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Unit operations for production of Clean Hydrogen-Rich Synthesis Gas from gasified biomass

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ABSTRACT
The rebuild of the Växjö Värnamo Biomass Gasification Center (VVBGC) integrated gasification combined cycle (IGCC) plant into a plant for production of a clean hydrogen rich synthesis gas requires an extensive adaptation of conventional techniques to the special chemical and physical needs found in a gasified biomass environment. The CHRISGAS project has, in a multitude of areas, been responsible for the research and development activities associated with the rebuild. In this paper the present status and some of the issues concerning the upgrading of the product gas from gasified biomass into synthesis gas are addressed. The purpose is to serve as an introduction to the scientific papers written by the partners in the consortium concerning the unit operations of the process.

1. Introduction

The CHRISGAS project, financed by the European Commission and the Swedish Energy Agency, has carried out research and development activities in a multitude of areas for over 5 years concerning the rebuild. In this paper the present status and issues concerning the upgrading of the product gas from gasified biomass into synthesis gas are addressed. The purpose is to serve as an introduction to the scientific papers produced by the partners in the consortium concerning the unit operations. The aim of the CHRISGAS (Clean Hydrogen-Rich Synthesis Gas) project was to support the rebuild of the VVBGC (Växjö Värnamo Biomass Gasification Center) demonstration plant from an IGCC (Integrated Gasification Combustion Cycle) plant into a synthesis producing unit with research and development [1]. Synthesis gas is a gas mixture of carbon monoxide, carbon dioxide and hydrogen which can be used for synthesis of different chemicals, for instance, synthetic liquid fuels such as methanol, di-methyl ether (DME) or Fischer-Tropsch diesel. The ratio between the different gases may vary depending on what synthesis process is used. Traditionally, synthesis gas is produced from fossil fuels such as natural gas or coal, but any carbon based fuel can be used. At the VVBGC plant the synthesis gas is to be produced by gasification of biomass – a renewable energy source.

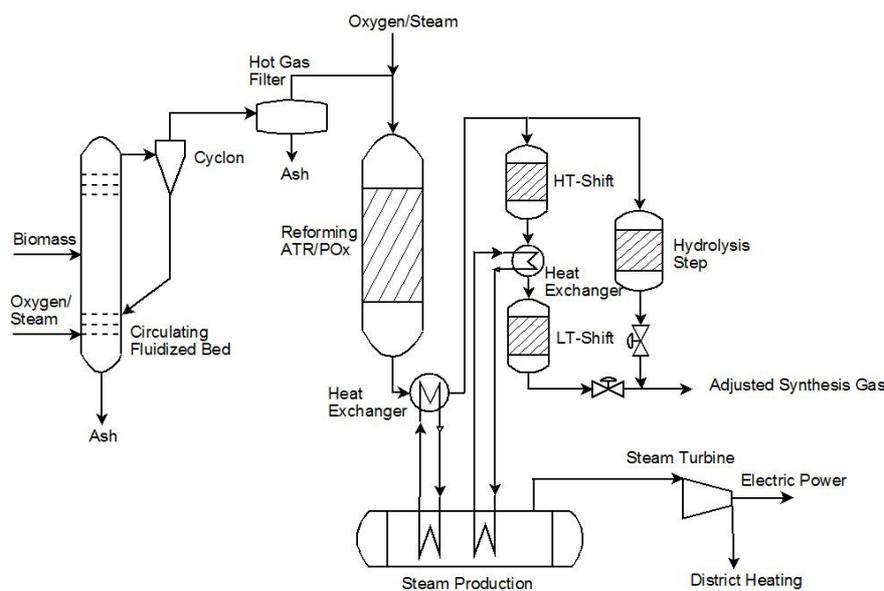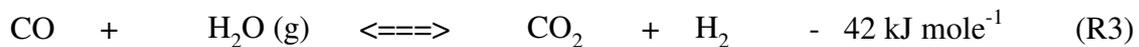Fig. 1 shows the configuration of the VVBGC plant after the planned rebuild. Modifications of old and introduction of new unit operations include:

1) The gasifier

2) The hot gas filter

3) The reformer unit

4) The shift reactor

Subsequent gas cleaning systems for removing contaminates such as sulphur, tars, ammonia etc., prior to the expected synthesis step(s) were not included in the CHRISGAS project.

2. The gasifier [1, 2]

In principle, thermochemical conversion of a biomass particle always begins with a drying step followed by a pyrolysis step, i.e. heating in an inert atmosphere. If the heating rate of the particle is fast, these processes will more or less coincide. Three phases are obtained in pyrolysis: a solid residue, char, consisting mainly of carbon and ash; a gas phase containing mainly carbon monoxide, carbon dioxide, hydrogen, methane, some C2-C3 hydrocarbons and light aromates; and a condensable phase consisting of tar and water. If more or less reactive gases such as oxygen, steam or carbon dioxide are present, the carbon in the solid residue will react with these and eventually also become gaseous. The final product gas composition will thus be the result of a multitude of different parallel and sequential heterogeneous as well as homogenous reactions. Char conversion takes place through a number of reactions, the most important being:

$$C \quad + \quad CO_2 \quad \Longleftrightarrow 2 \quad CO \qquad\qquad +172 \text{ kJ mole}^{-1} \qquad (R1)$$

$$C \quad + \quad H_2O(g) \quad \Longleftrightarrow \quad CO \quad + \quad H_2 \qquad +130 \text{ kJ mole}^{-1} \qquad (R2)$$

$$CO \quad + \quad H_2O \ (g) \quad \Longleftrightarrow \quad CO_2 \quad + \quad H_2 \qquad - \ 42 \text{ kJ mole}^{-1} \qquad (R3)$$

$$C \quad + \ 2 \ H_2 \quad \Longleftrightarrow \quad CH_4 \qquad\qquad\qquad - \ 71 \text{ kJ mole}^{-1} \qquad (R4)$$

