

A combined physical and statistical simulation model for Black Liquor Gasification

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Abstract: In this paper the development of a design model for Black liquor gasification is described, where factorial design is used for pilot plant experiments. The results from the experiments are then used to build multi-variate statistical models using PLS. These models are used to give the correlations between important variables and are later used in the physical simulation model to determine gas composition of the product gas, when operations under different conditions are made. The physical model adds the known physical relations as probable water content of the product gas from the shift reaction, selective absorption in a wet scrubber, heating value of the gas etc. From the simulation model we can then determine what the gas composition and the solids composition will be at different operating temperatures, production capacities, relative oxidation, composition of the black liquor and some other factors.

Back ground: During the 90th ABB developed a Black liquor gasification process. The process has as a goal to replace existing Tomlinson boiler in pulp and paper industry with a new process, where up to three times more electric power can be produced from the black liquor, a split of sulfides from the bed solids (primarily sodium carbonate) and elimination of the risk for a steam explosion if there is a break in a water tube in the reactor, something happening roughly twice a year somewhere in the world today, with enormous consequences for human lives and economy. The black liquor consists of roughly 1/3 organics (lignin, hemi-cellulose etc), 1/3 water and 1/3 in-organics like sodium/potassium carbonate, sulfate and chloride. In the process sulfates are reduced to sulfides for reuse in the digestion of wood chips into pulp in the Kraft process.

The specifics of the process are that the gasifier is a circulating fluidized bed gasifier. Black liquor is introduced into a fluidized bed with bed particles made of e.g. CaCO₃. When air is added, heat is generated and the gasification of the organics of the black liquor starts. Still we only add approximately 35 % of the air needed to combust the organics of the black liquor totally. This is called 35% relative oxidation. Hydrogen, carbon monoxide and methane are the products we want to get in the gasifier, as these can be combusted in a gas turbine, generating huge amounts of electric power. The heat in the product gas after the gas turbine is used to heat steam for a steam turbine, increasing the power generation even further. This is called a combined cycle.

We also get a reaction reducing sulfates in the black liquor solids to sulfides, and due to equilibrium constraints also a major part of the sulfides are evaporated as hydrogen sulfide. The hydrogen sulfide is absorbed in a gas scrubber using sodium carbonate and sodium hydroxide. To avoid simultaneous absorption of carbon dioxide, we have developed a selective absorption process, where approximately 20 times more hydrogen

sulfide is absorbed compared to the carbon dioxide, with respect to the incoming gas content. That means that twice as much sulfide is absorbed, although the carbon dioxide content is ten times higher in the product gas. The remaining hydrogen sulfide is converted into sulfur dioxide during the combustion in the gas turbine, so no hazardous gas is emitted.

In the further development of this process we also added Titanium dioxide to achieve direct caustization of sodium carbonate into sodium hydroxide, a process that is today taking place in a separate step in a lime kiln. By integrating this process into the gasification process we get a smaller apparatus, possibility to gasify at a higher temperature without risk for bed agglomeration and also lower total energy consumption. This add-on is not covered in this article, though.

Process description: The process consists of a circulating fluidized bed. In the pilot plant we had two cyclones in series for removal of solids in the gas for recirculation directly into the bed. After these the gas was cooled by a couple of heat exchangers, a bag house removed most of the remaining particles and there after the gas was scrubbed in a two step counter current scrubber. Finally the gas was combusted.

The air was heated to approximately 400 °C before entering the gasifier, and the black liquor was heated to approximately 120 °C, to make it fluent. (Black liquor at room temperature is a solid!). Different fillings were tested in the scrubber, to achieve the goal of selective absorption for sulfide.

The gas composition was measured on-line with respect to CO₂, CO, H₂ and CH₄, while H₂S was measured by extracting gas through a “Draeger tube”. Nitrogen and oxygen were given from measurements of air feed and knowledge about “organic” oxygen content of the black liquor from chemical analysis of this. Water content was calculated from condensate flow and temperature of extracted gas. Temperature was measured at a number of positions in the reactor.

