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THERMODYNAMIC ANALYSIS OF HIGH TEMPERATURE STEAM GASIFICATION OF BLACK LIQUOR FOR POWER GENERATION

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ABSTRACT

Today gasification of Black liquor at high temperature is a promising alternative to the conventional recovery boiler process used in chemical pulping. This study aims to develop a new conceptual model for black liquor gasification. The mixture of black liquor vapour and water vapour is passed through a regenerative system where the mixture is heated up at high temperature. The regenerative system uses an additional preheating system combusting part of the produced syngas. Hydrogen production increases with increase in steam/fuel ratio and decreases with increase in gasification temperature. For steam/fuel ratio 1.30, maximum hydrogen production is about 55.5%. The mass balance, energy balance of the system has computed to evaluate the efficiency of the system. Also the exergy value of produced syngas has computed. The result shows that both the energy value (LHV) and exergy value increases with the increase of gasification temperature. The maximum exergy 72.5% is achieved at 1100C and steam/fuel ratio 0.30. The largest part of exergy loss occurs in the gasifier which is 23.5%. The analysis also shows that power generation efficiency of the system is favoured by higher gasification temperature but disfavoured by higher steam/fuel ratio at a constant temperature. But in both cases the cold gasification efficiency (CGE) increases.

Keywords: Black liquor, Gasification, Syngas

1. INTRODUCTION

Today it has become very significant to use renewable and CO_2 natural fuels like biomass and waste due to the increased world energy demand and the alarming global warming. In paper industry when wood is converted to pulp by the Kraft process (or sulphate method), the fibre is released by dissolving the other organic constituents of the wood or nonwood lignocellulosics into an aqueous solution containing sodium hydroxide and sodium sulphide. After removal of the fibre product, the remaining spent solution, which is called black liquor, is an important industrial fuel in papermaking countries. It consists mainly of dissolved lignin degradation products from reacting an aqueous solution containing sodium hydroxide and sodium sulfide along with the hemicellulosic and cellulosic hexose and pentose sugars degradation products. Pulp and paper industry producing huge amount of black liquor can play an important role in the respective country energy system.

Gasification of Black liquor at high temperature is a promising alternative to the conventional recovery boiler process used in chemical pulping. Compared to the conventional recovery process, i.e. combustion of black liquor in a recovery boiler, the primary advantage of gasification is the potential to produce bio-fuels and chemicals. Black liquor with an integrated combined cycle has the potential to double the amount of net electrical energy for a Kraft pulp mill compared to an ordinary recovery boiler with a steam turbine. Among the several gasification processes, they can roughly be categorized into two processes. One is low temperature processes that work below 715°C and the other one is high temperature processes which operate above 900°C. For low temperature processes the inorganic salts are removed as dry solid and for high temperature processes the inorganic salts are removed as smelt. The main principal behind these technologies is to spray the black liquor as fine particles into the reactor where the temperature is high enough to gasify the black liquor droplets.

In this study, a conceptual model-high temperature steam gasification of black liquor (HTSG-BL)-has been developed as shown in figure 1. Chemical equilibrium calculation by using CEA code has been done to get the composition of syngas from black liquor gasification for different operational parameters (gasification temperature, steam/fuel ratio and gasifier pressure). Finally mass balance, energy balance, exergy and efficiency have been calculated to evaluate the model.

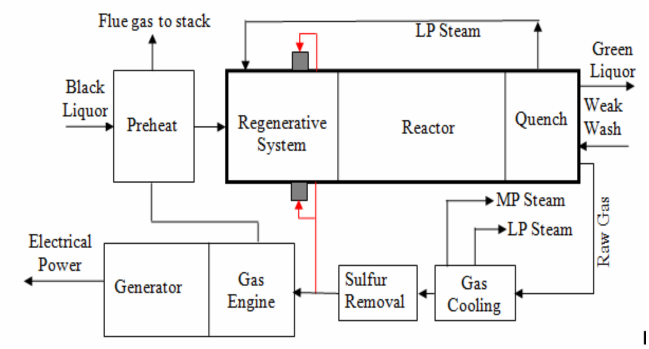

Figure 1: A new conceptual model of high temperature steam gasification of black liquor (HTSG-BL)

A compact regenerative system where a part of product gas is combusted to provide the necessary heat, can be used to produce a preheated mixture of black liquor vapour and steam above 1000C [1]. Figure 2 shows a conceptual model of such equipment.

