

Modeling of Black Liquor Gasification

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Abstract

The energy situation in both process industries and power plants is changing. It is becoming interesting to perform system analysis on how to integrate gasification into chemical recovery systems in the pulp & paper industry and into the CHP systems in power plant applications to complement with production of chemicals aside of heat and power. The potential chemicals are methane, hydrogen, and methanol. It is also interesting to estimate the potential to introduce combined cycles with gas turbines and steam turbines using both black liquors and other type of biomass like pellets, wood chips etc. To perform such type of analysis, it is vital to have relevant input data on what gas composition we can expect from running different types of feedstock. In this paper, we focus on black liquors as feedstock for integrated gasification systems. The experimental results are correlated into partial least squares models to predict major composition of the synthesis gas produced under different conditions. These quality prediction models are then combined with physical models using Modelica for the investigation of dynamic energy and material balances for complete plants. The data can also be used as input to analysis using e.g. ASPEN plus and similar system analysis tools.

Keywords: black liquor, gasification, CHP, Modelica, physical models, synthesis gas

1 Introduction and Literature Review

During the 70' s, there was a strong demand to increase steel production from the iron ore. ASEA together with Stora and LURGI thus started the development of a new process, the circulating fluidized bed gasification (CFBG). The CFBG process was tested at a demo-plant in Vasteras in a 0.5 m inner diameter reactor with 20 m height. LURGI built a number of coal gasification plants and ASEA became ABB and afterwards ABB acquired the American company Combustion Engineering in 1990. Then, black liquor gasification (BLG) became interesting and a pilot plant was operated in Västerås.

Dipal and Baruah (2014) made an overview of biomass gasification modelling recently and different modeling approaches were categorized based on criteria such as type of gasifier, feedstock, modeling considerations and evaluated parameters. Gómez- Barea and Leckner (2010) performed the modeling work performed with many different approaches from artificial neural nets to computational fluid dynamics. They covered conversion of single fuel particles, char, and gas and conclude that most of the different approaches fit quite well between models and experimental results. However, a very little work has been made on real gasifiers or systems at a larger scale. Capata and Veroli (2012) made a mathematical model over an air-blown CFB with a capacity of 100 kWth. They concluded that there were some problems to get reasonable predictions of the tar formation. It is interesting to note that we did not create any detectable amounts of tar at all while running our CFB gasifier (100-200 kWth) with wood pellets. This shows that the gasification results are influenced depending on the fuel and how the plants are operated. It becomes difficult to achieve accurate models correlating to the experiments, if the mechanisms are not completely understood. Blasi (2016) has made an overview of the kinetic processes in detail to describe tar formation from a theoretical perspective. Still, it is interesting to describe what is actually taking place inside the reactors to be able to predict the process.

2 Description of the Pilot Plant

The experimental work has been performed in a CFB gasifiers in Vasteras at ABB and was built on the design developed through the cooperation between ASEA and LURGI during the 70's. The reactor had a diameter of 170 mm and a height of 10 meters, integrated with one cyclone with a G-valve. The synthesis gas was cooled through a heat exchanger and the gas was cleaned in a bag filter first, then in a scrubber, and finally combusted. At the G-valve entrance, the dust was recirculated from the bag filter. The gas sampling was made using a NIR meter giving simultaneous analysis of several gases.

Table 1. Results from experiments with black liquor operations

Avg. Temp	Fuel feed	Relox	MC	CO	H ₂	CO ₂	CH ₄
T2-T6	tDS			%	%	%	%
655	8	0.45	0.35	2	4	13.5	1.2
597	8	0.54	0.35	2.2	7.5	16.1	1.2
686	16	0.29	0.35	4	11.7	15.7	2.1
703	16	0.36	0.35	3.3	13.3	19.1	1.9
705	20	0.35	0.35	3.9	12.2	18.8	2.3
646	11	0.45	0.35	4.1	8.7	16.7	1.6
654	19	0.26	0.30	3.7	15	14.5	1.8
676	17	0.36	0.30	3.9	12.9	14.2	1.1
613	14	0.38	0.3	2.8	12.3	9.5	0.9
678	14	0.36	0.3	2.5	12.4	8.9	1
677	14	0.35	0.3	2.2	9.3	6.9	1.1
674	13	0.52	0.42	2.8	8.3	15	1.2
677	13	0.53	0.42	2.8	8.1	15.8	1.1
611	15	0.36	0.32	3.7	12	15.2	1.4
612	16	0.33	0.32	3.6	12.4	15.1	1.5
678	15	0.34	0.3	3.4	11	6	1.1

The gas sampling was made at several points in the reactor, although the main position was after the filter. The black liquor gasifier was operated for several years and experiments run in accordance with factorial design

of the variation of the operating variables: temperature, relative oxidation, capacity, pressure, different black liquors, addition of KCl, operation with TiO₂, recycling of dust from bag house and others.

