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A simulation model of a sulphuric acid production process as an integrated part of an energy system

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Abstract

Power plant process simulation software is well-suited for the modelling of energy systems and more importantly, tools for analysing the energy efficiency are often built into the software. This work presents the development of a simulation model for a sulphuric acid plant using a commercial software package for power plant process simulation. This will be of value to for instance small consultant and engineering companies involved with audits and analysis of energy systems. For small sized companies the cost of acquiring and maintaining many different specialised software packages will be noticeable. However, companies involved with audits and analysis of energy systems will in most cases have access to at least one software package for power plant process calculations. The use of this kind of software for also modelling chemical plants would be valuable to these companies. The results of this work shows that it is possible to use an inexpensive but powerful power plant process simulation software for modelling a common chemical process as a part of a large energy system.

Keywords: Process plant model; Energy; Optimisation

1. Introduction

This paper presents the development of a simulation model for a sulphuric acid plant using a commercial software package for power plant process simulation.

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The focus is primarily on the energy system and many parts of the chemical process will thus be simplified.

Energy audits and analyses have in recent years become an important part of national climate strategies for reducing the impacts the process industry has on the environment [1]. The energy audits and analyses often include the evaluation of different modification to the process or processes. The modifications can be parametrical or structural. In most cases the processes being studied are a part of a larger and more complex system, and in order to accommodate this complexity it is common to disregard this fact and just analyse each process separately. In the worst case this can lead to recommendations for modifications that actually reduce the overall energy efficiency of the system even though the energy efficiency of the sub-process will be improved. This leads to a need for methods that can analyse the processes as an integrated part of a larger system. One way of doing this is to build a simulation model of the whole system. The simulation model can also be used as a source of data for building optimisation models, which is a common method for evaluating modifications. The data taken from the simulation model would then be in energy and mass balance which is seldom available from the actual processes. A brief description of the use of the simulation model presented in this work is given in Section 4.2. The choice of the software that suits the calculation needs is an important part of the analysis. Power plant process simulation software is well-suited for the modelling of energy systems and more importantly, tools for analysing the energy efficiency are often built into the software. Another important factor for choosing the software is the annual cost. Especially for small consultant and process engineering companies the cost of keeping many specialised simulation software packages will be relatively high. For these reasons it is interesting to know if it is possible to use power plant process simulation software for modelling a common chemical process as a part of a large energy system. There is a great number of software packages that could be used for this kind of simulation. The perhaps most known are *Aspen Plus* [11] by Aspen Technologies, Inc. and *Thermoflex* [7] by Thermoflow, Inc. In the article by Giglmayr et al. [6] a comparison between 18 different software packages capable of simulating a power plant was made. The software packages that was chosen for this work *Prosim* from Endat Oy, performed very well in the test and had a low annual cost in the comparison to the other tested software.

The sulphuric acid process modelled in this work is a part of a larger system. The larger system is the *Kemira Oyj*'s Siilinjärvi Plants situated in mid-Finland close to the town of Kuopio. The development of the simulation model followed a procedure consisting of the following steps *system identification*, *data extraction*, *data verification*, *simulation model building* and *simulation model verification*.

This paper is organised as follows: in Section 2 the modelled system is presented together with the most important sources for the data extraction. In Section 3 the sulphuric acid process is presented in more detail. The final simulation model of the system is presented in Section 4. This section also contains description on how the chemical process units were modelled using power plant modules. The conclusions of this work are summarised in Section 5.

2. The energy system

The Siilinjärvi plants consists of the following units: *three roasters* (for oxidation of pyrite), *two sulphuric acid plants*, *a phosphoric acid plant*, *a nitric acid plant*, *a power plant*, *a fertiliser plant* and *a gypsum pigment plant*. The two last units are not major contributers to the energy system and are therefore not included in the model. In addition there are offices, a workshop, a laboratory and a water effluent treatment plant that are not included in the model either as their impact on the energy flows is small enough to be ignored. Fig. 1 shows the main energy flows between the different units. The units that are modelled in greatest detail are *roaster III* and *sulphuric acid plant II*. The other plants and units are modelled so that their impact on the energy system is sufficiently taken into account; e.g. since the efficiency of the steam turbines is a function of the volume flow of steam through the turbine it is important that the steam production of the whole system is included. Another example is the district heating system which must be included so that the condensing water to the feedwater tank has the correct temperature and mass flow.