The first two reactions are the main gasification reactions, indicating that gasification consumes energy. This energy may be obtained by letting oxygen react with part of the char as follows:

$$C \quad + \ 1/2 \ O_2 \quad \Longleftrightarrow \quad CO \qquad\qquad\qquad -109 \text{ kJ mole}^{-1} \qquad (R5)$$

$$C \quad + \quad O_2 \quad \Longleftrightarrow \quad CO_2 \qquad\qquad\qquad -390 \text{ kJ mole}^{-1} \qquad (R6)$$

The energy needed for the endothermic gasification reactions (R1 and R2) above may also be supplied via sensible or indirect heat. If air is used as gasification agent the product gas will be diluted by nitrogen. Air gasification gives a relatively poor-quality gas (4–6 MJ Nm^{-3}) which is suitable for boilers but not for engine and turbine operation. One alternative to improve the gas quality, i.e. increase the heating value of the gas is to employ oxygen/steam instead of air as the gasification agent. Oxygen/steam gasification gives a better-quality gas (10–15 MJ Nm^{-3}) which is more suited for use as synthesis gas for subsequent upgrading to transportation fuel liquids or chemicals. Additionally, oxygen/steam gasification, in contrast to air gasification, gives a product gas with higher hydrogen content and also allows for a better possibility to tune the gas composition. Gas of this higher quality can also be produced through steam gasification, if the energy is externally supplied.

Many types of gasifiers with varying schemes for both reactor design and reaction media may be found. The most common types are counter- and co-current fixed beds, bubbling, circulating and fast fluidised beds. The gas flow is lowest in fixed-bed gasifiers, higher in bubbling beds and highest in the fast fluidised beds. The biomass capacity per unit cross-sectional area is thus largest for these beds. The processes can be either atmospheric or pressurised. The VVBGC gasifier today is an air-blown 18 MWth pressurised fast circulating fluidised bed gasifier (CFBG), providing a high capacity per unit cross-sectional area. It operates at a temperature above 900 °C for minimising tar levels and maximising char burnout. The bed material is MgO-based, as it allows for relatively high gasification temperatures. The pressure is about 2 MPa; a compressor will adjust to the pressure necessary

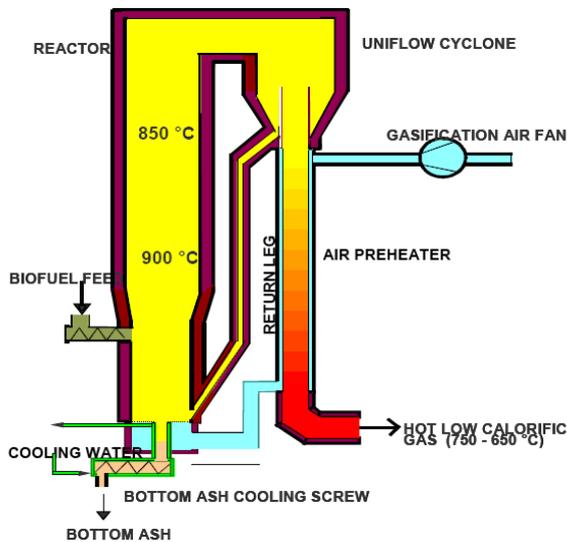for the subsequent synthesis processes. A schematic of the CFB gasifier concept is shown in Fig. 2 below.

Fig. 2 – Schematic of CFB gasifier concept

In a CFBG, the gas is introduced in the bottom, at a flow rate higher than the minimum fluidised bed velocity, and blown through a sand bed. This bed is not as thick as the bed in a bubbling fluidised bed gasifier (BFBG). The sand will be mixed with the fuel and a portion of the char and sand will, together with the gas, leave the reactor at the top and enter a subsequent cyclone, where the solids are separated from the gas and returned to the gasifier. Thus the char particles will encounter longer average reaction times in comparison to the gas compounds. In large CFBG-gasifiers is it preferable to use a number of smaller cyclones in parallel instead of one large cyclone. In gasifiers with a good and relatively long contact time between char and gas (bubbling fluidised bed gasifiers) the water gas shift equilibrium (R3) will usually be reached. However, the methane concentration will normally be far from the equilibrium because methane is primarily formed through tar decomposition, not via the methanisation reaction as shown above (R4). In the faster circulating fluidised bed gasifiers it is questionable if the water gas shift equilibrium (R3) can be reached. The presence of tar may be problematic during gasification. The amount of tar may be decreased by, if possible, increasing the temperature, for example, by adding additional oxygen. Catalysts may also be used for decomposing the tar. Char can be used as catalyst, but the result is often limited. An alternative inexpensive catalyst is calcined dolomite (CaO-MgO). Dolomite does not perform well in pressurised systems when the carbon dioxide partial pressure exceeds ≈ 1 atm, since the calcined dolomite then will revert to $MgCO_3$-$CaCO_3$. There is also the possibility of using more expensive catalysts, such as Ni-based, for tar decomposition. Biomass does not only contain carbon, hydrogen and oxygen; additional elements include nitrogen, chlorine and sulphur. Therefore the resulting gas will contain small amounts of a variety of contaminants, such as ammonia, hydrogen sulphide, carbonyl sulphide and hydrogen chloride. The ammonia will come from the fuel bound nitrogen. Ammonia can be an environmental problem, as nitrogen oxides (NOx) might be formed at some stage downstream. The chemistry of the nitrogen conversion during gasification of biomass is not fully understood today. One theory is that HCN is first formed, and then converted into ammonia. Usually about 70% of the fuel-bound nitrogen is converted into ammonia, HCN and NOx, and with the balance becoming N_2.

