

Modelling of non-process elements in a lime kiln burning renewable product gas

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1. Introduction

In this paper, a lime kiln firing renewable product gas is investigated with the help of VTT's KilnSimu program and chemical thermodynamic calculations. The aim of the work is to model the distribution and accumulation of non-process elements (from here on, NPEs) in the lime kiln.

Recausticizing is part of the recovery process in a kraft or sulfate pulp mill. In the recovery process, cooking chemicals NaOH and Na₂S are regenerated. The process involves a reaction turning CaCO₃ to CaO, which occurs in the lime kiln. The reaction is endothermic and requires a significant amount of energy. To provide this energy, a fuel must be burned in the kiln.

Lime kilns are often the last place in a pulp mill where fossil fuels are used, but recently, it has become more common to use fossil-free options in the lime kilns as well, making pulp mills completely fossil-free. Some alternatives to methane and fuel oil are wood powder, biomass-based oil and biomass-based gas [1].

One possible fuel for the lime kiln is bark, which is often a side-product, and is available in excess at the mills. However, combusting bark directly at the kiln is often not a viable option due to bark quality and therefore gasification is often used as a pre-process. In gasification, a CFB (circulating fluidized bed) boiler is used to gasify fuel in a reducing environment, creating a product gas that can be combusted later. Before bark can be fed to the gasifier, it must be dried to a humidity of less than 10% in a separate dryer. The operating temperature of the gasifier itself is typically 800-1000 °C, and it is often run at atmospheric pressure [2].

NPEs are elements not directly associated with the recovery reactions. In a pulp mill, most of the NPEs originate from the wood raw material, but a part of these elements may also originate from the product gas. Especially phosphorus, magnesium, and silicon are suspected to increase in burned lime if a bark-based product gas is fired in the lime kiln, although some of the ash in bark is removed from the gasifier through its bottom ash [2]. The NPEs are unwanted, because they may enrich in the recausticizing cycle and cause different problems, such as a decrease in causticizing efficiency and lime mud dry solids content.

2. Modelling methods

KilnSimu program [3] is used for the lime kiln simulations. In KilnSimu, the chemical reactions are calculated by combining Gibbs energy minimization method with reaction kinetics. The pure substance and solution databases [4] in FactSage 7.2 are used to describe the thermodynamic system of phases and constituents in the lime kiln. The included elements are:

- Main elements: C, Ca, H, O, N
- NPEs: Na, K, Mn, Mg, P, S, Al, Fe, Si, Zn, Cl

The phases consist of liquid and solid salt mixtures and several pure condensed phases, and altogether 369 phase constituents are included.

In KilnSimu, heat and mass transfer are assumed to occur in radial direction. An axial plug flow model is used for both the bed and gas flows. The unknown variables are the temperatures of the bed, gas, inner and outer wall, and the flow rates of the bed and gas species. The volume elements of the bed and gas are described as open thermochemical systems, which transform heat and mass with each other. The equilibrium states of the volume elements are calculated by minimizing their Gibbs energy and by taking into account the heat and mass transfer between the elements and their surroundings. The time-dependent reactions in the bed and the gas flow are considered in the Gibbs energy minimization by constraining the fractions of phases taking part in the equilibrium calculation (e.g. inert and reactive parts). The Gibbs energy minimisation is done by calling routines in the ChemApp library [5].

The unknown variables are determined at discrete reference points called calculation cells. Each cell represents a certain volume, and its temperature and composition are a measure of the average properties of that volume. The counter-current flow system in the kiln comprises a so-called two-point boundary value problem with a fixed boundary. It is solved iteratively until the composition and the temperature profiles of the bed and gas flows converge within a given tolerance.

A KilnSimu library has been made for the ExtendSim simulation program [6] so that it can be used as a GUI (graphical user interface) for designing process flowsheets and inputting the model parameters (see Figure 1).

3. Results

The data used in the presented modelling work is obtained from Metsä Fibre's Bioproduct mill in Äänekoski, Finland. Metsä Fibre is kindly acknowledged for providing data for this work.