After the identification of the system the next step is the data extraction. This is the most time consuming part of building a representative simulation model of a plant. The approach for verification of the data used here is that the ambiguous data are identified by using basic calculations of the mass and energy balances. In meetings with the plants' personnel the sources of the ambiguities are identified. At the same time also so-called trusted data are identified, i.e. data that is believed to be correct. This might be measurements for which it is known that the measurement instruments are good. The ambiguities are then replaced by new values calculated from the trusted data.

In the case of Kemira Siilinjärvi Plants the most important sources for the data extraction are:

- data from the flowsheets from the planning/design of the plant,
- data from the control and monitoring system of the plant,
- data given by the operating personnel and engineers at the plant,
- basic calculations of mass and energy balances.

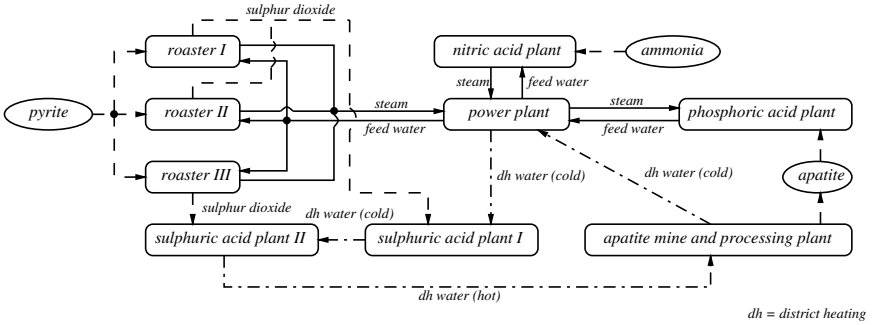

Fig. 1. The system's main energy flows except electricity.

The advantage of the data taken from the flowsheets is that the data already are in mass and energy balance, but since changes were made to the process the data does not necessary correspond with the actual data from the plant today. The second most important source is the data from the control and monitoring system, i.e. measurements from the actual plant. In addition to the general uncertainties connected with measurements a disadvantage is that it is almost impossible to get all the measurements taken at the same time. The measured data are thus from different operating situations, which can cause ambiguities. The necessary data that is not found from the flowsheets of the control and monitoring system is either collected from the operating personnel or calculated based on simple mass and energy balances.

3. The sulphuric acid process

The process of making sulphuric acid is a mature process. A good overview of the process can be found in [2]. The process is highly exothermic, and therefore the heat recovery is a substantial part of the process. A good introduction to heat recovery in sulphuric acid plants can be found in [8]. A more up to date presentation is given in [5].

The process can be divided into three main reactions, namely:

- combustion of sulphur: $S + O_2 \rightarrow SO_2$
- catalytic oxidation: $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$
- sulphur trioxide absorption: $SO_3 + H_2O \rightarrow H_2SO_4$

The total reaction can be written as $S + \frac{3}{2}O_2 + H_2O \rightarrow H_2SO_4$. The source of sulphur for the plant is pyrite. Pure pyrite, or iron disulfide (FeS_2), contains 46.67% iron and 53.33% sulphur. The overall reaction for oxidisation of pyrite is:

$$FeS_2(s) + \tfrac{11}{4}O_2(g) \rightarrow \tfrac{1}{2}Fe_2O_3(s) + 2SO_2(g) \quad (1)$$

However, the pyrite used in the process also contains iron sulfide (FeS) and impurities such as silicon dioxide (SiO_2). The pyrite that is used at the plant contains about 51% sulphur, 42% iron, 7% water and some other elements (e.g. silicon dioxide, zinc and arsenic). The overall reaction for oxidisation of iron sulfide is:

$$FeS(s) + \tfrac{7}{4}O_2(g) \rightarrow \tfrac{1}{2}Fe_2O_3(s) + SO_2(g) \quad (2)$$

The oxidation of SO_2 to SO_3 is slow without the use of a catalyst. In the process vanadium oxide, V_2O_5, mixed with alkali sulfate is used as a catalyst. The reactor has four stages and the gas is cooled after each intermediate stage. This heat is recovered and used to heat other process streams.