3. The hot gas filter

The hot gas filter shall remove dust, fly ash and char particles from the gas, to prevent clogging and contamination of downstream units. It would be relatively easy to reduce the gas temperature and then use standard filter equipment to clean the gas. This means, however, that the gas has to be re-heated, either by an external source, or by releasing a part of the chemically bond heat in the gas, resulting in loss of the already moderate, heat content of the gas. Thus a high temperature ceramic candle filter would be preferable. If the filter can be designed to work at 650 °C a large portion of heat in the gas stream may be preserved instead of being used for re-heating. Additionally attempts have been made to activate the ceramic wall in the filter with a catalyst, making the filter active for tar and methane decomposition. One of the main efforts in the CHRISGAS project was to test, investigate and optimize the hot gas filter design and performance in a biomass derived steam/oxygen gasification environment by improving removal efficiency, dust cake cleaning and related issues.

Table 1 – Estimated composition of the synthesis gas in Värnamo (Equilibrium calculations).

Component	After gasifier (vol %)	After ATR 1000 °C (vol %)	After POX 1300 °C (vol %)
Inlet O_2		6.5	9
Inlet Temperature °C		800	800
C2-hydrocarbons	1.6	-	-
CH_4	8.2	-	-
CO	12	17	17
CO_2	28	19	18
H_2	12	23	16
H_2O	38	42	49
NH_3	0.3	0.2	0.2
H_2S	0.01	0.01	0.01
Tars	0.3	-	-
LHV MJ kg^{-1} (wet)	4.6	3.8	3.2
LHV MJ Nm^{-3} (wet)	6.0	4.6	3.9

4. The reformer unit

The unconverted hydrocarbons in the produced gas represent a large part of the heating value of the produced gas; CH_4 + C2 about 50%, and the tars about 10–20% of the LHV [7]. This means that the hydrocarbons must be converted into synthesis gas if the process should have good efficiency. This is done in the reformer unit. Reforming of hydrocarbons is an old, well

proven industrial process where the hydrocarbon reacts with steam forming CO, CO_2 and H_2; as, for example, the reaction with methane:

$$CH_4 + H_2O ==> CO + 3H_2 \qquad\qquad \Delta H = 206 \text{ kJ mole}^{-1} \text{ } CH_4 \qquad\qquad (R7)$$

The reaction is endothermic, i.e. it consumes heat. This means that heat has to be added to the reactor, otherwise the temperature will drop and the reaction will eventually stop. In classical steam reforming, the reactor is heated by an external source. This means that the heat must be transferred through the reactor wall. Since high temperature and pressure mean material issues, steam reforming is conducted at relatively low temperature (about 850 °C) with a water to carbon ratio of about 3 [4]. This is due to the equilibrium between methane and the synthesis gas. If more water is added the equilibrium state of the gas is shifted in favour of the conversion of methane. The conversion of methane is unfavoured of an increased pressure due to the equilibrium. This is an important thing to remember since the gasification processes in industrial scale are usually pressurized. In Fig. 3 the equilibrium conversion of methane is shown for 1, 10 and 20 bar at a steam/C-ratio of 3.
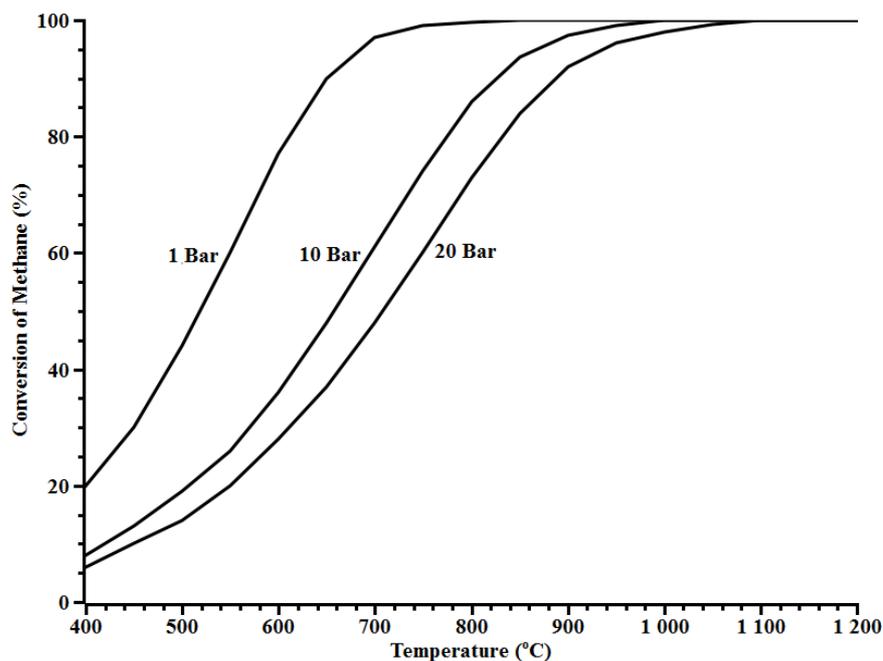

Fig. 3 – Equilibrium Conversion of methane into synthesis gas (CO, CO_2 and H_2) versus temperature with steam/C-ratio of 3. Calculations performed at 1, 10 and 20 bars pressure. Calculations performed with HSC Chemistry 6.1.

