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Integration of SuperCritical Water Gasification (SCWG) in Pulp and Paper Production – A Feasibility Study of Integration Options

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By means of supercritical water gasification (SCWG) different types of wet biomass can be gasified resulting in a hydrogen-rich product gas. The product gas can be used as such or be further refined into for example renewable traffic fuels or chemicals. The dry matter content of the feed is preferably 1-20 wt%. In pulp and paper production several streams of wet biomass are produced, these have large potential in being used as feed in SCWG as they contain considerable amounts of organic material and water. There are several options for integrating a SCWG plant in pulp and paper production; in this initial study two possibilities of integrating a SCWG plant into pulp and paper production have been investigated. The results are based on mass and energy calculations for a pulp and paper mill and laboratory experiments using black liquor and paper sludge as feed. The experiments have been carried out in temperatures of 600-700°C and pressure of 25 MPa.

1. Introduction

The research in SCWG has in recent years boomed. With this method biomass can be fully converted into syngas utilising the properties of water at supercritical conditions. In water at normal conditions there is a significant difference between the liquid and the vapour phase. The supercritical point of water is reached when the pressure is 22.1 MPa and the temperature is 374 °C (Antal et. al., 2000). At these conditions there is no significant difference in the physical properties between the liquid and vapour phase; there is only one phase, the supercritical phase. Supercritical water acts as, in contrary to water at normal conditions, a non-polar solvent; organic material is hence fully soluble and inorganic material is practically insoluble (Kruse and Dinjus, 2007). A large variety of raw material can be gasified in supercritical water; also biomass containing inorganic material is possible to make use of. The products from SCWG are gases, such as hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4), and product liquid that contain the inorganic part of the raw material and organic material that has not been gasified. The reactions in SCWG are mostly endothermic and constant heating of the reactor is hence required (Kruse and Dinjus, 2007). In order to develop a feasible process efficient heat recovery is required for larger scale applications of SCWG. Up to 70 % of the inserted heat can be recovered from the

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products; consequently additional heating is required continuously. By using part of the product gas for generation of the additional heat, there is no need for additional heating and the process is in this way self-sufficient (Naqvi, Yan, and Fröling, 2010). The SCWG method has great potential in being implemented as a waste treatment method for wet waste streams and preferably integrated at the site where the waste material is produced; reducing the need for drying and transportation of the feedstock.

2. Experimental methods

The laboratory experiments were conducted in a laboratory scale reactor system using industrial biomass from pulp and paper industry as feedstock.

2.1 Laboratory reactor system

The laboratory scale reactor system consisting of a pressurisation unit, a reactor and a cooling and separation unit. Reaction conditions such as temperature and pressure are measured and controlled. The quantity of the product gas and liquid are measured and the composition of the product gas is analysed after each experiment. The composition of the product gas is analysed with a gas chromatograph.

2.2 Raw material

As raw material for this study black liquor and primary paper sludge from Finnish pulp mills have been used. Black liquor is spent cooking chemicals from the kraft pulping process. In the process the black liquor is evaporated and incinerated recovering the chemicals and generating heat for the pulping process. The primary paper sludge originates from the pulp and paper making processes, this sludge is normally treated at the waste water treatment plant. For every t of pulp produced is 1.7 t of black liquor produced (Gullichsen and Fogelholm, 1999).

Two different types of primary sludge have been chosen to investigate the differences in the two sources. In pulp production 20-25 kg sludge is produced per metric ton pulp produced and the corresponding amount of sludge produced in paper production is 5-10 kg/t of paper produced (Hynninen, 1998).

Table 1: Elemental composition, dry matter content and HHV for the raw material.

wt %	Black liquor	Paper sludge 1	Paper sludge 2
C	27.8	43	25.1
H	3.2	4.9	3.3
N	0.1	0.5	0.2
S	7.5	0	0.01
O	6.4	52	19.4
Inorganic material	55	0	52.0
Dry matter content	16.1	5,0	4.6
HHV (MJ/kg)	12.8	N/A	8.7

The elemental composition, dry matter content and the higher heating value are presented in Table 1. The carbon content in the first paper sludge sample is almost double the amount in the second sample. The amount of inorganic material differs as well when the two sources of primary paper sludge are compared. The inorganic content can have a catalysing, inhibiting or no effect on the gasification. The inorganic material in black liquor has been proved to have catalysing effect (Rönnlund et al, 2010) and the inorganic material in paper sludge has in experiments been observed to have no or inhibiting effect.

3. The kraft pulping process

The kraft pulping process has been used for more than hundred years; the main process steps have not been changed. There have however been some change and the most remarkable one is the size of the plant; when the pulp production has been increased the chemical recovery plant has been scaled-up using known technology. In Figure 1 a basic flow scheme of the kraft pulping process including a paper mill is illustrated.

At UPM-Kymmene’s pulp and paper mill in Kaukas 720 000 t pulp and 580 000 t paper is produced annually. When minimal amount of primary sludge production is assumed, the total amount is 17 300 t of primary sludge annually. By mixing primary paper sludge and black liquor the yield from the gasification is increased; the more black liquor the higher is the yield (Rönnlund et al., 2010). If the main purpose of the gasification plant is waste water treatment of the wet primary sludge and black liquor is used as an additive the maximal amount of black liquor is 50 % on dry basis in the feed stock to the gasification plant. At the Kaukas mill this will correspond to 1.4 % of the total black liquor production annually.