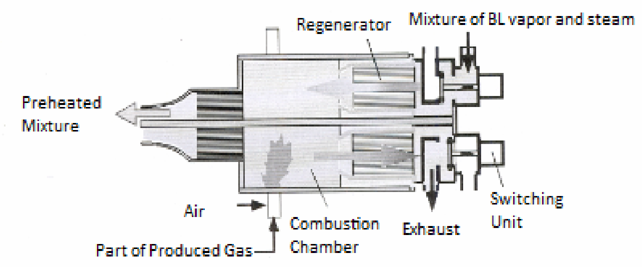

Figure 2: Concept of regenerative system for high-temperature gasification

The regenerator is located at the bottom of a combustion chamber and is heated up by the flue gases. The mixture of BL vapour and steam to be heated passes the regenerator on top and takes up previously stored heat. Heat storage and heat release in the regenerator are repeated periodically when combustion gases and cold BL vapour-agent are alternatively provided to the two regenerators by on-off action of a switching valve located on the low temperature side. The preheated gas continuously discharges from each exit nozzle on the left-hand side section and combustion gas exhausts from the right-hand side section.

2. METHODOLOGY

2.1 Gasification Equilibrium Model

The composition of a mixture at equilibrium can be estimated using different methods. The gasification equilibrium model used here is based on the **CEA** (Chemical Equilibrium with Applications) **code.** This code is suitable for calculations of the equilibrium state of systems comprising of one or more phases. The chief advantage of this method is that it does not require selecting a number of ‘‘representative” chemical reactions allowing the formation of (equilibrium) products; it is nevertheless necessary to establish a list of chemical species inclusive of the ones expected in the product mixture. Other approaches to estimate the product composition are available, such as kinetic/dynamic models [2] and neural network applications [3] allowing in some instances to obtain a better accuracy. Nevertheless, the proposed approach has a more general application with predictive capability, without requiring an extended set of data to fit/train the model itself.

The model considers 78 chemical species. The chosen compounds are combinations of C, H, O, Na and S that are the typical elements of black liquor. The model results show that only a small number of species is present in the product of mixture after gasification in a significant fraction. The black liquor composition was assumed to be $CH_{1.25}O_{0.70}Na_{0.24}S_{0.04}$ which corresponds to typical Kraft liquor with a molar ratio of S/Na is 0.30.The following assumptions were made during the simulation:

1. The residence times of reactants were considered as high in order to reach the chemical equilibrium.
2. Whole carbon contained in fuel is gasified. Therefore, charcoal was not formed
3. The reactions are at thermodynamic equilibrium
4. The reactions proceeds iso-thermally
5. The gasification reactor temperature varied between 700C and 1200C
6. The pressure varied between 1 bar and 35 bar.

7. Steam/fuel ratios varied between 0.30 and 1.30 [mol/mol]

2.2 Model Equation

The steam gasification is represented by the following equation:

$$C_nH_mO_p + wH_2O \rightarrow aCO + bH_2 + cCO_2 + dCH_4$$

Where, n, m and p are number of moles of feedstock compositions; carbon, hydrogen and oxygen respectively. w isNumber of moles of steam (H_2O). a, b, c and d are number of moles of the fuel gases; carbon monoxide, hydrogen, carbon dioxide and methane respectively.

The LHV of fuel gases was calculated by using the following equation [4,5]:

$$LHV[KJ/\ Nm^3] = (30*CO + 25.7*H_2 + 85.4*CH_4 + 151.3C_nH_m)*4.2$$

Where, CO, H_2, CH_4 and C_nH_m are molar ratio of the CO, H_2, CH_4 and hydrocarbon (C_2H_4 and C_2H_6) in the gas product. The energy balance was calculated by the following equations:

$$\sum H_{input} = \sum H_{output}$$

The energy input was calculated by the formulas:

$$\sum H_{input} = H_{CH,BLV} + H_{SG,RS}$$

The chemical energy of feedstock was calculated as follows:

$$H_{CH,BLV} = LHV_{Feedstock} * \overset{o}{m}_{DryFeedstock}$$

Where, $LHV_{Feedstock}$ - Lower heating value of feedstock [MJ/Kg $_{\text{feedstock}}$]

Energy required for the regenerative system:

$$H_{SG,RS} = H_{SS} + H_{BLV}$$

The sensible heat of gaseous mixture at a defined temperature was calculated as the weighted average of the sensible heat for the pure species:

$$H_{mix} = \sum_i h_i$$

$$h_i = h_{i,sensibleheat} + h_{i,latentheat}$$

The sensible heat at a defined temperature relative to the standard state can be computed by the Shomate equation:

$$h_{i,sensibleheat} = A*t + B*\frac{t^2}{2} + C*\frac{t^3}{3} + D*\frac{t^4}{4} - E*\frac{1}{t} + F - H$$