Since it is difficult to obtain full conversion of the hydrocarbons, especially for methane, a secondary reformer unit is often used. In this type of reformer air or oxygen is added to a part of the gas and burnt in a burner within the reactor itself. The reactor is lined with a high temperature resistant ceramic layer, making it possible to use temperatures of 1000–1100 °C inside the reactor. This type of reactor has been developed into a stand alone process called Autothermal Reforming (ATR), mainly used for gaseous fuels like methane. The catalysts used both for steam reforming and ATR are based on nickel. Unfortunately these nickel catalysts are sensitive to sulphur compounds and fossil fuels, like natural gas, thus require

desulfurisation before the reforming step. However, the biomass generated gas will contain between 50–150 ppm (Table 1) of hydrogen sulphide, H_2S, and there is no obvious way of removing it prior the reforming step. The sulphur poison of the catalyst strikes especially hard against the methane reforming; the heavier hydrocarbons can be reformed despite of the high sulphur content. It might, however, be possible to successfully convert the methane at the high temperature present in an ATR unit [6,7]. This is due to the fact that:

a) The rate of reaction increases with temperature.

b) The coverage of sulphur on the catalyst nickel surface decreases with temperature.

This has also been demonstrated in laboratory tests during the CHRISGAS project [7, 8]. However, operating at higher temperatures than conventional will increase the rate of sintering of the catalysts; at least if the catalysts have high loading of nickel. In the project, new Rh based reforming catalysts have been tested with promising results. The Rh is, however, very expensive.

An alternative option to the conventional methane and hydrocarbon reformation alternatives discussed above would be to employ monolith catalysts. This would allow for the use of catalysts even in dusty environments, which can be advantageous if problems arise with the high temperature filter. For this a suitable catalyst, for example nickel, may be applied on the monolith surface. If monolith catalysts are to be used though the fuel ash may not melt, hence deactivating the catalyst. Thus the temperature must not exceed the ash melting point. Additionally, as the decomposition of methane is endothermic the reaction heat must be supplied in-situ. One way of doing this could be to stage the oxygen supply, hence mount the monolith catalyst in sections. The staging is for preventing the peak-temperature to become too high. Computations indicate that the temperature in the reformer will drop by about 50 °C per % decrease in absolute methane concentration. Hence a 10% initial methane concentration will correspond to a ~ 500 °C total drop in temperature. Therefore an absolute 10 % decrease in methane concentration calls for ~3–4 monolith sections with oxygen addition in between the sections for maintaining an acceptably high temperature throughout the whole reformation process. The temperature should preferably not go below 850 °C. The minimum temperature limitation is for reasons of reaction kinetics as well as for equilibrium considerations. If the catalytic approach fails, however, there is still the possibility to use a non catalytic process, i.e. Partial Oxidation (POX). This process uses a very similar reactor as ATR, but without the catalytic bed. Both ATR and POX utilize an open flame in the reactor to generate the heat necessary for the temperature increase in the reactor. Figs. 4a and 4b show the result of a kinetic simulation of partial oxidation in, and above, a burner stabilized premixed flat flame, a simplified model of the real case. Input data for the simulation is the gas composition "After gasifier" in Table 1, an inlet temperature of 1073 °C and a pressure of 1 bar (isobaric operation). As oxidizer, 12 vol% of oxygen is added in the inlet. The simulation can be regarded as a POX reaction taking place in an adiabatic tube with the burner at the entrance. As can be seen in Fig. 4a the temperature peaks at 1300 °C after approximately 35 ms, representing the flame peak. After this, the temperature decreases due to the endothermic reforming reaction while the gas travels down the tube, away from the burner. The temperature drop is about 40 °C during the 3 seconds the simulation lasts. The reason for the moderate temperature drop is that the concentration of hydrocarbon to convert in the product gas is low. However, the temperature drop is sufficient to almost stop the reaction and the remaining amount of methane decreases very slowly (Fig. 4b).
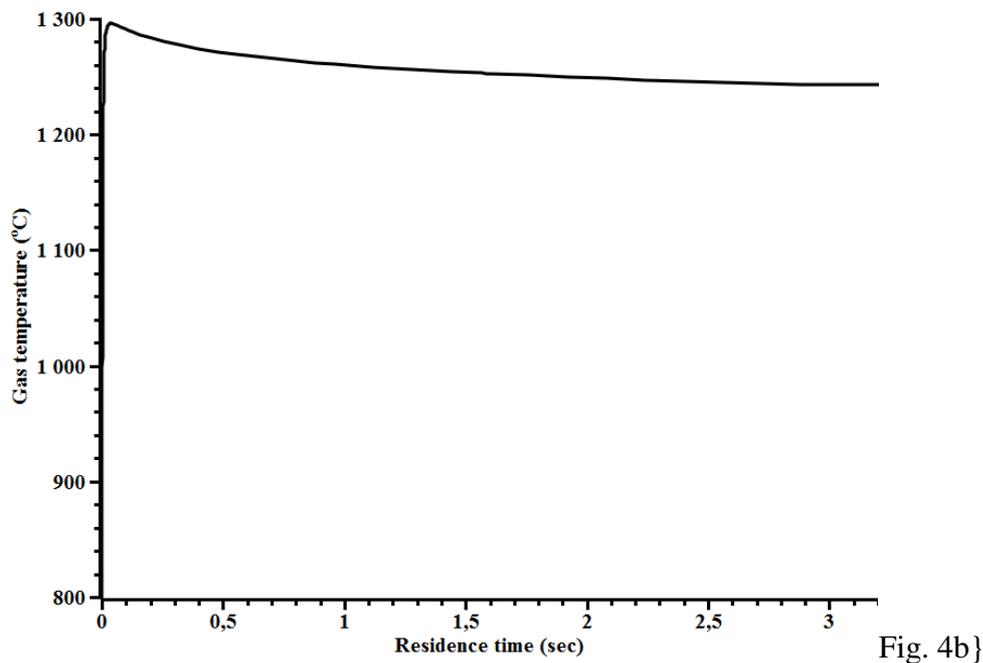
Fig. 4b}