3 Experimental results

In Table 1, we have presented few results extracted from our large data set. The selections have been made to have representation of the whole operational volume with similar amount of samples for each condition, to get balanced models. Every experimental test has been operated at least four hours under as steady state conditions as possible. The fuel rate is shown in ton DS/h.m² based on the reactor size. The 20 kg/h fuel load in the reactor corresponded to 1.13 ton tDS/m².h. The relative oxidation (Relox) means the amount of air (m³) needed for the 100 % oxidation of 1 kg of fuel (dried solids). In this case, approximately 4.9 m³ of air is needed for the 100 % oxidation of 1 kg of feed. The moisture content means the moisture including the steam added. The amount of tar was found to be very low that could not be determined accurately during steady state operations, although some tar was formed during the start-up phase. Since tar were not found considerably, they are excluded under the synthesis gas compositions. In addition, N₂ and H₂O are also not included in Table 1. It is found that there is a significant difference between the gas composition obtained from black liquor and wood, gasified in principally using the same reactor (Naqvi et al, 2010, 2016, 2017a).

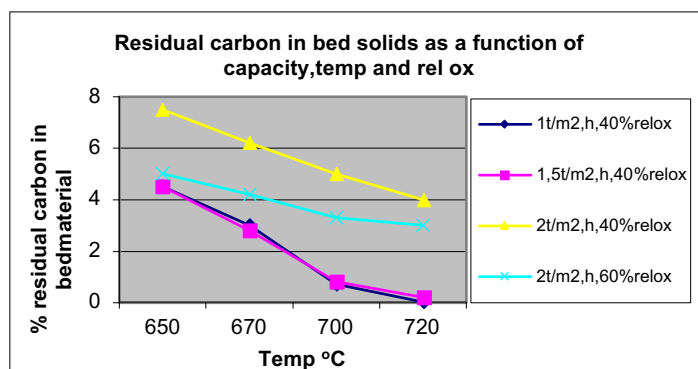
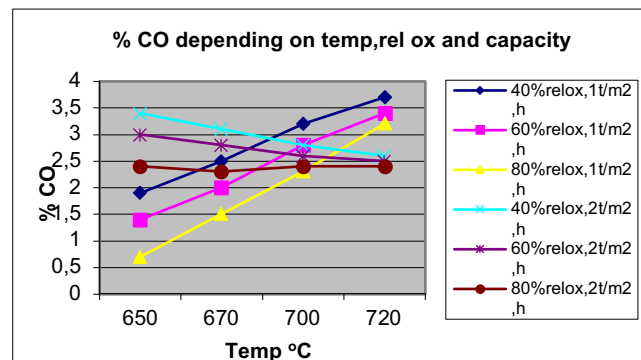
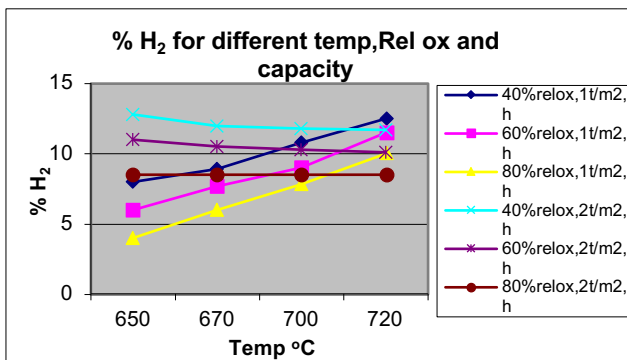
**Figure 1.** Correlation between H₂ and CO composition as well as residual carbon in fly ash

Table 2. Results from the simulation with black liquor gasification using the combined physical model for energy and material balances and PLS models for gas composition