The plant could be operated up to a pressure of 5 bar absolute

Experiments in pilot plant: When we started the project the goal was to identify operational parameters such as what was possible max operating temperature, max and min fluidization velocity, max capacity (ton per m² reactor area and h), minimum relative oxidation or maximum heating value of the product gas, relation between equilibrium calculations and real plant data, where also kinetics was considered, maximum water content possible to use in the black liquor, minimum residual carbon possible to achieve in the bed ash, reduction of sulfate to sulfide and how much of the sulfide was evaporated as hydrogen sulfide, how much of this hydrogen sulfide could be absorbed, and how much carbon dioxide was absorbed “by accident” at the same time. So there were many unknowns to determine. Also operations at atmospheric conditions in relation to pressurized conditions should be found.

So we started with identifying a factorial design for the experiments to perform. First some over view experiments were done, to identify what variable were the most important. These turned out to be the black liquor load (ton per m² bed area and hour, t/m²,h), the relative oxidation and the temperature. The full factorial design was focused on these variables, while other variables were done at some few points of the total operational area. In figure 1 the pilot plant set up is seen.

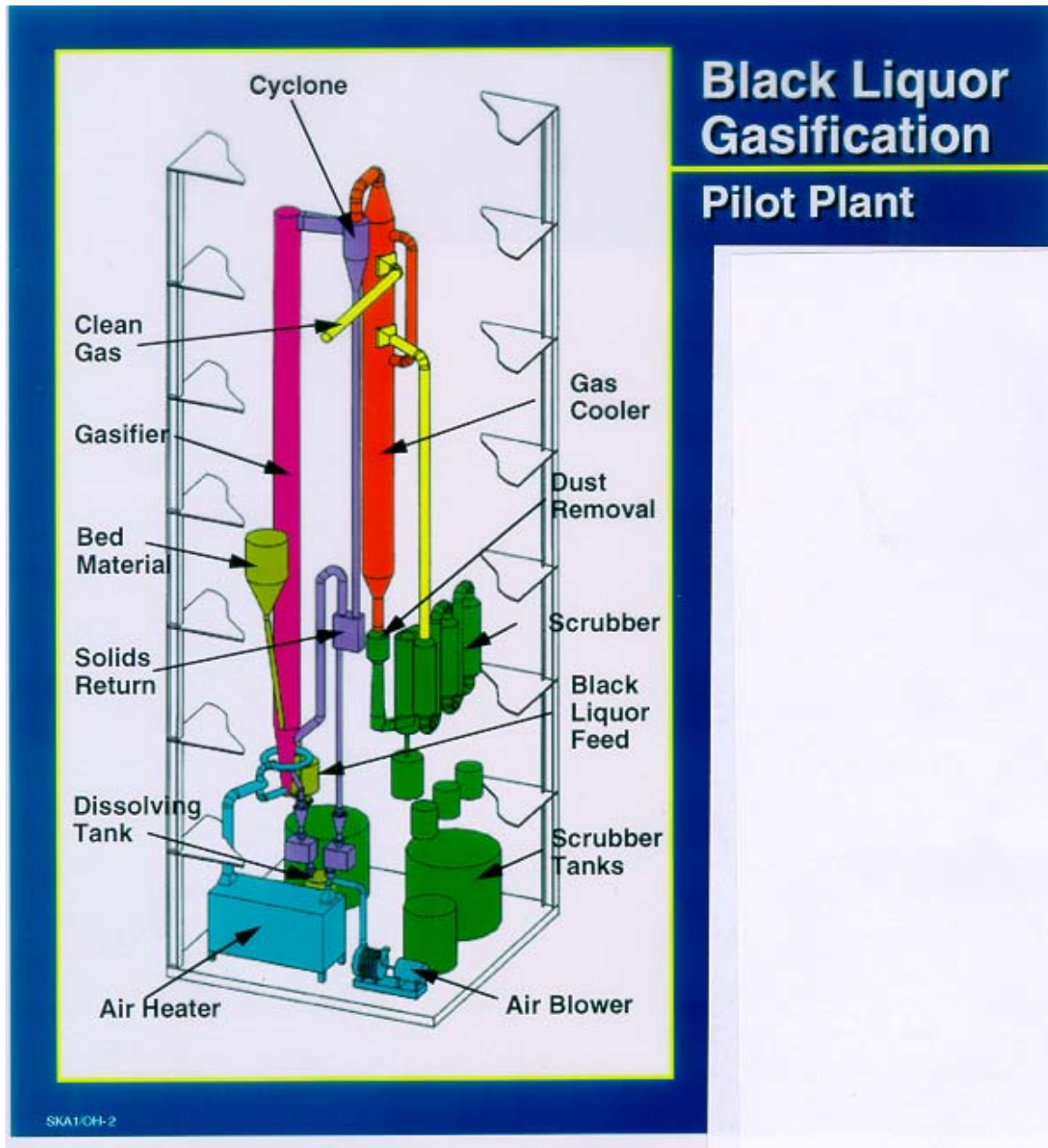
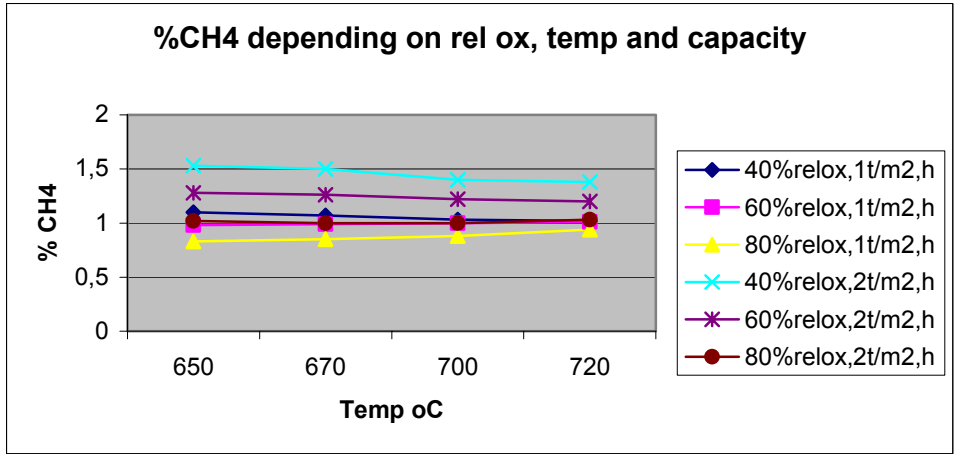
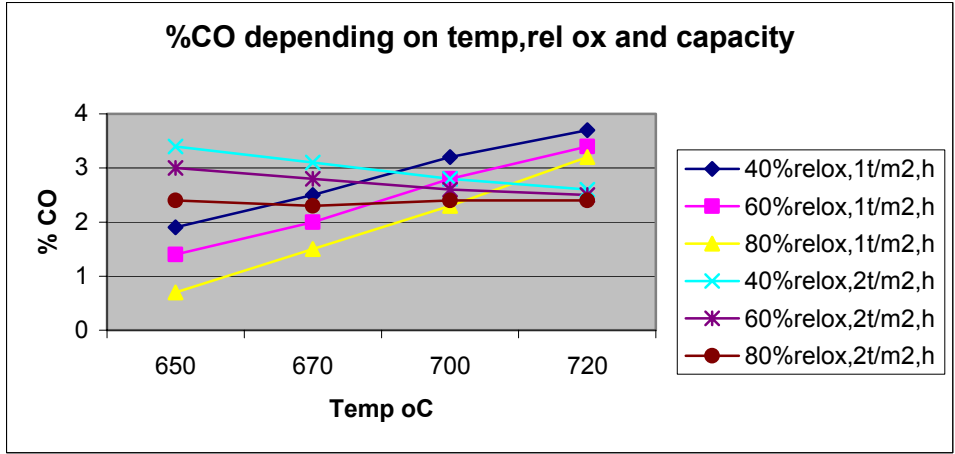
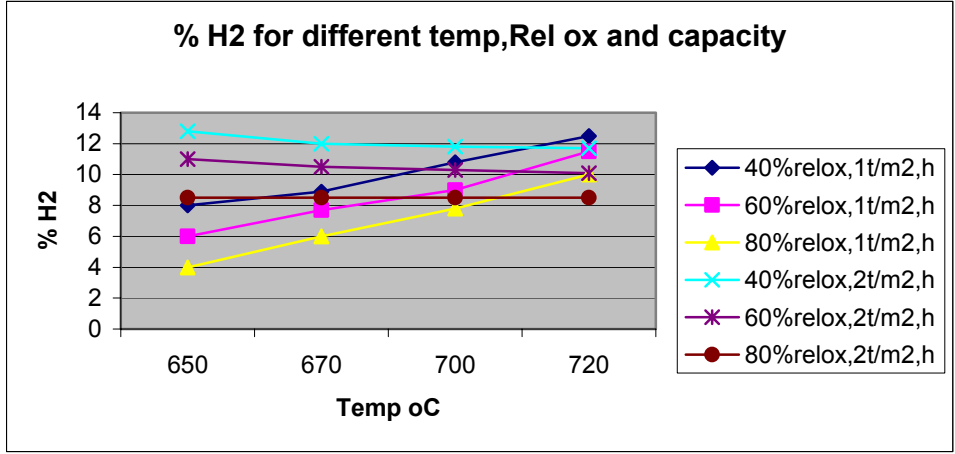