4. The simulation model

The simulation software used in this work is *Prosim* from Endat Oy. Prosim is a module based steady state simulation system for thermal power plant processes [3,4].

To find the thermodynamic properties for the substances Prosim uses a mixture of functions and tables. The basic process in Prosim consists of modules connected through streams. In this case the streams are fuel, air, flue gas, water and steam. Most of the typical modules for power plants are included in the software package. For example the burner module is used to model the oxidation of pyrite. The module calculates the adiabatic flame temperature based on the chemical reactions of the fuel. The burning power can be adjusted by either specifying a known burning power, the fuel flow or the flow of the flue gases. In addition various parameters for the module can be set, e.g. stoichiometric air ratio, oxygen content in the flue gas and unburned coal in ash. The calculations of the steam and superheated steam are done in two similar modules, namely the boiler (evaporator) and the superheater. The parameters that determines the mass flow of the steam produced is the pressure of the saturated water and the massflow and inlet and outlet temperatures of the flue gases. The superheater module does not calculate the mass flow, so the outlet temperature of the steam is determined by either a given exit temperature of the flue gas or by the pinch point. The steam turbine efficiency, η is calculated by Prosim using the following formulas:

$$\eta = 0.023521 \cdot \ln(v) + 0.749538 \tag{3}$$

The average volume flow, v, is calculated as follows

$$v = \frac{m \cdot \mathrm{d}h_s}{P_{in} - P_{out}} \tag{4}$$

where m is the mass flow of the steam, $\mathrm{d}h_s$ is the isentropic enthalpy change and P is pressure. The formulas are based on late 1990 turbine design specifications.

Figs. 2 and 3 show the flowsheet for the simulation model. The process parts that are included in the model in addition to the power plant are the roasters, the second sulphuric acid plant, the nitric acid plant, the phosphoric acid plant and the district heating network.

The roaster process can be divided into three tasks: *pyrite conversion*, *steam production* and *flue gas cleaning*. The combustion of pyrite takes place in a fluidised bed reactor. The combustion of pyrite (FeS_2 and FeS) is not included in the simulation software. The combustion is therefore modelled in a burner module as combustion of pure sulphur (S). In the simulation model a modified heating value of sulphur was used so that it corresponded to that of pyrite. The iron oxide (Fe_2O_3) enters the process together with silicon dioxide (SiO_2) as ash. The cooling of the fluidised bed reactor is modelled by a boiler module, where the exit temperature of the flue gas is set to match the temperature of the real process. This is the parameter that controls the amount of steam generated in the boiler module. The rest of the steam generation takes place in the boiler where the flue gas is cooled down and some of the ash is removed. This is modelled as a boiler module combined with a superheater module. Finally the ash is removed in an ash separator module. The steam that enters the superheater module comes from a steam drum module. In the steam drum the feedwater that in this case is not at the saturation temperature is heated to the saturation temperature with saturated steam. The remaining steam is sent to the