	EXPERIMENTAL RUNS								
Input	1	2	3	4	5	6	7	8	9
DS, %	70	70	70	70	70	70	70	70	70
Feed rate, ton DS/m ² h	1.8	1.8	1.8	2.4	1.2	1.8	1.8	2.4	1.8
Relox, %	35	45	25	35	35	35	35	35	35
Temp bottom, °C	700	700	700	700	700	725	700	725	725
Temp at BL-injection, °C	695	695	695	695	695	720	695	720	720
Temp after scrubber, °C	65	65	65	65	65	65	40	40	40
Output									
Theoretical possible heat prod, kW	-137	-139	-136	-161	-96	-143	-137	-169	-143
Heat consumed in reactor, kW	44	48	40	58	29	48	44	66	48
Vol. % in wet gas									
H ₂ O	33	29.4	37.3	34	32.2	35.1	33	39.9	35.1
H ₂	10.5	8.7	12.8	9	10.6	13	10.5	9.6	13
CH ₄	1.16	0.96	1.43	1.26	1	1.33	1.16	1.33	1.32
CO ₂	12	11.2	12.9	10.6	12.9	10.8	12	9.8	10.8
CO	2.5	2.1	2.85	1.8	2.7	2.8	2.5	1.68	2.9
N ₂	40.3	46.9	32.1	42.6	40	36.5	40.3	37.2	36.5
H ₂ S	0.57	0.56	0.6	0.7	0.56	0.43	0.58	0.52	0.43
Heating value dry gas, kJ/kg of BL	-4635	-4284	-5039	-3883	-4633	-6147	-4635	-4668	-6147
Heating value wet gas, kJ/nm ³	-1887	-1580	-2290	-1672	-1874	-2268	-1888	-1753	-2268
Velocity upper reactor, m/s	5.5	6.1	4.9	6.95	3.7	6.2	5.5	8.2	6.2
Flame temp (°C), Air surplus 1.1	1221	1154	1293	1182	1231	1246	1315	1274	1336
Flame temp (°C), Air surplus 1.0	1272	1197	1354	1229	1282	1305	1376	1334	1405
Condensate, mol/kg of BL	9.4	6.4	12.2	9.9	8.8	12.8	25.2	34	30.2
Vol. % in gas after scrubber									
H ₂ O	26.7	25.5		27	26.4	27.4	13	15.8	13.5
H ₂	11.5	9.2		9.95	11.5	14.5	13.6	13.5	17.3
CH ₄	1.27	1		1.39	1.1	1.48	1.5	1.87	1.77
CO ₂	13.1	11.9		11.7	14	12.1	15.6	13.7	14.4
CO	2.7	2.3		2	2.9	3.2	3.2	2.4	3.8
N ₂	44.1	49.5		47.1	43.5	40.8	52.4	52.1	48.7
H ₂ S	0.63	0.59		0.78	0.61	0.48	0.75	0.73	0.57
Heating value of dry gas, kJ/nm³	-2065	-1668		-1848	-2035	-2536	-2452	-2457	-3021
Product gas/air	1.96	1.68		1.85	1.97	2.16	1.96	2.13	
Air, nm ³ /h per ton DS/m ² h	3222	4143		4296	2148	3222	3222	4296	
H ₂ S removal, %			46.9	58.5	50	41.8	50.7	49.7	41.9
SO ₄ reduction, %			90.8	86.9	93.3	92.2	91.3	87.9	92.2
C-conversion			91	78	98.9	97.6	92.8	82.5	97.6

There are much lower levels of H₂ in wood gasification than BLG but instead higher CO levels. For wood pellets gasification, higher CH₄ concentrations are obtained as compared to black liquor gasification.

The experimental data (not shown here) has also been gathered for the reduction of SO₄ and calculation of the carbon conversion, i.e. balance between what is gasified respective to unconverted carbon in the bed solids dust. In the scrubber, a selective absorption of H₂S takes place while limiting the absorption of CO₂ as far as possible.

In the experiments at the pilot plant, we have achieved 1 M (32 g S/l) at a selectivity of 20 by avoiding turbulence in the liquid, but promoting turbulence in the gas phase. In addition, pH is kept as constant as possible at 10.5, to give fast reaction of H₂S. While CO₂ get a back pressure in the liquid film reducing the absorption that is kinetically much slower than the one for H₂S absorption. Few examples of the simulation results are shown in Fig. 1 for the black liquor.