Figure 1. Black liquor gasification pilot plant in Vasteras, Sweden.

Statistical model using multi-variate data analysis: From the factorial designed experiments we received a lot of data. These were used to build PLS-models for the

different gas components (CO, CO₂, H₂, CH₄, H₂S) and the inorganics in the bed solids leaving the reactor (residual carbon, sulfate, sulfide). We were using the program SIMCA from Umetri for this, but other programs like Unscrambler or PLS-toolbox would have given the same results. Graphs for the different polynoms acquired from the results of the pilot plant experiments are shown in figure 2 below:



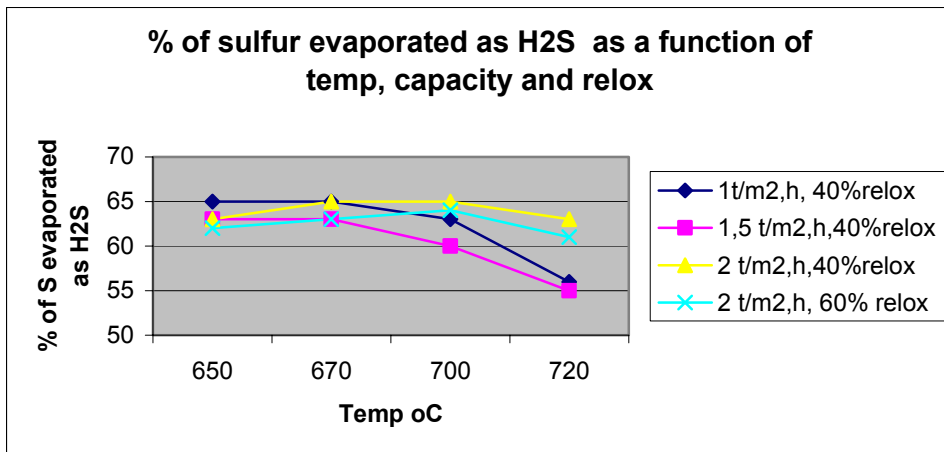
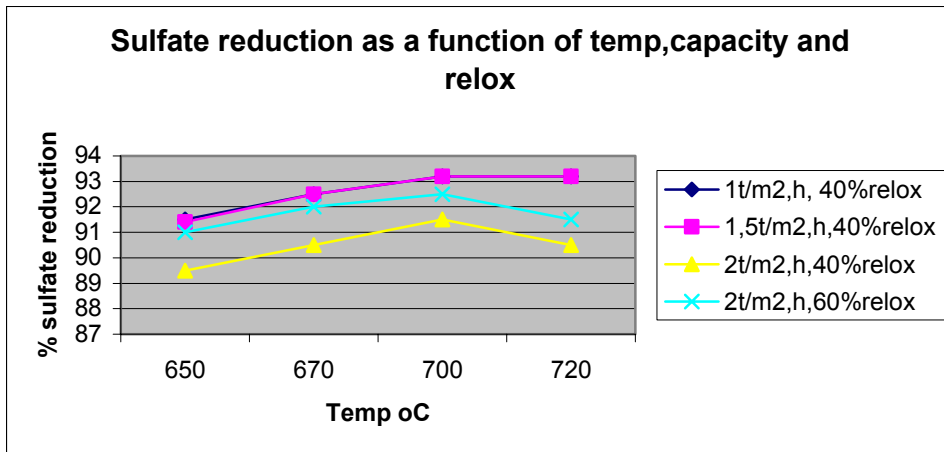
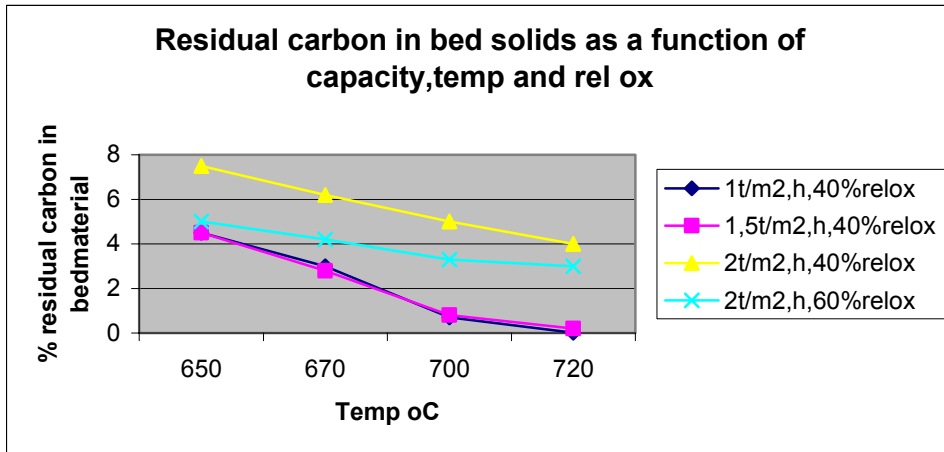
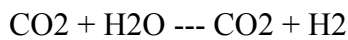