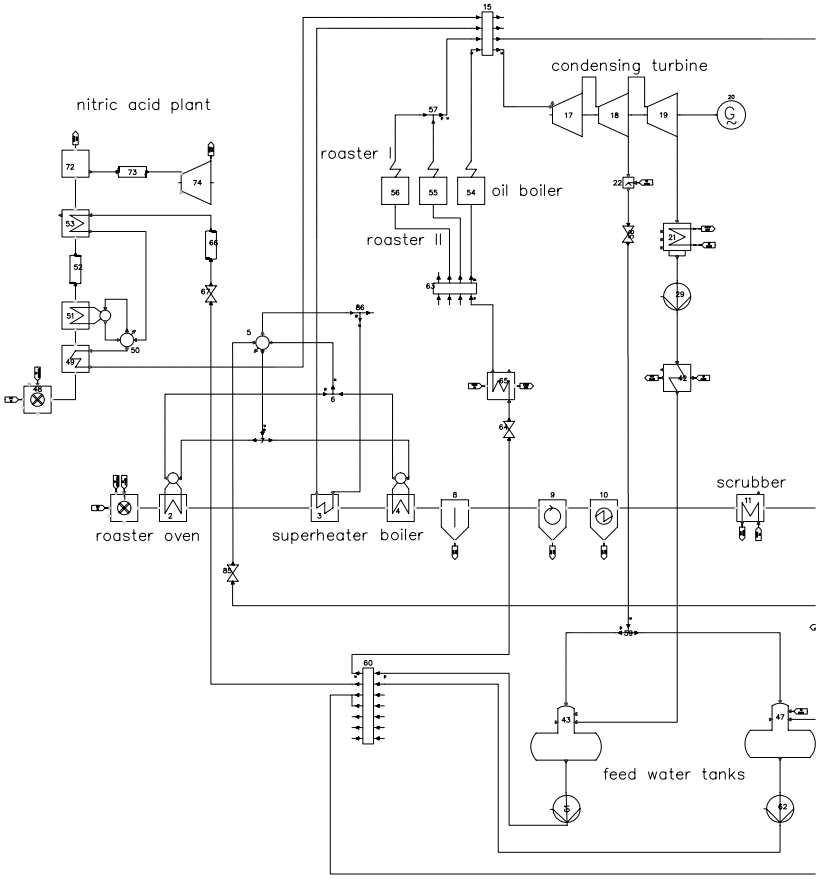

Fig. 2. First part of the Prosim simulation model of the energy system (continuous from the right in Fig. 3).

superheater, from which the steam is sent to the power plant. The flue gas is then sent to a cyclone module followed by an electrostatic precipitator module.

The sulphuric acid plant is primarily modelled as a system of heat exchangers. The flue gas from the roaster process is cooled further down in the flue gas cleaning units before the blower module. Additional air is added and the water is also separated from the gas stream. After the blower the gas is heated before it enters the first reactor stage. The reactor stages are modelled as pipes with negative heat loss. As the fourth reactor stage and the absorbers do not add valuable information regarding the energy of the system, they are not included in the simulation model.

In the nitric acid plant ammonia and air is burned in the burner and the flue gas continues to the superheater and boiler. The chemical reactions are shown in Eqs. (5)–(7)