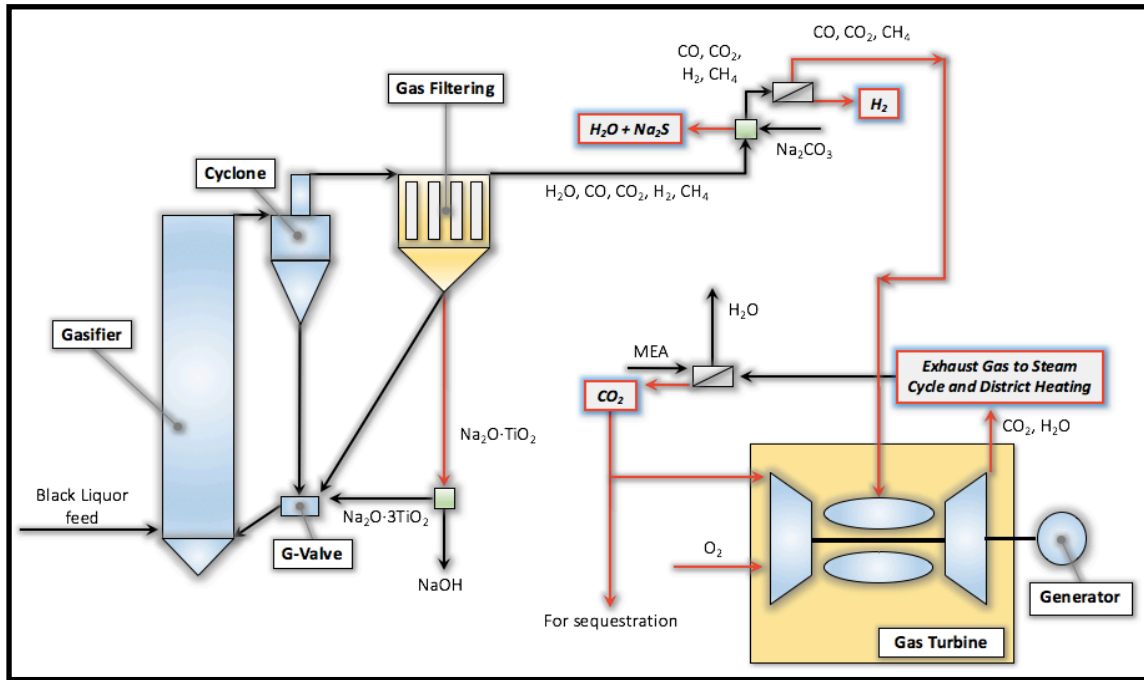


Figure 2. Different solutions can be either integrated as shown in the figure or operated separately

In Table 2, we have summarized the results from the simulations using different conditions with respect to calculated gas composition using the PLS-models. The energy and material balances are performed using the physical model. The physical model takes into account endothermic and exothermic reactions like reduction of SO₄ respective to oxidation of C and H.

The heat transfers through walls, in heat exchanger and scrubber are calculated as well as particle separation in the cyclone and the bag filter. However, the absorption of H₂S respective to CO₂ in the scrubber as a function of pH of the scrubber solution is not included here. The recycling of ash from the bag house is also not included in this simulation.

For the black liquor gasification, we found that there is residual carbon not converted during the gasification. By recirculating the solids from the bag-house into the reactor, the amount of residual carbon dropped to below 4% in the filter ash at stabilized conditions. This resulted in a carbon conversion of higher than 96-99% at steady state with recycled dust from the bag house to the down-comer of cyclone 1.

The results showed that the H₂ content is in the range 9 -17%vol., while the CO content is only 2-4%. The CH₄ content is in the range 1-1.9%, which is quite high in relation to the CO content. Since H₂S is stripped off, the concentration of H₂S is found to be 0.5-0.8% with SO₄ reduction of 87-93%, which is as good or better as in a conventional recovery boiler.

The moisture (H₂O) is calculated from the shift reaction with the constant K_T given for the average temperature (T) at steady state conditions as shown in

$$K_T = \frac{[CO][H_2O]}{[H_2][CO_2]} \quad (1)$$

This is for the actual gasification. For the moisture content in the synthesis gas after the scrubber, the water content of the synthesis gas at saturation for the given scrubber temperature is used. From this we recalculate the gas composition used in the simulations later on as a function of operating conditions, but then combining also with energy and mass balances.

4 System Studies

The experiments are not always easy to control as exactly as wanted in the pilot scale plants. For the analysis of impacts of different variables (like temperature, relative oxidation, organic load and impact of water/moisture for the black liquor), the model still is good enough in relation to other uncertainties. By inserting the conditions and gas composition, the material and energy balances are determined for the systems studied in addition to the dynamics and controllability. The detailed system analysis is not possible to include in this paper due to the limited number of pages available, and thus will be presented in future studies.

