

Waste to energy by industrially integrated SCWG – Effect of process parameters on gasification of industrial biomass

Lillemor Myrén, Ida Rönnlund, Kurt Lundqvist, Jarl Ahlbeck, Tapio Westerlund
Process Design and Systems Engineering Laboratory
Faculty of Technology, Åbo Akademi University
Piispankatu 8, FIN-20500 Turku, Finland
e-mail: lillemor.myreen@abo.fi

In supercritical water gasification (SCWG) complete gasification of biomass can be achieved resulting in a valuable hydrogen-rich product gas. Potential raw material sources for this process are wet organic waste streams containing more than 80 wt-% water. The large variety of industrial biomass is challenging and needs to be further investigated for future industrial applications of the SCWG process. Moreover, the impact of process parameters in SCWG is essential. In this study the behaviour of glucose, paper sludge, black liquor and peat in SCWG have been examined. The effects of temperature and residence time in gasification of black liquor have been investigated. This study has been done to verify the performance of the laboratory scale reactor.

1 Introduction

During the last decades the research in the field of SCWG has increased rapidly. In this process biomass is gasified using the supercritical conditions of water at temperatures above 374°C and pressures above 22.1 MPa. The produced gas consists mostly of hydrogen (H₂), carbon dioxide (CO₂), methane (CH₄) and carbon monoxide (CO). Also hydrogen sulphide (H₂S) is formed when sulphur-containing biomass is used as raw material. As the water acts as solvent, catalyst and reaction media in SCWG there is no need for drying, and in this way the energy efficiency is increased. This method can be utilized in processes where wet waste streams consisting of organic material are formed. Model compounds such as glucose have been investigated to achieve a better understanding of industrial biomass (Antal et al., 2000; Boukis et al., 2006). Studies concerning industrial biomass have been done as these contain substances that can inhibit and/or enhance the gasification (García Jarana et al, 2008; Sricharoenchaikul, 2009).

In the pulp and paper industry today, dried paper sludge is dried and combusted in a fluidized bed boiler. Black liquor is first evaporated and then combusted in a recovery boiler, generating heat and recovering valuable chemicals for the sulphate pulping process. Production of more refined products is with these methods not possible. By integrating a SCWG plant in existing processes, more valuable products are produced.

2 Experimental methods

2.1 Laboratory reactor system

The experiments were performed in a laboratory scale tubular reactor with plug flow behaviour; the reactor is made of Inconel alloy 625. The length of the reactor is about 0.5 m and the inner diameter is 14 mm. The reactor has a total volume of about 83 ml, due to corrosion and deposits during experiments the exact volume of the reactor is hard to determine. The reactor material has been showed to have catalytic influence on the gasification after oxidisation of the reactor surface (Boukris et al., 2006).

2.2 Equipment and methods for analysis

In all parts of the process measurements and analyses are done before, during, and after an experiment. The composition of the feed is analysed, the amount of feed inserted into the reactor system and the dry matter content of the feed are measured. During experiments are the temperature and pressure controlled. The product gas is analysed in a Clarus 5000 gas chromatograph from Perkin Elmer. Elemental analysis is done in a Flash EA1100 with a TC detector from Thermo Quest; an ICP-OES has also been used.

2.3 Raw material

One of the most important compounds in biomass is cellulose. In gasification of cellulose the first step is hydrolysis to glucose and fructose, this occurs rapidly when the temperature reaches 200-250°C (Sasaki et. al., 1998). Gasification of the intermediate product glucose is believed to give similar results as gasification of cellulose (Lee et. al., 2002). For the experiments glucose is dissolved in distilled water achieving a 0.1 M solution that is easily inserted to the reactor system.

Paper sludge and weak black liquor were obtained from local pulp and paper mills. The dry matter content of the paper sludge as received was too high for using in the experiments as such; too high dry matter of the feed inhibits the gasification (Sricharoenchaikul, 2009). Before experiments water was added to the paper sludge achieving a dry matter content of 2-10 wt-%. The black liquor had a dry matter content of 17-18 wt-% when received. Black liquor consists of about 60% inorganic material and 40% organic material. As a result of the high alkali concentration, black liquor has slippery behaviour and can easily be fed as such into the reactor system. Peat was sent from a Finnish condensing power plant. The dry matter content of the peat as received was too high for experiments; the peat was therefore mixed and water was added achieving a dry matter content of about 10 wt-%.

The elemental composition of the different feeds used in the experiments can be seen in Table 1. Glucose and paper sludge have about the same composition with the exception of that paper sludge contain some nitrogen (N). The black liquor contains less carbon (C) and oxygen (O) than the other feeds, but on the other hand it contains sodium (Na), potassium (K) and chlorine (Cl). Peat has the highest content of C and the amount of O is about the same as for black liquor.