Fig. 4a – Adiabatic flame temperature versus residence time. Simulation of a burner stabilized, pre-mixed and adiabatic flat flame. Simulation done in Matlab with the Cantera toolbox [12] and Gri-mech 3.0 [13] as kinetic model. Input data: Gas composition "After gasifier" in Table 1, Inlet temperature 1073 K, Pressure 1 bar (isobaric).
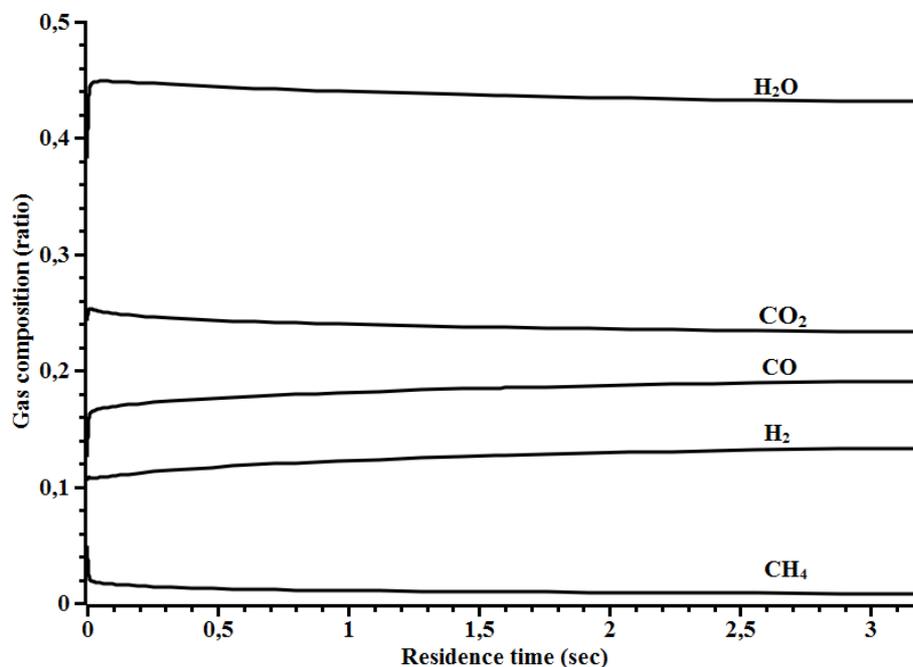

Fig. 4b – Gas composition versus residence time. Simulation of a burner stabilized, pre-mixed and adiabatic flat flame. Simulation done in Matlab with the Cantera toolbox [12] and Gri-mech 3.0 [13] as kinetic model. Input data: Gas composition "After gasifier" in Table 1, Inlet temperature 1073 K, Pressure 1 bar (isobaric)

9

Due to the fact that POX is a non catalytic process, a higher temperature (1200–1400 °C) must be used to run the reforming reactions. This means that yet more of the chemically bonded heat has to be released to increase the temperature than in the case of ATR (See Table 1). Based on a gas composition, after the gasifier in (Table 1), a calculation of the adiabatic equilibrium composition as function of equi-molar O_2/steam addition was performed (Figs. 5a and Fig. 5b).
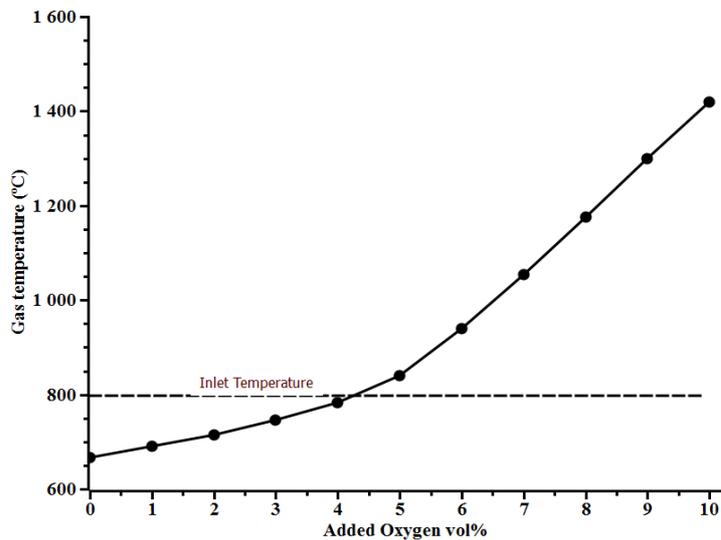