$$NH_3 + \tfrac{5}{4}O_2 \rightarrow \tfrac{6}{5}H_2O + NO \tag{5}$$

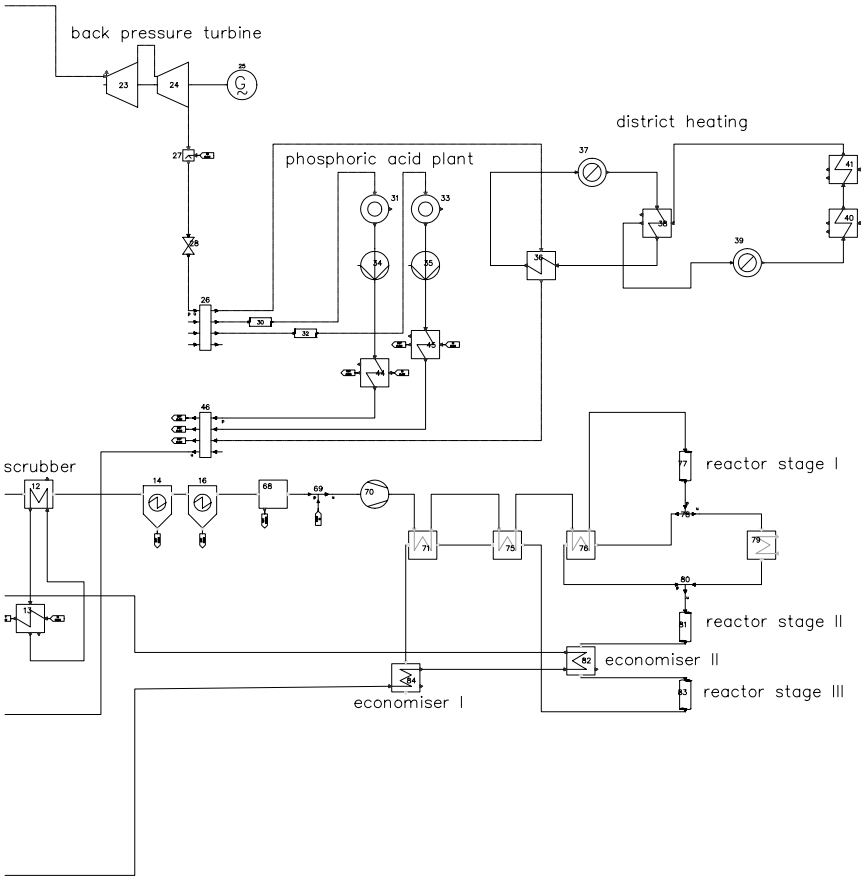

Fig. 3. Second part of the Prosim simulation model of the energy system (continued from the left from Fig. 2).

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \tag{6}$$

$$NO_2 + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2 \rightarrow HNO_3 \tag{7}$$

As the simulation software does not contain physical properties for nitric oxides the two reactions shown in Eqs. (5) and (6) are modelled as the chemical reaction shown in Eq. (8)

$$NH_3 + \tfrac{3}{4}O2 \rightarrow \tfrac{3}{2}H_2O + \tfrac{1}{2}N_2 \tag{8}$$

In addition the heat value for NH_3 used in the simulation model is modified to match that of the real process. This is done in order to get a better approximation of the flue gas temperature and energy content. After the boiler the flue gas is cooled down. This is modelled as a pipe module with heat loss. In the economiser the flue gas is cooled further.

The conversion of nitric dioxide to nitric acid shown in Eq. (7) is not modelled in the simulation model, instead the nitrogen from the combustion air is separated and heated to the right temperature in a pipe. The nitrogen then continues to the expander. The heat loss from the feed water tank is modelled as a pipe with constant heat loss. The feed water goes through the economiser to the steam dome. In this case the feedwater leaving the economiser is not yet saturated, so it is heated to the saturation temperature by a fraction of the steam from the boiler. The remaining steam continues to the superheater and to the powerplant's turbines.

The main components for the power plant simulation model are the two turbines, the two generators and the condenser. The phosphoric acid plants are the major consumers of low pressure steam, and since the focus of the simulation model is on the steam generators the phosphoric acid plants are not modelled in detail. The plants are simply modelled as pipes with pressure loss, steam consumers and water pumps. The district heating system is a major consumer of heat. District heating is mainly used in the mine and to heat facilities at the plant.

4.1. Simulation model verification

Verification of the simulation model can be done by comparing snapshots from the monitoring system at the plant with the similar values obtained from the simulation model. For practicable reasons it is next to impossible to get snapshots of the whole process from the plants to compare with the simulation model. This makes it considerably more difficult to verify how well the simulation model perform. However, it is possible to get quite a good picture of how sensitive the simulation model is to changes in the parameters. In Table 1 the way a ±5% change in some selected parameters affect the amount of generated electricity is presented. From the table it can be seen that changes in the pyrite mass flow has the biggest effect on the amount of generated electricity. In contrast, a change in the inlet make up water temperature does not seem to have any major effect. If possible, more effort should then be put into getting the values for the pyrite mass flow right than the values for the make up water temperature. In fact, during the verification of the simulation model it was found that the scale that was used to monitor the mass flow of pyrite at the plant was faulty and needed to be calibrated.

