

Evaluation of process configurations to produce hydrogen from black liquor

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Introduction

In order to reach a more sustainable society in the future, it is necessary to use other types of energy carriers than today. The hydrogen society has been proposed as the ultimate goal for a sustainable society, especially if the hydrogen is produced from renewable resources, such as biomass.

Black liquor is the residue from the kraft paper pulp process and consists, mainly, of water, lignin, organic residues from cellulose and hemicelluloses and inorganic matter (mostly sodium, potassium and sulfur). Before any combustion or gasification, the dry content of the black liquor is increased, typically from 14-18% to 75-80%, to permit autogenous combustion and high conversion efficiency of the fuel value to superheated steam. The main reason to produce hydrogen or other energy carriers in a pulp mill is that there is a surplus of energy and fuel available, from wood waste and spent pulping liquor, in modern, stand-alone pulp mills. The reason to use black liquor to produce hydrogen is that it is easier to process black liquor, a pumpable liquid, and an extremely reactive fuel, in a pressurized gasifier than it is to process solid biomass.

The study reported here was done to evaluate the potential for hydrogen production by gasification of black liquor. The objective was to maximize the hydrogen yield, given a purity requirement on the hydrogen product, constraints on the range of operating conditions in the different unit operations (gasifier, steam reformer and water-gas shift reactor) and the overall process configuration.

Method

The system boundary is shown in Figure 1. Systems analyses were made for cases where the gasifier, gas cleanup train, and hydrogen separation plant were included within the system boundary. In those cases, a simulated black liquor and an oxidant (air or oxygen) were the input streams. In other cases, systems analyses were made where the process boundary included only the hot gas cleanup train and the hydrogen separation plant. The input streams for these cases was the raw syngas from the gasifier.

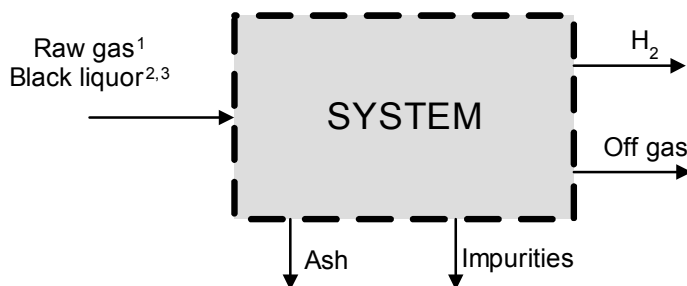


Figure 1. System boundary

In this investigation, a typical Swedish black liquor was used as the raw material. It had a dry solids content of 75% (0.34 kg water / kg black liquor solids). The elemental composition of the dry black liquor solids is seen in table 1.

Table 1. Elemental composition in the used black liquor

Element	% (by weight) as dry solids
C	36.33
H	3.52
O	34.38
K	1.90
Na	18.87
S	5.00

Process calculations were made for different cases. The calculations were made in the flowsheeting program Hysys 3.1. Necessary complementary calculations, regarding the membrane separation, were made using an Excel spreadsheet. The results were used in the flowsheeting program as inputs for a component splitter, i.e. the splitter were defined by the external calculations.

The investigation were separated into three categories, depending on the method to simulate the raw gas production. The three simulation methods for raw gas production were (a) kinetic controlled gasification (e.g. entrained flow gasifier) at high temperature and pressure (900°C and 30 bar); (b) an equilibrium gasifier (representing a fluidized bed gasifier) at high temperature and pressure (900°C and 30 bar); and (c) an equilibrium gasifier at high temperature and low pressure (900°C and 5 bar). The temperature at which gasification proceeds in a flow reactor is determined by the air ratio used and the amount of heat transferred to or from the gasifier. In the cases investigated here, the temperature of the gasifier was adjusted by both methods. Entrained flow gasification of black liquor has been simulated elsewhere (Marklund, 2003). One result from that study is the synthesis gas composition found in Table 2.

Table 2. Main species in the synthesis gas from an entrained black liquor gasifier at 900°C and 30 bar.

Species	%-weight
H ₂	5.07
CH ₄	8.49
CO	67.49
CO ₂	13.26
H ₂ S	5.69

The equilibrium reactors were modeled by a Gibbs reactor in the flowsheeting software. The algorithm for that reactor is based on Gibbs free energy minimization.

