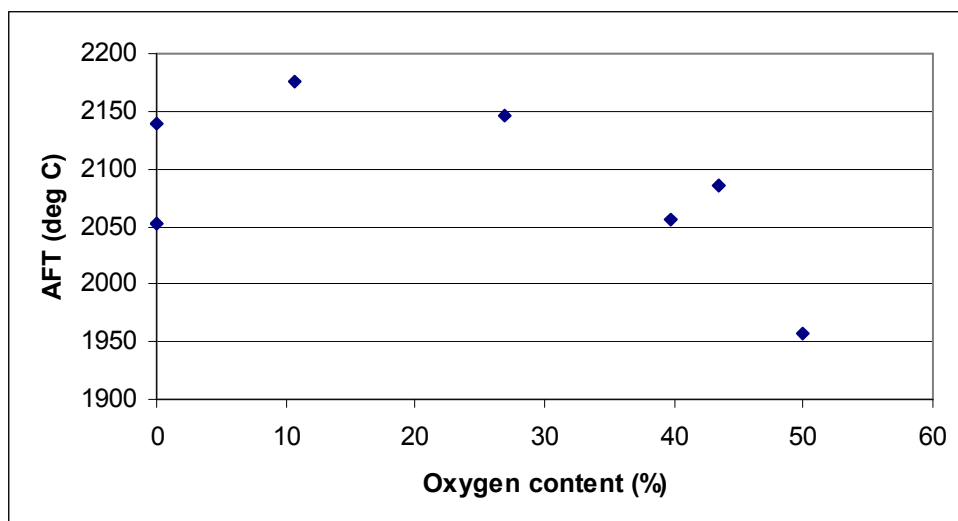


Figure 17. Correlation between adiabatic flame temperature and carbon content for a number of fuels.