Figure 1 shows the ExtendSim model of the Äänekoski lime kiln system and a comparison table between the measured and calculated values of some of the process parameters. Lime mud feed rate (2600 t/d wet) is set so that the lime production rate is close to the measured rate. Bark gas feed rate (10.5 Nm³/s wet) is set so that the bed maximum temperature in the kiln stays below 1200 °C and the residual CaCO₃ remains greater than zero (0.5%). In the cyclone, 91% of the solids are separated and recycled back to the lime kiln, and 99.75% of the remaining solids are separated in the ESP (electrostatic precipitator). In the dust splitter, 71% of these solids are recycled back to the lime kiln and the rest are purged to control the NPE enrichment in the recausticizing cycle.

Table 1 shows the elementary composition of the feed and the product streams. The main phases in the lime mud feed are CaCO₃ and H₂O. The other elements are given as suitable phases (carbonates, phosphates, sulphates and chlorides) in the feeds so that the elementary compositions of the feeds remain fixed.

Figure 2 shows the calculated temperature and CaCO₃/CaO profiles. The combustion of the bark gas is controlled by simple first order reaction kinetics.

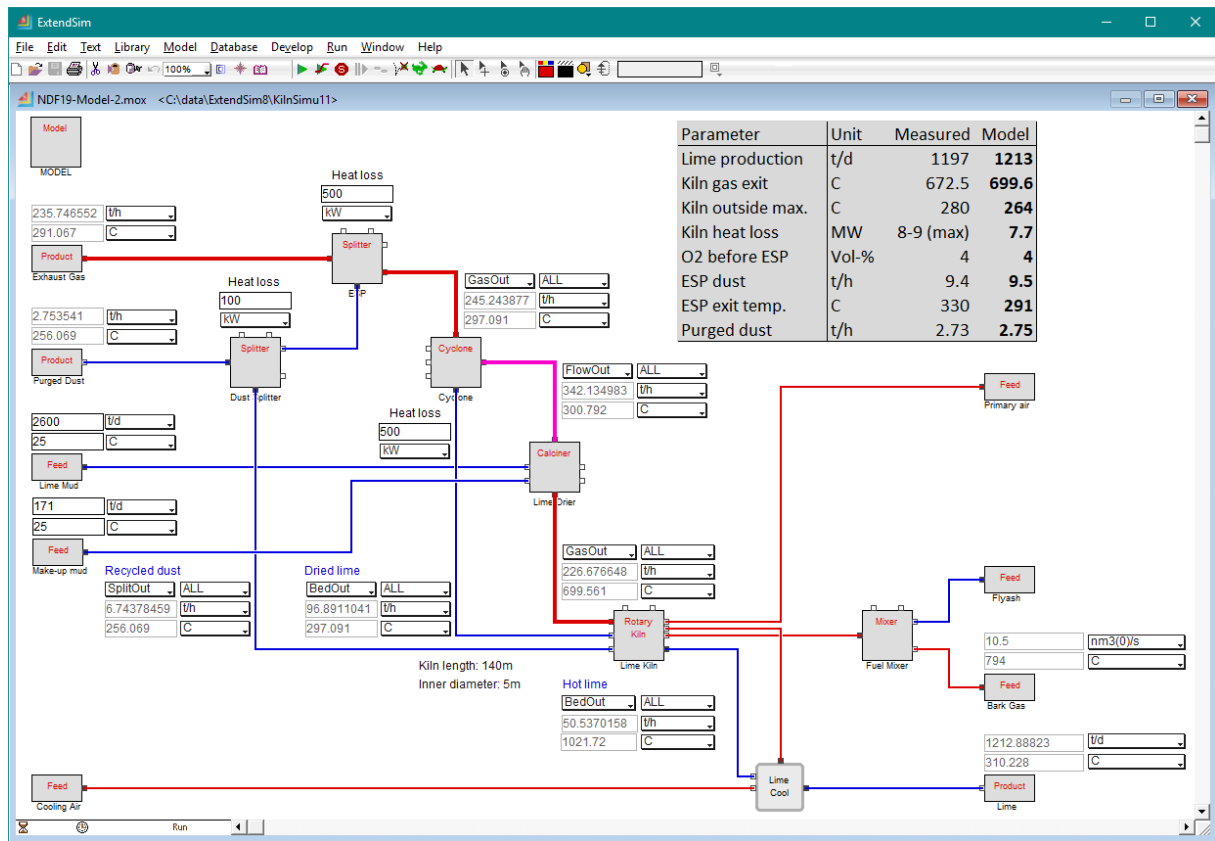


Figure 1. ExtendSim model of the Äänekoski lime kiln. The model contains lime flash drier (calciner), cyclone, ESP (splitter), dust splitter (splitter), lime kiln (rotary kiln) and lime cooler blocks.