Fig. 5a – Equilibrium adiabatic gas temperature versus added amount of oxygen (equi-molar O_2/H_2O addition at 1073 K). The calculation was done in Matlab with the Cantera toolbox [12], by the use of the chemical equilibrium routine, and the Gri-mech 3.0 [11] as kinetic model. Input data: Gas composition "After gasifier" in Table 1, Inlet temperature 1073 K, Pressure 15 bar (isobaric).
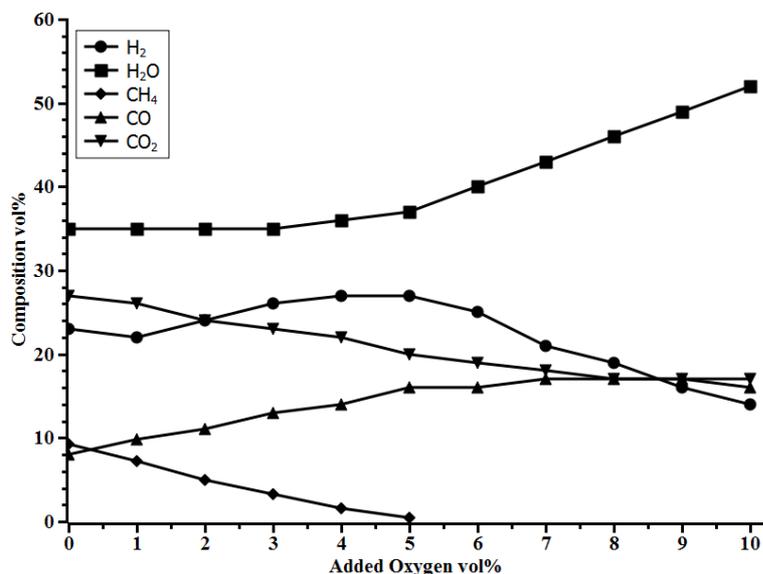

Fig. 5b – Equilibrium gas composition versus added amount of oxygen (equi-molar O_2/H_2O addition at 1073 K). The calculation was done in Matlab with the Cantera toolbox [12], by the use of the chemical equilibrium routine, and the Gri-mech 3.0 [11] as kinetic model. Input data: Gas composition "After gasifier" in Table 1, Inlet temperature 1073 K, Pressure 15 bar (isobaric).

In the calculations the inlet temperature was set to 800 $^{\circ}$C and the total pressure to 15 bars. In Fig. 5a the calculated adiabatic temperature, and in Fig. 5b the calculated gas composition are shown. It can be seen that addition of at least 4 vol% O_2 is required in the reactor to avoid temperature drop. If it is assumed that the ATR requires 1000 °C and the POX 1300 °C, the required oxygen addition becomes 6.5 vol% for the ATR and 9 vol% for the POX. The corresponding gas compositions are given in Table 1.

Table 2 – Required H_2/CO for different synthesis processes.

Product	H_2/CO-ratio
Methanol	2
DME	2
FT	2
SNG	3

5. Water-gas shift step

When the synthesis gas leaves the reformer unit (ATR or POX) the H_2/CO ratio will not be suitable for the subsequent synthesis step. Depending on the synthesis process chosen, the required H_2/CO ratio will differ (Table 2). The ratio between H_2/CO is tuned by the water-gas shift reaction (R3). Due to the fact that the WGS reaction is an exothermic reaction and that the hydrogen content in the gas is limited by the temperature, a two step process (High Temperature (HT) and Low Temperature (LT) steps with cooling in between the reactors is used industrially when the required hydrogen content of the gas is high [4]. The equilibrium state is, however, not affected by the total pressure since this is an equi-molar reaction.
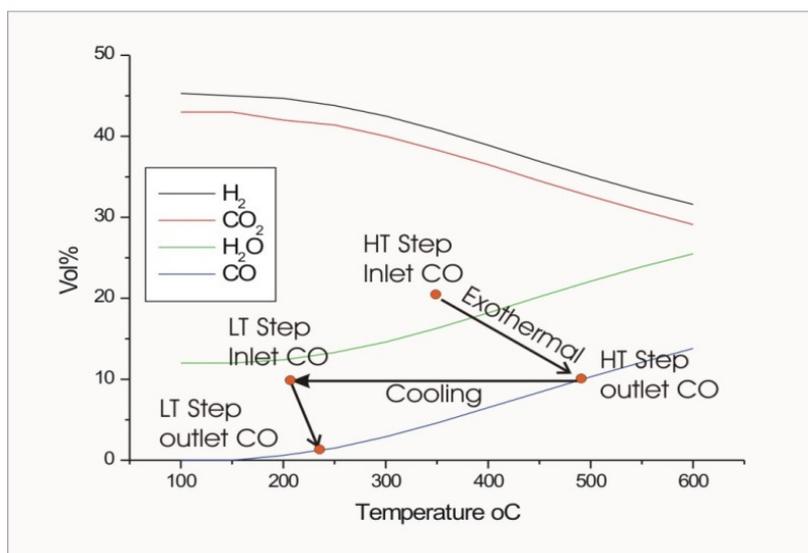

Fig. 6 – Combined High and Low temperature water gas shift step with cooling in between (2)