In each of the cases, different high-temperature operating conditions for the steam reforming units were tested as well. These were; adiabatic reformer, maximum H₂ yield, and isothermal reformer. One simulation were also performed at low temperature (300°C).

The gas cleaning system consisted of: a cyclone for particulate separation, a tar cracker that uses dolomite as catalyst, a condensate separator and a desulphurization unit (either a scrubber or a high temperature adsorbent based on ZnO). There was also a gas conditioning unit which consisted of: steam reformer (mainly for conversion of the methane produced in the gasifier to CO and H₂), water shift gas reactors (WSGR) and pressure swing adsorption (PSA) units for final separation and purification of hydrogen, as shown in Figure 2.

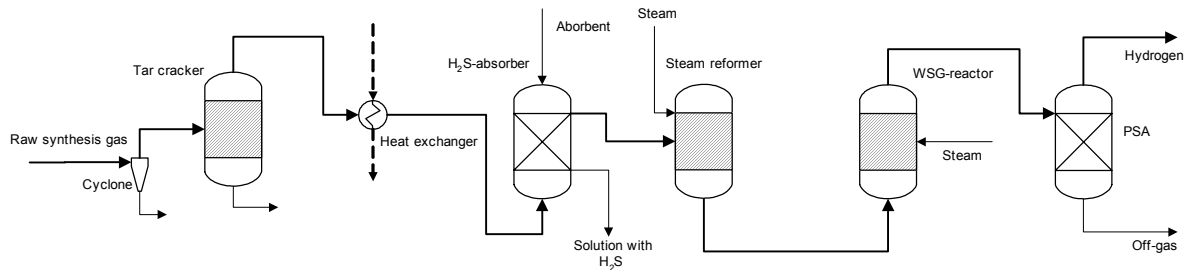


Figure 2. Gas cleaning and conditioning process configuration.

Results and Discussion

The first important characteristic of the process noted during the simulations was that if a scrubber were to be used for sulfur gas removal there would be a substantial temperature decrease between the gasifier and to the scrubber since a suitable temperature on the incoming gases to the latter was found to be 40°C. Therefore, it is necessary to include a heat exchanger between the tar cracker and the absorber. This will decrease the overall second law efficiency of the process as it is not possible to utilize the high quality energy content of the hot gas stream for other than heating. However, this case was further investigated since the main task was about maximizing the hydrogen production. Furthermore, the amount of weak white wash needed to scrub H₂S from the raw gas became very large to be able to decrease the H₂S-concentration below 3 ppm (higher concentration might poisoning the catalysts in the steam reformer). This led to a high amount of CO₂ absorbed in the liquor as well. The latter is not good with respect to operability in the pulp mill and leads to a higher demand of energy input in the lime kiln (more NaOH must be produced). Another option would be to use a liquor with more base and thereby be able to decrease the amount of liquor, but with the drawback of having to produce more NaOH. The wet scrubber was thus replaced by other methods, such as adsorption/reaction at high temperature using a bed of ZnO.

The next piece of equipment considered was the steam reformer. The first trial was at low temperature and high pressure (300°C and 30 bar). The reason for this trial was to find how much the temperature needs to be increased before the steam reformer, provided that a cold sulfur gas removal method were used.. This is not a favorable condition for the reactor since the high pressure prevents steam reforming from occurring, Eq 1, due to the formation of 4 moles of gas for each 2 mol of reactants. The reaction is also endothermic, which thereby favors high temperature for the reaction to occur fast.



It was found that methane actually was formed in the reformer, when modeled as a Gibbs reactor. In fact it has been shown by Xu and Froment (1989) that there will be very low conversion of methane at low temperature and high pressure (they found that the conversion of methane to H₂ and CO was only 10% at 500°C and 30 bar).

The next step was to investigate what temperature should be used in the reformer. This was done by operating the reactor in different modes; adiabatic and non-adiabatic. It was clear that (a) the amount of methane reformed increased with increasing temperature, (b) that the conversion in the adiabatic reactor was not high enough (the outlet temperature became about 650°C) and that the temperature in the reformer had to be increased to at least 700°C. Therefore, it was clear that a non-adiabatic reactor had to be chosen.