Table 1
The effect of a ±5% change in selected parameters on the amount of electricity generated

Parameter	Base case	Unit	Change in generated electricity
Pyrite mass flow	6.1	kg/s	±2.4%
Additional air to reactor	7.7	kg/s	±0.2%
Steam drum blowdown	0.8	kg/s	±0.2%
Gas outlet temperature (boiler)	340.0	°C	±0.8%
Gas outlet temperature (economiser II)	160.0	°C	±0.5%
Make up water inlet temperature (tank)	20.0	°C	±0.0%

One way to get an indication of how the simulation model performs is to choose a few important values and compare these. For this case the most important parameters are related to the steam production. The values that were chosen were the amount of superheated steam from the roaster and mass flows and temperatures in the economisers in the sulphuric acid plant. Time series of these values would be necessary in order to be able to perform a valid statistical analysis, e.g. statistical and systematic error, but these time series are unfortunately not available. This means that the comparison between the data and the simulation model presented below will at the most be indicative.

The production of steam in the roaster oven and in the boiler is in the simulation model determined by the exit temperature of the hot gases. Some of this steam is used to heat the water coming to the drum to the saturation temperature. The remaining steam is sent to the superheater. The heat load in the superheater is determined by the exit temperature of the steam. The amount of superheated steam produced in the roaster process calculated by the simulation model is 9.7 kg/s, which is approximately 11% more than the value obtained from measurements at the plant. The other steam producing processes are tuned to produce steam corresponding to measured values at the plant, so the difference between the total amount of superheated steam to the power plant is small. This can for instance be seen as the difference between the measured electricity generated and the simulated is only about 1%. Table 2 shows a comparison between the simulated and measured values of mass flows and temperatures for the two economisers at the sulphuric acid plant. The heat load for the economisers are in the simulation model determined by the exit temperatures of the gas flows, i.e. the inlet temperatures are calculated in the previous modules and the exit temperatures of the feed water are calculated in the economisers. Again it should be stressed that due to the lack of good statistical analysis the comparison is only at best indicative, but it seems that the values taken from the calculations made with the simulation model corresponds well with the values measured at the actual plant. This is strengthen by letting engineers and operating personnel at the plant look at and comment the results from the simulation model.

Table 2
Comparison between simulated process values and values measured at the plant for two economisers at the sulphuric acid plant (see Fig. 3)

		Economiser I		Economiser II	
		Measured	Simulated	Measured	Simulated
Feed water	Mass flow	10.0	9.6	10.0	9.6
	Temperature in	125	128	163	164
	Temperature out	163	164	214	208
Gas flow	Mass flow	30.9	26.8	30.9	26.8
	Temperature in	213	215	496	496
	Temperature out	160	160	430	430

Mass flows are in kg/s and temperatures in °C.

4.2. Application of the simulation model

One of the major uses for the simulation model was to simulate changes to the process. The simulation model was for example used to demonstrate a new methodology for improving large scale thermal energy systems [9]. The methodology combines simulation, experimental design and mathematical programming to achieve cost-effective modifications. The simulation model was used to model changes to the system and then to generate data for the regression models [10]. The changes to the system that were investigated where the addition of four different heat exchangers, for preheating combustion air and feed water entering the feed water tanks. The different heat exchangers were added to the simulation model and different start and ending temperatures were given. The relevant results from the simulation runs are presented in Table 3. The simulation runs were made according to a 2^4 factorial design. For the preheating of the combustion air temperature, the temperature can be directly varied from 4 to 80 °C. This temperature is labelled x_1. For the preheater after the condensing turbine the mass flow of district heating water to the new heat exchanger can be varied from 0.0 to 2.0 kg/s. At the maximum mass flow the minimal temperature difference is achieved. The mass flow of district heating water to the heat exchanger is labelled x_2. The independent variables for the new heat exchangers at the phosphoric acid plant will be the exit temperatures of the hot water to the heat exchangers. These will be labelled x_3 and x_4. The temperatures can vary from 150 to 125 °C, where an exit temperature of 150 °C corresponds to the non-