In Fig. 6 the principal operation of a two step shift unit is shown. The curves drawn represent the equilibrium state of the synthesis gas as a function of temperature. Only the CO that enters the reactor is shown, as a simplification. Since the reactors operate adiabatic, the temperature increases during the reaction limiting the obtainable conversion. The original plan for the Värnamo plant included both HT and LT shift steps. However, if one analyzes the resulting HT shift composition "After ATR" in Table 1 it becomes clear that one HT step suffices for generating a synthesis gas with a H_2/CO ratio of 2–3; thus being suitable for methanol, DME, FT or SNG production.
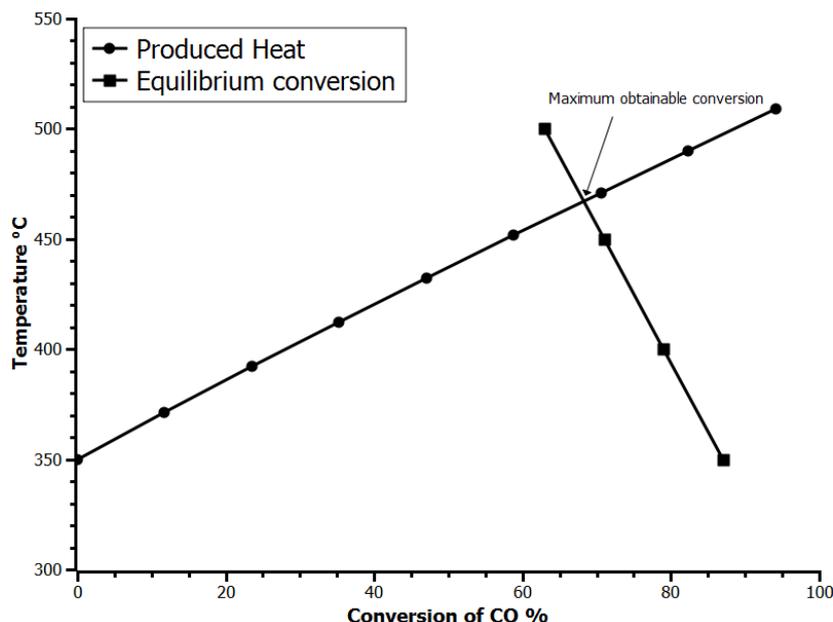

Fig. 7 – Determination of the maximum obtainable water gas shift conversion of CO, in one HT shift steep. Inlet gas composition: "After ATR" in table 1 and inlet reactor temperature of 350 °C.

In Fig. 7 the adiabatic temperature increases (produced heat) due to the reaction enthalpy is plotted versus the conversion of inlet CO in gas for the "After ATR" composition. Overlaid is also the equilibrium conversion in the same gas calculated with HSC Chemistry 6.1. The intersection point represents the maximum obtainable conversion for the given conversion and inlet temperature, 68% at 467 °C. This yields a H_2/CO ratio of 5; sufficient to produce gas for the subsequent synthesis processes, like methanol, DME, or FT. To obtain a flexible unit, useful for different types of synthesis processes, the H_2/CO ratio should be tunable. This can be achieved by letting part of the synthesis gas bypass the shift steps (Fig. 8).
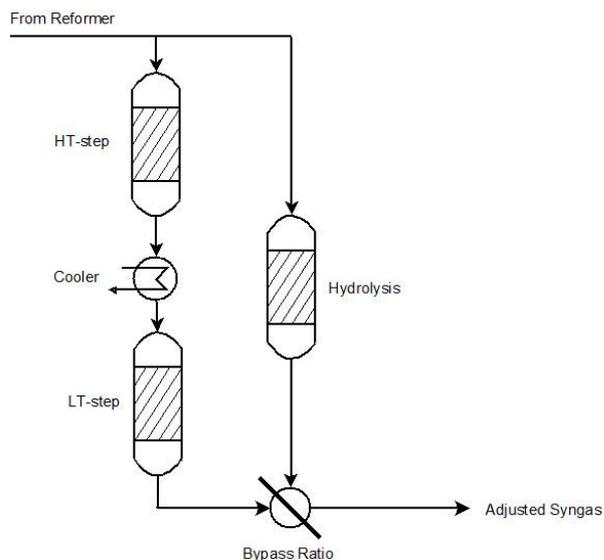
Fig. 8 – Originally planned shift step in the Värnamo, with bypass and hydrolysis reactor.

In this way the H₂/CO ratio can be set by changing the bypass ratio. In the bypass line (Fig. 8) there is a third catalytic reactor, a hydrolysis step. The reason for this step is the presence of carbonyl sulphide, COS, in the gas. Sulphur in the form of carbonyl sulphide cannot be removed from the gas by the same methods that are used for H_2S removal, i.e. absorption by ZnO. The COS is normally converted into H_2S by a hydrolysis reaction [10], assumed to occur in the WGS step:

$$COS + H_2O \longleftrightarrow CO_2 + H_2S \tag{R8}$$

The COS in equilibrium with a gas of initial composition corresponding to "After ATR" in Table 1 is shown in Fig. 9.
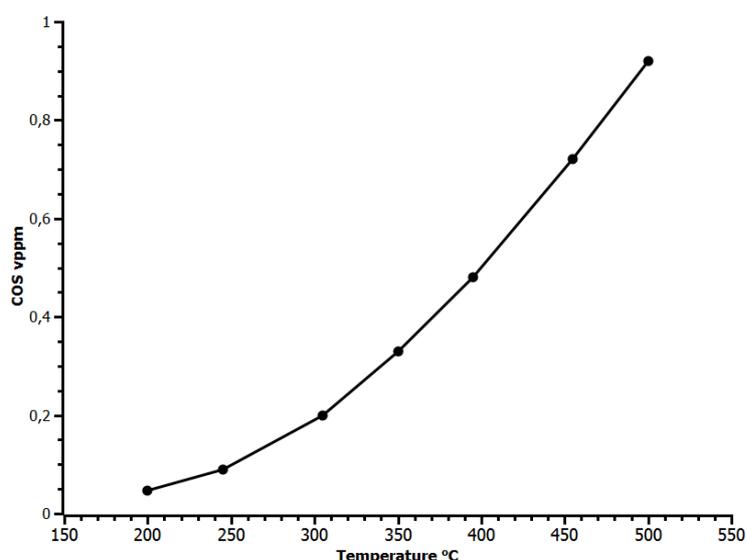

Fig. 9 – Equilibrium carbonyl sulphide (COS) concentration in gas of the "After ATR" composition. Calculated with HSC Chemistry 6.1.