Figure 2. Plots of the different polynoms made by PLS for a number of variables from the pilot plant experiments.

The PLS polynoms we got were then used later on to determine the gas composition and bed solid composition for different operational conditions of the reactor.

Physical model incorporating the statistical models: The polynoms for the gas composition etc were used in the physical simulation model to get the real kinetic data for the gas composition. These differed quite a lot from what was calculated using equilibrium calculations in Aspen + ,EquiCalc and other programs, using Gibbs free energy minimization. The CH₄ was significantly higher and the CO significantly lower than what was predicted from the equilibrium calculations. Still, the HHV (Higher heating value) was approximately the same.

In the physical simulation model we determined water content from the water-gas-shift reaction:



$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}$$

$$\text{where } \ln K = 4397 / T_k - 4.0566$$

K is the equilibrium constant and T_k the temperature in kelvin

A separate model was developed for selective absorption of H₂S compared to CO₂, heat losses where calculated, energy balances were calculated to determine what amount of oxygen should be needed from a theoretical point of view to run the process, and was compared to the actual air feed and gas composition was calculated at different positions in the reactor, taking into account water condensation, particle removal and gas absorptions.

A model for the absorption of H₂S and CO₂ was developed in cooperation with Mats Wallin at Lund University. Hydrogen sulfide is absorbed very rapidly in liquor with pH 10- 11, while CO₂ has a slow reaction.

$$[\text{H}_2\text{S}]_{\text{absorbed}} = [\text{H}_2\text{S}]_{\text{gas}} * K_{\text{H}_2\text{S}}$$

$$[\text{CO}_2]_{\text{absorbed}} = [\text{CO}_2]_{\text{gas}} * K_{\text{CO}_2} / [\text{CO}_3^{2-}]_{\text{liq}} * [\text{H}^+]_{\text{liq}}^2$$

where K_{H₂S} >> K_{CO₂}

For the CO₂ we also have to take into consideration the diffusion of CO₂ and the equilibrium with Carbonates [CO₃] and Hydrogen ions [H]. A high pH will give high absorption, while a low pH will give no absorption at all. Concerning the diffusion of CO₂ into the liquid phase from the surface we will have :

$$\partial[\text{CO}_2] / \partial t = D * \partial^2[\text{CO}_2] / \partial^2 x$$

This means that the diffusion will depend on the liquid thickness. A high thickness will give a strong resistance to absorption, and also lead to high concentrations of CO₂ in the surface closest to the gas phase. D is the diffusion constant.

By having a good gas mixing we can have a maximum concentration of H₂S at the liquid surface and thus high absorption of H₂S.

The model could predict the selective absorption for most conditions pretty well, but not all. Still, the absorption mechanisms described above could be verified and proved.

Other variables calculated are adiabatic flame temperature, amount of condensate, heating value of the gas, heat losses, full gas composition of both wet and dry gas and some other factors.