Table 1. Elemental composition of glucose, paper sludge, black liquor and peat

Element	Glucose wt-% of dry solid	Paper sludge wt-% of dry solid	Black liquor wt-% of dry solid	Peat wt-% of dry solid
C	40.0	43	32	56
H	6.7	4.9	3.3	6.1
N	0	0.5	0.1	0.2
S	0	0	5.5	0
O	53.3	52	36	38
Na			19	
K			3.3	
Cl			0.4	

2.4 Experimental parameters

The initial experiments have been carried out in temperatures of 500-650°C and residence times of 1.9-4 min. The pressure in the reactor was kept constant at 25 MPa. No catalysts were added to the biomass; notable is that black liquor has catalytic properties in thermal gasification (Jaffri and Zhang, 2008). Experiments with alkali catalysts (potassium hydroxide, KOH and sodium hydroxide, NaOH) been done in the reactor during the time period when most of the experiments for this study has been done. The use of these alkali compounds has resulted in an oxidation of the reactor surface resulting in a catalysing layer (Boukis et al., 2006). The surface is consequently activated and catalyses the gasification although no catalysts are added to the feed.

2.4.1 Residence time and temperature

In SCWG of glucose the gas yield has been reported to increase with residence time until complete gasification is reached (Hao et al., 2003; Antal et al., 2000; Sricharoenchaikul, 2009). Likewise has the temperature an increasing effect on the gas yield in SCWG of glucose (Hao et al., 2003). Non-catalytic SCWG of cellulose has by Resende et al. (2007) been showed to increase with temperature. The yield of product gas in the experiments was according to this presumed to increase with increase in residence time and temperature also when black liquor is used as feed.

3 Results and discussion

Due to different elemental composition of the feeds and different complexity of the biomass, the yield and composition of the product gas from gasification varies noticeable. To illustrate these differences experiments has been done with glucose, paper sludge black liquor and peat; maintaining other parameters, such as temperature, pressure, dry matter content, and residence time, as constant as possible. The different experiments have been done in temperature of 600°C, pressure of 25 MPa, dry matter content of 6-10 wt-% organic matter and residence times of about 2 min. The results from these experiments can be seen in Figure 1. The experiments with glucose have been done before the activation of the reactor material.

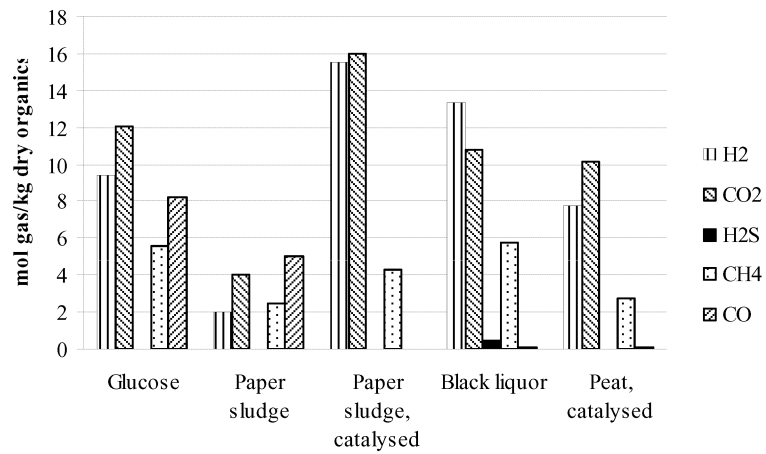


Figure 1. Yield of mol gas per kg dry organics in feed as function of different biomass at 600°C and 25 MPa and with residence time 2 min

The effect of activating the reactor surface can be seen when comparing the results from gasification of paper sludge in the reactor before and after activation. Peat has been gasified in the already activated reactor. The yield of gas in gasification of peat is lower than for gasification of paper sludge in the activated reactor. The composition of the product gas is affected by the reactor surface activation. Before the activation there is a notable amount of CO in the product gas and after activation the CO levels are low.

3.1 Effect of residence time

The experiments concerning the residence time have been done at four different residence times at 600°C and 25 MPa, using only black liquor. The results from this study can be seen in Figure 2 where trend lines have been added for better visualisation of the effect of residence time.

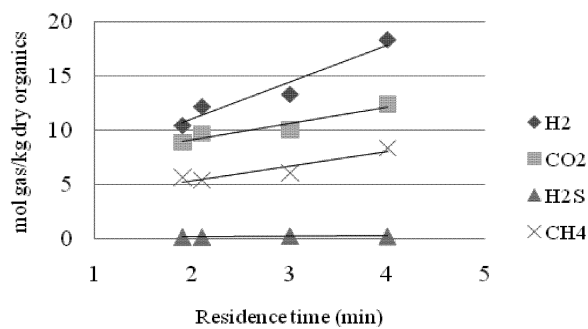


Figure 2. Yield of mol gas per kg dry organics in feed as function of residence time in gasification of black liquor at 600°C and 25 MPa.