Where t = T/1000

The energy output has calculated by the following formulas:

$$\sum H_{output} = H_{CH,SG} + H_{PH,CG} + H_G + H_{FG}$$

The fuel gas energy was calculated from the following equations:

$$H_{CH,SG} = LHV_{SG} * \overset{o}{m}_{Syngas}$$

$$H_{PH,SG} = \sum_i \left[\overset{o}{m}_{Gi} \int_{T_{in}}^{T_{out}} CpdT \right]$$

Assumptions made during the energy balance:

1. The energy loss in gasifier was assumed to be 10% of the chemical energy of the syngas, i.e. $H_G = 10\% * H_{CH,SG}$
2. The thermal loss through flue gas was assumed to be 5% of energy used in the regenerative system, i.e. $H_{FG} = 5\% * H_{CG,RS}$

The electrical power output from the system is,

$$P_{Electrical} = H_{SGE} * \eta_E * \eta_G$$

Where, H_{SGE} -Energy of syngas used in engine [KW], η_E -Efficiency of engine 30%, η_G -Efficiency of generator 95%

Total exergy of syngas can be found as:

$$E_{total,SG} = E_{CH,SG} + E_{PH,SG}$$

The chemical exergy relative to a standard environmental state (298K and 1 bar) was calculated with:

$$E_{CH,SG} = \overset{o}{m}_{SG} \left[\sum x_i \varepsilon_{0,i} + RT_0 \sum x_i \ln(x_i) \right]$$

The physical exergy relative to a standard environmental state (298K and 1 bar) was calculated with:

$$E_{PH,SG} = \overset{0}{m}_{SG} \left[\left(h_i - h_{0,i} \right) - T_0 \left(s_i - s_{0,i} \right) \right]$$

The entropy of species at different temperatures was also calculated by using the Shomate-equation:

$$s_i = A\ln(t) + B*t + C*\frac{t^2}{2} + D*\frac{t^3}{3} - E*\frac{1}{2t^2} + G$$

Where t = T/1000

For black liquor fuel, thermodynamic properties are not available. Therefore, the statistical correlation of Kotas was used to calculate the exergy of formation for black liquor [6]:

$$E_{BL} = LHV_{BL} \left[\frac{1.0438 + 0.1882 \frac{g_{H_2}}{g_C} - 0.2509 * \left(1 + 0.7256 \frac{g_{H_2}}{g_C} \right) + 0.0450 \frac{g_{Na}}{g_C}}{1 - 0.3035 \frac{g_{0_2}}{g_C}} \right]$$

Where, LHV_{BL} is the lower heating value i.e net enthalpy of combustion of black liquor and g_{H_2} , g_C , g_{O_2} , g_{Na} are the mass fraction of hydrogen, carbon, oxygen and sodium respectively.

The net electrical efficiency of the system [%]

$$\eta_{Total} = \frac{P_{Electrical}}{\overset{0}{m}_{Feedstock} * LHV_{Feedstock}} * 100\ \%$$

The cold gasification efficiency (CGE) is a measure of gasifier performance. It is defined as the ratio of energy in the gas and the energy contained within the fuel.

$$\eta_{CGE} = \frac{LHV_{gas} * V^{0}_{gas}}{\overset{0}{m}_{Feedstock} * LHV_{Feedstock}} * 100\ \%$$

3. RESULT AND DISCUSSION

3.1 Syngas Composition

The CEA code enabled to obtain the syn gas composition after gasification of black liquor. Among the 78 species only several species are presented in the gasification product in a significant percentage. The quench-cooler is used to separate the products exiting the reactor (gases and smelt). Table 1 shows the syngas molar composition equilibrium calculations for different operational parameters (reactor temperature, steam/fuel ratio and reactor pressure). Smelt generally consists of inorganic salts like Na_2CO_3, Na_2SO_4, Na_2S, NaOH, Na+, COS etc.