Table 3
Selected results of the simulation runs, where x_1 is the combustion air temperature, x_2 is the mass flow of district heating to feed water heater, x_3 and x_4 are the exit temperatures of district heating from feed water heater (phos I) and district heating from feed water heater (phos II) respectively

x_1 (°C)	x_2 (kg/s)	x_3 (°C)	x_4 (°C)	y_1 (kg/s)	y_2 (kg/s)	y_3 (kg/s)	y_4 (MW)	y_5 (MW)	y_6 (MW)
4.0	0.0	125.0	125.0	3.4077	22.5991	26.01	3.0890	14.1968	17.29
4.0	2.0	125.0	125.0	3.4077	22.5991	26.01	3.1644	14.1968	17.36
4.0	0.0	150.0	125.0	3.4009	22.6059	26.01	2.7231	14.2011	16.92
4.0	2.0	150.0	125.0	3.4009	22.6059	26.01	2.7979	14.2011	17.00
4.0	0.0	125.0	150.0	3.4042	22.6026	26.01	2.9057	14.1990	17.10
4.0	2.0	125.0	150.0	3.4042	22.6026	26.01	2.9807	14.1990	17.18
4.0	0.0	150.0	150.0	3.3977	22.6092	26.01	2.5415	14.2031	16.74
4.0	2.0	150.0	150.0	3.3977	22.6092	26.01	2.6009	14.2031	16.80
80.0	0.0	125.0	125.0	3.7751	22.5991	26.37	3.4611	14.1968	17.66
80.0	2.0	125.0	125.0	3.7751	22.5991	26.37	3.5367	14.1968	17.73
80.0	0.0	150.0	125.0	3.7683	22.6059	26.37	3.0939	14.2011	17.30
80.0	2.0	150.0	125.0	3.7683	22.6059	26.37	3.1688	14.2011	17.37
80.0	0.0	125.0	150.0	3.7716	22.6016	26.37	3.2770	14.1990	17.48
80.0	2.0	125.0	150.0	3.7716	22.6026	26.37	3.3524	14.1990	17.55
80.0	0.0	150.0	150.0	3.7650	22.6092	26.37	2.9114	14.2031	17.11
80.0	2.0	150.0	150.0	3.7650	22.6092	26.37	2.9862	14.2031	17.19

The variables y_1 and y_2 are superheated steam going to the condensing turbine and back pressure turbine respectively. The total amount of superheated steam produced is y_3. The shaft power from the condensing turbine and back pressure turbine are y_4 and y_5 respectively. The sum of the shaft powers is y_6.

existence of the heat exchanger. The most interesting effects of the changes to the process will be the production of high pressure steam and the turbine shaft work. The high pressure steam going to the condensing turbine and to the back pressure turbine will be labelled y_1 and y_2 respectively. The sum of these will be the total amount of high pressure steam produced and will be labelled y_3. The total turbine shaft work is labelled y_6 and is the sum of the shaft work for the condensing turbine, y_4, and for the back pressure turbine, y_5. The results of the investigation was that a 4% increase in the turbine shaft power could be achieved by adding three heat exchangers to preheat feed water. The suggested changes have not as yet been made to the actual process.

5. Conclusions

The simulation model shows that it is possible to model a sulphuric acid process with a power plant simulation software and that it is possible to include the process in a larger energy system. In effect simulation software for power plant simulation can be used as a part of energy auditing or energy analysis of some chemical processes. The comparison between the given values for the real processes and the ones calculated by the simulation model indicates that the model is well suited for calculating parametric changes that has an effect on the steam and electricity production of the plants, for example the calculation of the effect of preheating the combustion air to one of the roasters. Other possible studies can include the changes to the pressure and temperature levels, changes to the low pressure steam consumption, either by adding new units that require steam or reducing the steam consumption in existing units, and changes to the district heating system. The simulation model may also be a good basis for changes involving structural changes to the processes. This depends on how fundamental the structural changes are to the process.

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