Table 1. Modelled elementary compositions (mg/kg_{dry}) of product flows and the enrichment factors (EF) from lime mud to lime and ESP ash. Error columns show the relative difference between calculations and measurements.

NPE	Lime			ESP ash		
	mg/kg _{dry}	Error (%)	EF	mg/kg _{dry}	Error (%)	EF
Al	1020	3.7 %	1.12	646	-6.4 %	1.18
Ba	803	0.4 %	1.00	479	-4.2 %	0.99
Cl	87	15.4 %	2.02	74	-1.7 %	2.85
Fe	726	-9.2 %	1.10	419	-0.3 %	1.05
K	748	16.8 %	3.08	443	23.0 %	3.02
Mg	17000	1.4 %	1.00	10200	-6.8 %	0.99
Mn	1360	4.4 %	1.02	800	-4.7 %	1.00
Na	10200	-0.9 %	0.99	6780	-8.3 %	1.09
P	9200	3.3 %	0.98	6890	-6.8 %	1.22
S	1140	4.6 %	1.08	692	-28.7 %	1.08
Si	2690	-0.3 %	1.45	1430	1.8 %	1.28
Zn	474	7.8 %	1.01	279	-6.8 %	0.99

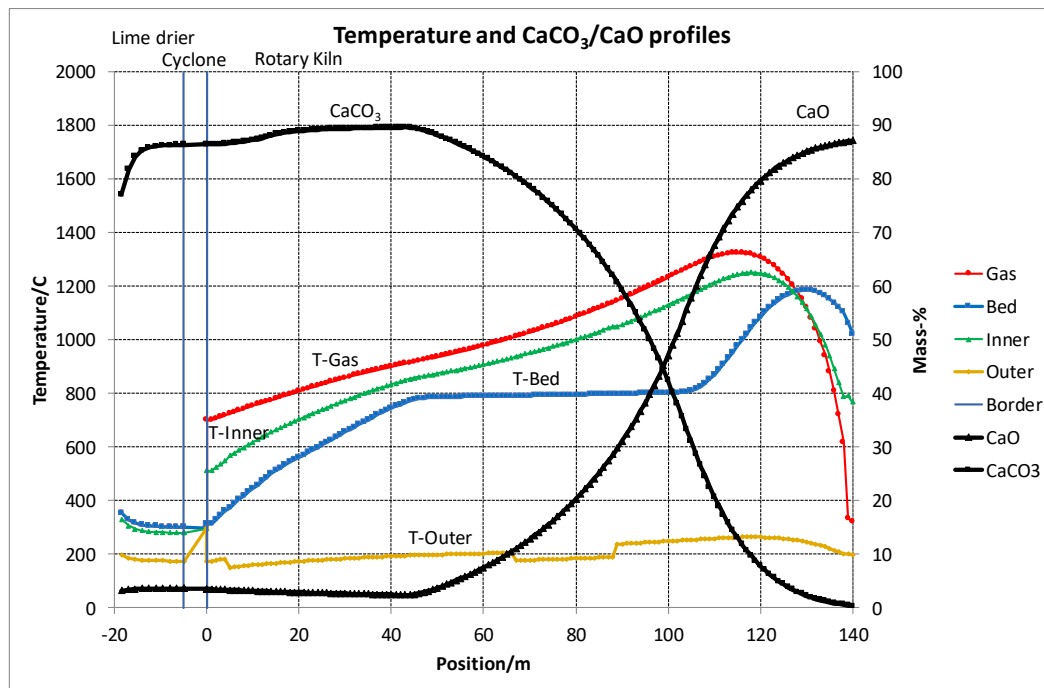


Figure 2. Calculated temperature and CaCO_3/CaO profiles in the lime drier, cyclone and lime kiln (the last 140 m represents the lime kiln).

4. Conclusions

The presented modelling method can be used to predict the effect of NPEs from the bark product gas to the lime kiln, and the enrichment of the NPEs to the product of the process, lime. For the easily volatilizing components like alkali chlorides, this requires optimizing their reaction rate parameters in the lime kiln. Based on the modelling and measurement results, the enrichment of the NPEs to lime is not a problem in the modelled example case, but the actual enrichment factors depend on the composition of the lime mud, make-up lime and the product gas in question.

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