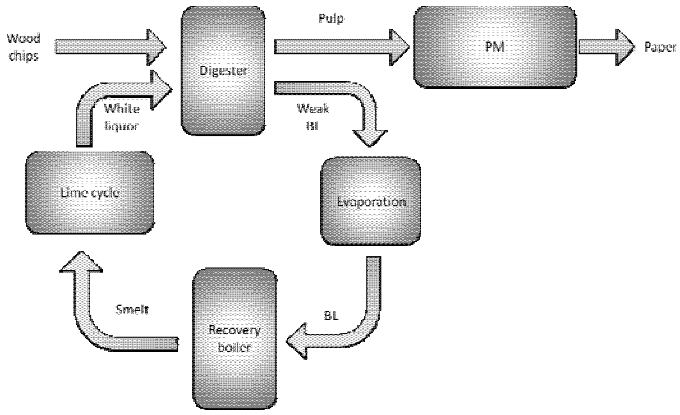

Figure 1: Simplified flow scheme of the Kraft pulping process.

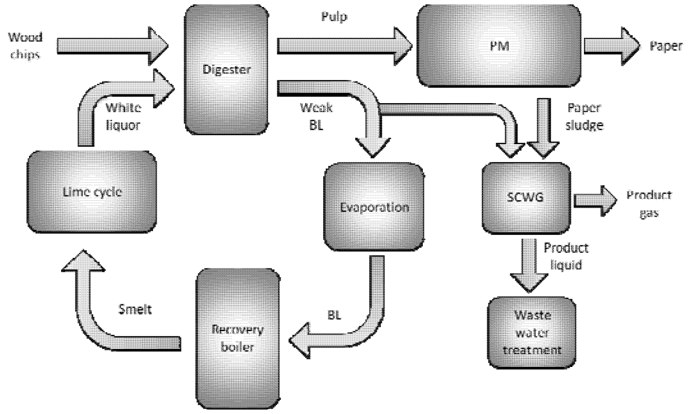

Figure 1: Integration of a SCWG plant, scenario 1.

3.1 Integration scenario 1

The first integration scenario is to gasify primary paper sludge from pulp and paper production together with a side stream of black liquor. The main idea of this integration scenario can be seen in Figure 2. The primary paper sludge is normally treated in the water treatment plant; by gasifying the sludge instead the load on the water treatment is diminished. The product liquid from gasification is however sent to the waste water treatment and the load on the waste water plant can be assumed to be equal to having no gasification plant.

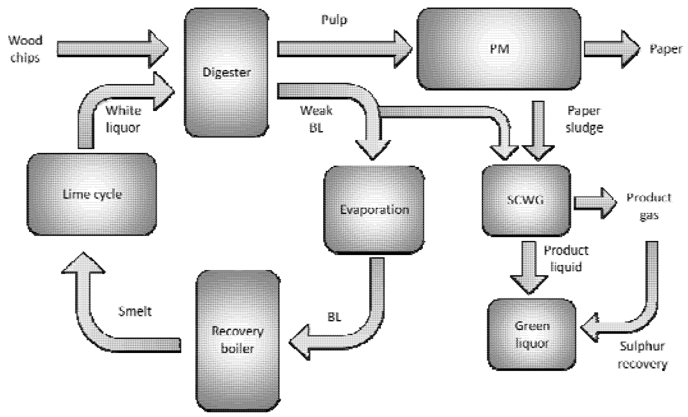

Figure 2. Integration of a SCWG plant, scenario 2.

3.2 Integration scenario 2

In the second integration scenario the gasification plant is a step more integrated in the pulping process, the integration scheme is illustrated in Figure 3. In this scenario the product liquid from gasification is added to the green liquor and the sulphur in the product gas is recovered in an acid gas removal unit and recycled back to the pulping process in the green liquor. In this way the load on the water treatment system is decreased. This scenario builds upon the assumption that the product liquid from gasification can be added to the green liquor, this hypothesis needs to be further investigated.

4. Results and discussion

In an earlier study have process parameters such as residence time and temperature been investigated as well as different sources of biomass (Myréen et al., 2010). The study showed that the gasification process is applicable for several types of biomass and by controlling process parameters the desired product can be achieved. The gasification results for the different raw materials are shown in Table 2. In the table the HHV of the product gas is calculated as MJ/kg dry feed in order to include the effect of the gasification efficiency. With higher gasification efficiency the HHV would be increased for the three raw materials; in the experiments for this study only the Paper sludge 1 has a higher HHV than the raw material had intially.

If the primary sludge produced at Kaukas pulp and paper mill would be gasified the thermal efficiency of the waste would be increased by 50 % from roughly 5 MWth to 7.5 MWth. Considering that the carbon gasification efficiency is low and that the gasification yield and efficiency can be increased by adding black liquor there is potential in increasing the thermal efficiency of the waste product even more.

Table 2: Gasification yield, carbon gasification efficiency and HHV for the product gas.

Mole gas/kg dry feed	Black liquor	Paper sludge 1	Paper sludge 2
H_2	5.61	15.52	1.89
CO_2	6.20	16.02	7.28
C_2H_4	0.05	0.00	0.13
C_2H_6	0.80	0.42	0.30
H_2S	0.00	0.00	0.00
CH_4	5.10	4.3	1.87
CO	0.04	0.00	0.24
Carbon GE (%)	49 %	27 %	50 %
HHV of the product gas (MJ/kg dry feed)	9.2	13.4	5.1

5. Conclusions

The integration of a gasification plant in an existing pulp and paper mill will facilitate production of more valuable products than the heat that is generated today. An integration of a SCWG plant would facilitate a development of a traditional pulp and paper mill into a modern-day biorefinery. Future research in the field of recycling of chemicals in the pulping process is essential in design of the industrial scale SCWG plant. The recycling of chemicals is an important issue for the size of the integrated plant. The reactor material and construction of the gasification plant is as well important issues. Before an industrially applied SCWG process can be built a cost efficient way more research needs to be done.

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