For system analysis, one study on H₂ production in a CHP plant is presented in Naqvi et al (2017b). Yang and Ogden (2007) made an overview of production costs for Hydrogen production as well. Another study was made on black liquor gasification systems Dahlquist et al (2017), where different cycles and solutions were compared, including among others CO₂ removal. Asadullah (2014) has made a critical review of downstream gas cleaning after biomass separation, which includes the particle and tar removal.

In Fig. 2, we have a gasification process that could be used for black liquors or another biomass. The BLG

with addition of titanate (TiO_2) can give a solution with direct caustization for conversion of Na_2CO_3 to NaOH , as well as selective absorption of H_2S for the chemical recovery. The gas then can be separated to extract hydrogen, while the residual gas is combusted directly in a boiler, or in an external gas turbine combustor, making a combined cycle possible. Heat from the steam turbine condenser then can be used for e.g. district heating. Even CO_2 can be removed at the far end of the exhaust gas train. The BLG with direct causticization at the pulp mill is an interesting option (Dahlquist, Jones, 2005). The alternative with a combi-cycle could give an electric to fuel heating value efficiency of up to 38%, which is high for a process with such a poor fuel.

5 Conclusions

In this paper, we have presented that how regression models such as PLS, PCA and similar can be made from experiments and combined with dynamic physical models developed in e.g. Modelica. Such developed models can be used to study different systems from the energy and material balance perspective, but also investigate how to go from one process mode to another in a smooth way. This will be more important as the economic conditions will vary much more in the future from one part of the day to another, as well as over the season, making it much more complex to fulfil all different demands. When earlier the focus has been on conversion processes like gasification, we will see an increasing demand also for gas separation like membrane separation for developing efficient system solutions. New demands like CO_2 removal may give quite different economical optima, if CO_2 is valued significantly higher than today. This also will shift the use of fossil fuels for production of chemicals into a demand to use biomass, which will give new incentives to the proposed processes for production of base chemicals like CH_4 and hydrogen.

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References

- A. Gómez-Barea and B. Leckner. Modeling of biomass gasification in fluidized bed. *Progress in Energy and Combustion Science*, 36(4): 444–509, 2010.
- C. Di Blasi. Kinetic modeling of biomass gasification and combustion. Intelligent Energy Europe (PyNe). Available via <https://pdfs.semanticscholar.org/dddc/d68110b3f918f67a9800a311ab2481db12ef.pdf> [accessed January 5, 2016].
- C. Roberto and M. D. Veroli. Mathematical Modelling of Biomass Gasification in a Circulating Fluidized Bed CFB Reactor. *Journal of Sustainable Bioenergy Systems*, 2: 160–169, 2012.
- C. Yang, and J. Ogden. Determining the lowest-cost hydrogen delivery mode. *International Journal of Hydrogen Energy*, 32: 268–286, 2007.
- D. Baruah and D. C. Baruah. Modeling of biomass gasification: A review. *Renewable and Sustainable Energy Reviews*, 39: 806–815, 2014.
- E. Dahlquist and A. Jones. Presentation of a dry black liquor gasification process with direct caustization. *TAPPI Journal*: 15–19, 2005.
- E. Dahlquist, M. Naqvi, E. Thorin, J. Yan, K. Kyprianidis, and P. Hartwell. Experimental and numerical investigation of pellet and black liquor gasification for polygeneration plant. *Applied Energy*, 204:1055–1064, 2017.
- M. Asadullah. Biomass gasification gas cleaning for downstream applications: A comparative critical review. *Renewable and Sustainable Energy Reviews*, 40: 118–132, 2014.
- M. Naqvi, E. Dahlquist, and J. Yan. Complementing existing CHP plants using biomass for production of hydrogen and burning the residual gas in a CHP boiler. *Biofuels*, 8(6): 675–683, 2017.
- M. Naqvi, J. Yan, M. Danish, U. Farooq, and S. Lu. An experimental study on hydrogen enriched gas with reduced tar formation using pre-treated olivine in dual bed steam gasification of mixed biomass compost. *International Journal of Hydrogen Energy*, 41(25): 10608–10618, 2016.
- M. Naqvi, J. Yan, and E. Dahlquist. Synthetic natural gas (SNG) production at pulp mills from a circulating fluidized bed black liquor gasification process with direct causticization. *In Conference proceedings of ECOS 2010*.
- M. Naqvi, J. Yan, E. Dahlquist, and S. Naqvi. Off-grid electricity generation using mixed biomass compost: A scenario-based study with sensitivity analysis. *Applied Energy*, 201: 363–370, 2017.