However, if a part of the gas is bypassed in the WGS step, this gas stream will contain COS. This means that a separate hydrolysis step is necessary in the bypass stream. This hydrolysis reaction, and eventually hydrolysis of CS_2 and HCN, is not extensively studied in the project and remains an issue for later work. In the CHRISGAS project the behaviour of WGS catalysts in biomass generated synthesis gases have been investigated and FeCr has been selected as possible useful catalyst. This catalyst seems resistant towards sulphur but is seriously affected by eventual ammonia and volatile chlorides, for instance HCl [11]. The ammonia present in the product gas, 3000 ppm (Table 1), should be decomposed, into N_2 and H_2, in the catalytic reformer step, a process also known as ammonia cracking. However, it cannot be expected that the gas after the reformer is completely free from ammonia; 95% conversion means that there is still 150 ppm of ammonia in the gas. The presence of HCl is more uncertain; the ash and dust is strongly alkaline and should capture the acidic gas. There may, however, be other, yet not identified, volatile chlorides present in the gas with similar impact on the activity. Further work is still necessary to ensure operation of a FeCr based WGS step in an industrial biomass gasification plant. After the WGS step, the synthesis gas will be free from dust and hydrocarbons and the H_2/CO ratio will be suitable for the subsequent synthesis steps. The gas will, however, contain contaminates such as hydrogen sulphide, chlorine and carbon dioxide that must be removed before the subsequent synthesis steps. However, these steps are not included within the CHRISGAS project.

6. Summary

The CHRISGAS project ran for over 5 years and an array of different issues concerning the gasification of biomass and upgrading of product gas into synthesis gas were addressed. New technologies have been developed and old ones have been adapted to the special conditions that emerge in the product gas. There are, however, issues, for instance regarding the catalytic reforming and the water gas shift, that are not resolved and new ones have appeared. The CHRISGAS project has brought the large scale synthesis gas production from gasified biomass closer to realisation, nevertheless the research and development work needs to continue.

REFERENCES

[1] S. Albertazzi, F. Basile, J. Brandin, J. Einvall, C. Hultberg, G. Fornasari, V. Rosetti, M. Sanati, F. Trifiro, A. Vaccari, The Technical Feasibility of Biomass Gasification for Hydrogen Production. Catalysis Today 106 (2005) 297-300.

[2] P. Quaak, H.E. Stassen and H. Knoef. Energy from Biomass: A Review of Combustion and Gasification technologies, World Bank technical paper no. 422, Energy series. The World Bank, Washington, D.C. ISBN 0821343351 (1999).

[3] Thermal Biomass Conversion, Eds: A.V. Bridgwater, H. Hofbauer and S. van Loo, CPL Press, November 2009. ISBN 9781872691534.

[4] Kirm, I. Brandin J., Sanati M., Shift Catalysis in Biomass Generated Synthesis Gas. Topics in Catalysis, Volume 45, number 1-4/August 2007.

[5] Hulteberg C, Brandin J Fuel Production from Gasified Biomass; A Feasibility Study, World Bioenergy Conference Jönköping, Sweden 30 May-1 June. 2006

[6] Koningen J., Sjöström K., Sulfur –deactivated steam reforming of gasified biomass. Ind. Eng. Chem. Res. 37, 1995, pp. 341-346.

[7] Einvall, J.; Albertazzi, S.; Hulteberg, C.; Malik, A.; Basile, F.; Larsson, A.-C.; Brandin, J.; Sanati, M., Investigation of Reforming Catalyst Deactivation by Exposure to Fly Ash from Biomass Gasification in Laboratory Scale. Energy & Fuels 2007; 21(5); 2481-2488.

[8] Albertazzi S., Basile F., Brandin J., Einvall J., Fornasari G., Hulteberg C., Sanati M., Trifirò F. and Vaccari A. Effect of Fly Ash and H2S on a Ni-based Catalyst for the Upgrading of a Biomass-generated Gas. Biomass and Bioenergy , 32(4), 345-353, 2008

[9] Albertazzi S., Basile F., Brandin J., Einvall J., Fornasari G., Hulteberg C., Sanati M., Trifir F. and Vaccari A., Pt−Rh/MgAl(O) Catalyst for the Upgrading of Biomass-Generated Synthesis Gases. Energy & Fuels, 2009, 23 (1), pp. 573–579

[10] Rhodes C., Riddel S., West J., Williams P., Hutchings G., The low-temperature hydrolysis of carbonyl sulfide and carbon disulfide: a review. Catalysis today, V50, 3-4, 2000, pp. 443-464

[11] Einvall J., Parsland C., Benito P., Basile F., Brandin J., High Temperature Water Gas Shift Step in the Production of Clean Hydrogen-Rich Synthesis Gas From Gasified Biomass. Submitted to Biomass & Bioenergy.

[12] Cantera. An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes. http://code.google.com/p/cantera/

[13] Smith G.P., Golden D.M., Frenklach M., Moriarty N.W., Eiteneer B., Goldenberg M., Bowman C.T., Hanson R.K., Song S.,. Gardiner W.C., Lissianski V.V., and Qin Z., Gri-Mech 3.0, http://www.me.berkeley.edu/gri_mech/