The experiments showed that with increase of residence time, the total yield of product gases is increased; the composition of the product gas is as well affected by the increase in residence time. As expected is the dependence of the residence time is according to the experiments virtually linear in this temperature range.

3.2 Effect of temperature

Experiments have been done at three temperatures using black liquor as feed keeping the other parameters constant; the pressure is 25 MPa, the dry matter is 18 wt-% and the residence time is 2 min. The result of these experiments can be seen in Figure 3 where the temperature dependence of the yield of product gas is illustrated.

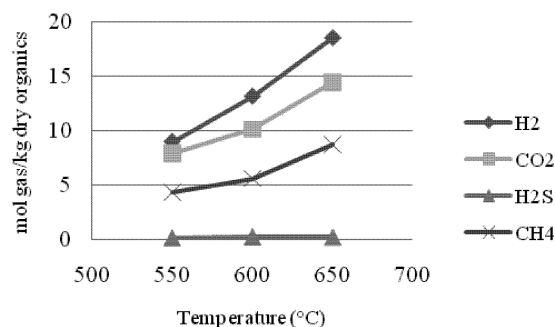


Figure 3. The temperature dependence of the yield of mol gas per kg dry organics in feed

The experiments have been done after activation of the reactor surface; therefore is no carbon monoxide formed during the experiments. With increasing temperature the total yield of product gas increases. As can be seen in the figure no optimum level of the temperature has been found in this temperature range. The yield of CH₄ is increased more than the yield of H₂ and CO. The yield of H₂S has an optimum at 600 °C. For this study are only three series of experiments done and the temperature range is rather small, for better understanding of the effect of the temperature the temperature range needs to be widened. In higher temperatures the amount of product gases is increased, which is in agreement with results reported by others (Sricharoenchaikul, 2009).

4 Conclusions

The experiments show that the SCWG process is temperature and time dependent, when using real biomass the highest gasification yield is for these two parameters obtained in the upper end of the investigated range. Due to different elemental composition of industrial biomass the yield of product gas varies with the feed used. Due to inhibition of the gasification not all types of industrial biomass are suited for this process. If the temperature could be increased, better results from gasification could be achieved. The limiting factor in SCWG is the reactor material and the materials and apparatus used in the reactor system. The results of this study correspond with results published by others and show that there are potential for integrating SCWG in existing processes. The

findings are important for further research in this field at the Laboratory. More research needs to be done in this field before an industrially applied SCWG process can be built a cost efficient way.

5 Acknowledgements

The financial support from the Fortum Foundation to the first author is gratefully acknowledged.

6 References

- Antal, M. J., Allen, S. G., Schulman, D., Xu, X. and Divilio, R. J., 2000, Biomass Gasification in Supercritical Water. *Ind. Eng. Chem. Res.*, 39, 4040-4053.
- Boukis, N., Diem, V., Galla, U. and Dinjus, E., 2006, Methanol Reforming in Supercritical Water for Hydrogen Production. *Combustion Science and Technology*, 178, 467-485.
- García Jarana, M. B., Sánchez-Oneto, J., Portela, J. R., Nebot Sanz, E. and Martínez de la Ossa, E. J., 2008, Supercritical water gasification of industrial wastes. *The Journal of Supercritical Fluids*, 46, 329-334.
- Hao, X. H., Guo, L. J., Mao, X., Zhang, X. M. and Chen, X. J., 2003, Hydrogen production from glucose used as model compound of biomass gasified in supercritical water. *International Journal of Hydrogen Energy*, 28, 55-64.
- Jaffri, G.-e.-R. and Zhang, J.-Y., 2008, Catalytic gasification characteristics of mixed black liquor and calcium catalyst in mixing (air/steam) atmosphere. *Journal of Fuel Chemistry and Technology*, 36 (4), 406-414.
- Lee, I.-G., Kim, M.-S. and Ihm, S.-K., 2002, Gasification of Glucose in Supercritical Water. *Ind. Eng. Chem. Res.*, 41, 1182-1188.
- Resende, F. L., Neff, M. E. and Savage, P. E., 2007, Noncatalytic Gasification of Cellulose in Supercritical Water. *Energy and Fuels*, 21, 3637-3643.
- Sricharoenchaikul, V., 2009, Assessment of black liquor gasification in supercritical water. *Bioresource Technology*, 100 (2), 638-643.
- Sasaki, M., Kabyemela, B., Malaluan, R., Hirose, S., Takeda, N. and Adschiri, T., 1998, Cellulose hydrolysis in subcritical and supercritical water. *Journal of Supercritical Fluids*, 13, 261-268.