Table 1: Gasification conditions and syn gas compositions for black liquor

Case number	1	2	3	4	5	6	7	8
Temperature(^{0}C)	900	1000	1100	1100	1100	1100	1100	1100
Pressure(bar)	1	1	1	1	1	1	5	10
Steam/fuel ratio	0.30	0.30	0.30	0.48	0.66	0.84	0.30	0.30
CH_4(mole %)	0.59	0.25	0.11	0.0044	0.0021	0.0011	0.71	1.44
CO(mole %)	43.17	47.23	51.86	46.65	39.35	32.88	45.22	43.73
CO_2(mole %)	0.52	0.16	0.06	1.21	2.64	3.89	0.23	0.44
H_2(mole %)	54.88	52.07	47.86	49.33	50.97	51.92	53.29	53.32
H_2O(mole %)	0.84	0.29	0.11	2.80	7.03	11.33	0.55	1.06
H_2S(mole %)	0.00	0.00	0.00	0.0012	0.0032	0.0081	0.00	0.0011
LHV(MJ/Nm^3)	9.66	10.06	10.52	10.00	9.50	9.20	9.90	9.80

The yields of the different species as a function of steam-fuel ratio is presented in figure 3. Analyzing the thermodynamic equilibrium composition of syngas in figure 3, it can be seen that hydrogen and carbon dioxide formation are favoured at higher steam-fuel ratio and at lower steam-fuel ratio carbon monoxide and methane are the dominant equilibrium products. It also can be seen that the LHV decreases from 10.52 MJ/Nm^3 to 8.20 MJ/Nm^3 with increasing steam-fuel ratio from 0.30 to 1.30 respectively.

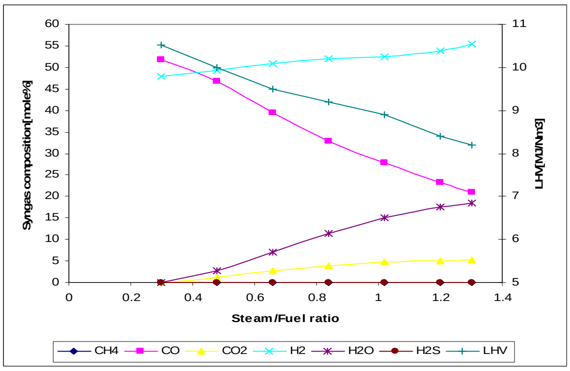

Figure 3: Syn gas equilibrium composition and LHV vs. steam/fuel ratio at temperature 1100^{0}C and pressure 1 bar.

Analyzing the thermodynamic equilibrium composition of fuel gas as a function of temperature, it can be seen that carbon monoxide formation is favoured at higher temperature and at lower temperature hydrogen, carbon dioxide and methane are the dominant equilibrium products. The LHV also increases with increasing temperature.

3.2 Quality of Syngas

Figure 5 shows the energy value (LHV), the exergy value of the produced syngas, hydrogen/carbon monoxide ratio and carbon dioxide/ carbon monoxide ratio as a function of the gasification temperature. By analyzing the figure it is clear that the higher gasification temperature has beneficial effect on the both energy and exergy density of the produced gas. This is mainly due to the fact that as the gasification temperature increases the dilution by carbon dioxide decreases. The figure also shows that the hydrogen/carbon monoxide ratio and carbon dioxide/ carbon monoxide ratio also deceases from 2.38, 27.52 to 0.86, 0.04 respectively as the gasification temperature increases from 700^0 C to 1200^0 C respectively. It is also clear that the decreasing ratio for carbon dioxide/ carbon monoxide is more stripper than the decreasing ratio for hydrogen/carbon monoxide. Figure 4 also shows that for a corresponding temperature rise the exergy value increases more rapidly than the energy value of produced syngas for the same temperature rise.

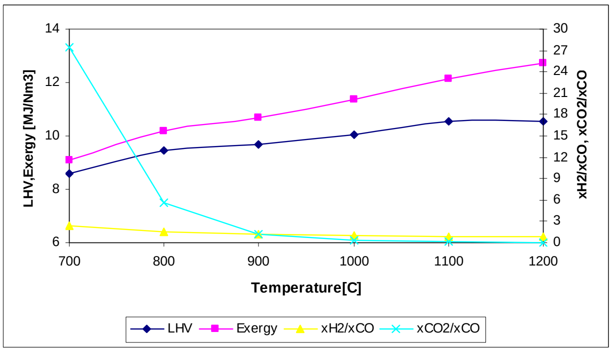

Figure 4: Energy value (LHV), Exergy value, xH2/xCO, xCO2/xCO of the produced syn gas as a function of temperature at pressure 1 bar, steam/fuel ratio 0.30

The quality of syngas has also been analyzed for different steam/fuel ratio. Figure 5 shows the hydrogen/carbon monoxide ratio, carbon dioxide/ carbon monoxide ratio as a function of the steam/fuel ratio. Analyzing the figure it can be seen that both the hydrogen/carbon monoxide ratio and carbon dioxide/ carbon monoxide ratio increases with increasing steam/fuel ratio. This increase is mainly due to the fact that hydrogen and carbon dioxide formation are favoured at higher steam/fuel ratio and at the same time carbon monoxide formation is disfavoured at higher steam/fuel ratio which is well described in figure 3. Actually, hydrogen and carbon dioxide formation is favoured mainly for the so-called water gas reaction ($C+H_2O = CO+H_2$) and the water gas shift reaction ($CO+H_2O = CO_2+H_2$) by the addition of steam as a gasification agent.