Regarding the WSG-reactor, the equilibrium, Eq. 2, is shifted towards formation of more hydrogen at low temperature. However, the reaction kinetics are slow at low temperatures. Therefore, it is practical to have at least two water gas shift units where the temperature is gradually decreased with residence time. Having two reactors also gives the possibility of using two different catalysts if desired).



Furthermore, it is clear from reaction 2 that it would be beneficial to remove the hydrogen from the gas before the WSG-reactor, thereby pushing the reaction further toward the right side. This was confirmed by the results of the simulation. Therefore, an extra unit was incorporated in the virtual process. This is a membrane separation unit, which is selective to hydrogen. This is not a feature existing in Hysys and it had to be calculated in a separate program. In order to do that and incorporate permeability of other compounds than hydrogen, e.g. CO₂, data was taken from Mulder (1996) and Perry (1997). The new improved process configuration scheme is shown in figure 3.

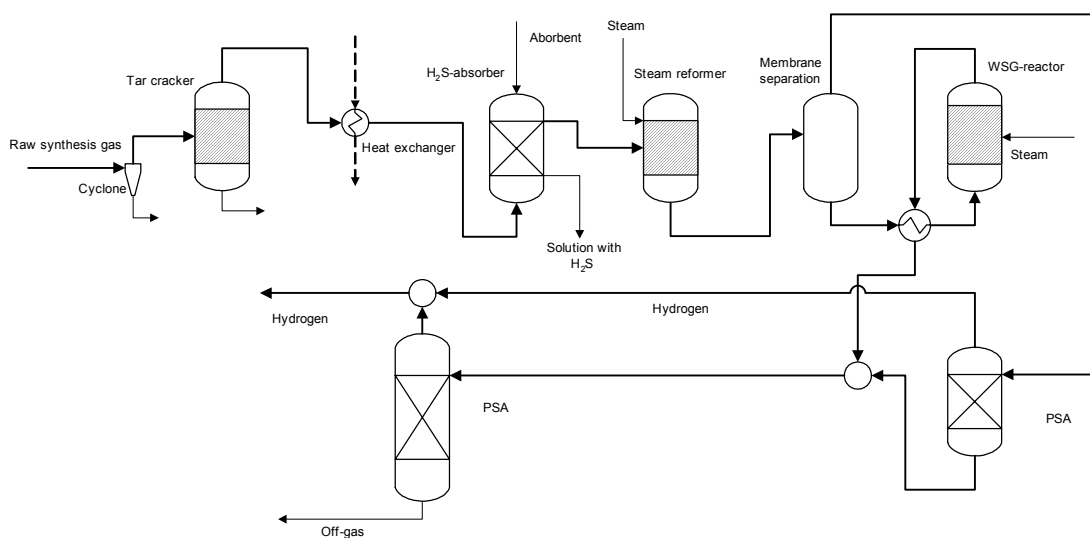


Figure 3. Process configuration for maximum hydrogen yield from black liquor gasification.

The membrane separation unit introduced operates unfortunately best at low temperatures, and it is therefore necessary to have internal heating of the gas coming to the WSG-reactor with the reacted gases. In Figure 3, an additional PSA-unit were installed. It operates selectively on the gas stream from the membrane. Due to the relative high concentration of hydrogen in that stream this unit could be much smaller and less costly than the main PSA.

The same process configuration was then used for the last two cases, fluidized bed gasifier at 30 bar and 5 bar respectively (both operating at 900°C). It became clear that a pressure of 30 bar was more efficient with respect to hydrogen production and is also better with respect to the overall energy efficiency of the entire process.

Conclusions

It was found that hot gas cleaning methods are advantageous to have a high hydrogen production, given a specific black liquor feed rate. It was also shown that high pressure operations gave higher production rates of hydrogen (both yield and purity) as well as better energy efficiency.

A pressure swing absorption unit was used to purify the hydrogen in the end and simultaneously open the possibility for CO₂ capture. It turned out that the highest potential for CO₂ capture was realized with the same process configuration that also had the highest hydrogen production. This can be explained by the water gas shift reaction, where CO₂ and hydrogen are in equilibrium with water vapor and CO, which basically means that a high hydrogen production in this step produce more CO₂.

References

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