The output from the model is all the information needed for the design of a process, and the influence of changing the different variables can directly be seen both qualitatively and quantitatively. Also the effect of changing operational mode can be determined by the model, when the plant is once up and running.

In a second step the steady state model was also made dynamic by numerical differentiation of the equations. This could be done relatively easy with the approach with a combination of physical and statistical models, while it is normally not that easy with a pure statistical model.

The results from simulations are shown for different conditions where we combine the polynoms produced from experimental data with physical relations. These are compared to equilibrium calculations for the gas composition using good equilibrium calculation programs like Aspen plus and Solgasmix. What can be seen is that the real plant will get quite different gas composition compared to the equilibrium calculations. Methane concentration is significant in real life, while the equilibrium calculations predict no methane at all. Instead the CO concentration is much lower in real life than predicted by the equilibrium calculation. The H₂S concentration is also lower in real life than predicted from equilibrium calculations. This shows that the kinetics is of major importance, and can not be neglected in the design of the process. The simulation also calculate a lot of other important factors of interest for dimensioning the process like gas velocity in different parts of the system, heat and material balances over the gasifier, cyclones and scrubber, absorption of H₂S respectively CO₂ in the scrubber, gas composition of also wet gas, total gas production, adiabatic flame temperature, ratio product gas volume in relation to air injected, comparison between theoretically predicted oxygen consumption and the actual consumed oxygen as air. These other results are not presented here, but will be presented in some later paper. When we compare real measurements from the process and what is predicted by the simulation we can see that the residual carbon in bed solids will have too high values when the carbon conversion is high. When ash is recirculated back to the reactor from the bag filter, also the carbon conversion is increased. This has not been included fully in the simulation model at the moment. Direct caustization by addition of Titanium dioxide, TiO₂, has also been tested, but has not been included in the simulation model yet. With this process much more H₂S

is stripped off, but also CO₂ from Na₂CO₃, and thus we get NaOH in the leaching of the bed material, which means direct caustization. The results are seen in the table 1 below.

no	Input data						Dry Gas composition									
	%DS	tDS/m2h	Relox	T _{bot} °C	T _{inj} °C	T _{scrub} °C	CO %	H ₂ %	CO ₂ %	H ₂ O %	CH ₄ %	H ₂ S %	SO ₄ _{red} %	H ₂ S _{strip} %	C _{conv} %	HHV _{drygas} KJ/Nm ³
1	70	1,8	35	700	695	65	2,7	11,5	13,1	26,7	1,3	0,63	91,3	50,7	92,8	2066
2	70	1,8	45	700	695	65	2,3	9,2	11,9	25,5	1	0,59	91,9	53,9	94,3	1668
3	70	2,4	35	700	695	65	2	9,9	11,7	27	1,4	0,78	86,9	58,5	78	1848
4	70	1,2	35	700	695	65	2,9	11,5	14	26,4	1,1	0,61	93,3	50	98,9	2036
5	70	1,8	35	670	650	65	3,1	11,6	12,1	24,2	1,3	0,8	88,5	60,2	84,5	2118
6	70	1,8	35	725	720	65	3,2	14,5	12,1	27,4	1,5	0,48	92,2	41,9	97,6	2537
							Dryer Gas composition									
7	70	1,8	35	700	695	40	3,2	13,6	15,6	13	1,5	0,75	91,3	50,7	92,8	2458
8	70	2,4	35	725	720	40	2,4	13,5	13,7	15,8	1,9	0,73	87,9	49,7	82,5	2456
9	70	1,8	35	725	720	40	3,8	17,3	14,4	13,5	1,8	0,57	92,2	41,9	97,6	3022
ref equilibrium calculations																
	70		36		725		6,5	13,3	10,8	13	0	1,06				2800
	70		45		725		4,2	9	11,1	13,2	0	0,95				2100
	70		36		675		7	13,5	16,4	17,5	0	1,33				2800

Table 1. Results from simulations with polynoms made from real plant operations and physical relations. These are compared with equilibrium calculations.

Conclusions: What have been shown here is that the combination of statistical models built from systematically designed experiments (factorial design) can be used very efficiently in a physical simulation model, to give all the information needed. The model can also be made dynamic with this approach, something that is normally not the case for a pure statistical model.

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