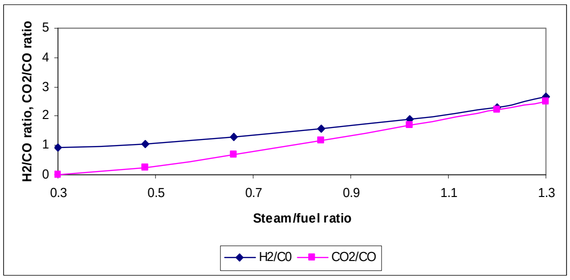

Figure 5: H_2/CO ratio and CO_2/CO ratio of the produced syn gas as a function of steam/fuel ratio at pressure 1 bar and temperature 1100^0 C

3.3 Energy and Exergy Flow

In figure 6, an energy flow diagram of the gasifier model with T=1100C, P=1 bar and steam/fuel ratio 0.30 is shown. Also in figure 7, an exergy flow diagram of the gasifier model with T=1100C, P=1 bar and steam/fuel ratio 0.30 is shown. It is seen that energy loss in gasifier is higher than loss through flue gas. The physical energy of syngas is 15% of the total out put energy which could be utilized to produce steam.

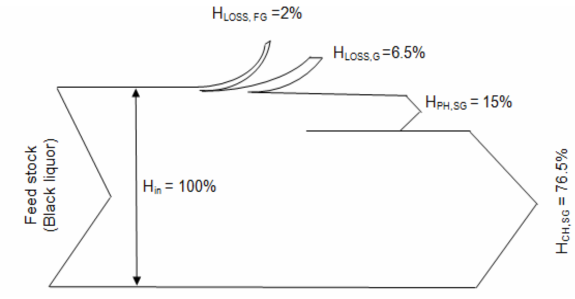

Figure 6: Energy flow diagram for gasifier energy model at temperature 1100^0C, pressure 1 bar and steam/fuel ratio 0.30

The largest part of exergy loss occurs in the gasifier, where the highly order chemical energy of feedstock converted into chemical energy of fuel gas and heat. The exergy loss in the gasifier decreases with the increase of gasification temperature. In this gasifier model total exergy loss is 27.5%. But from figure 6 it is clear that total energy loss for the same model is only 8.5% of the total out put energy.

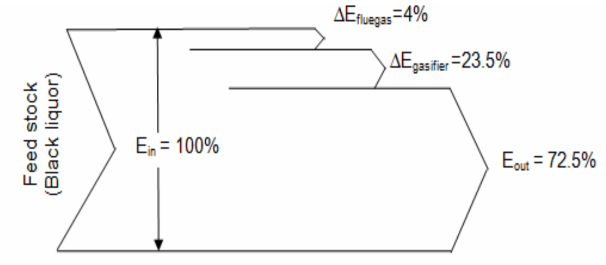

Figure 7: Exergy flow diagram for gasifier model at temperature 1100^0 C, pressure 1 bar and steam/fuel ratio 0.30

3.4 Efficiency

The total system efficiency and cold gasification efficiency as a function of gasification temperature is presented in the figure 8. Both the system efficiency and cold gasification efficiency increases with the increase of temperature.

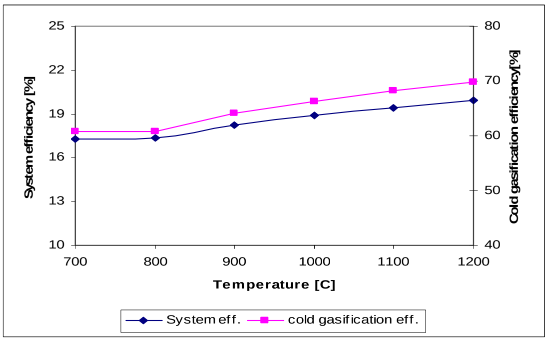

Figure 8: System efficiency and cold gasification efficiency vs. temperature at pressure 1 bar and steam/fuel ratio 0.30

The total system efficiency and cold gasification efficiency as a function of steam/fuel ratio is presented in the figure 9.

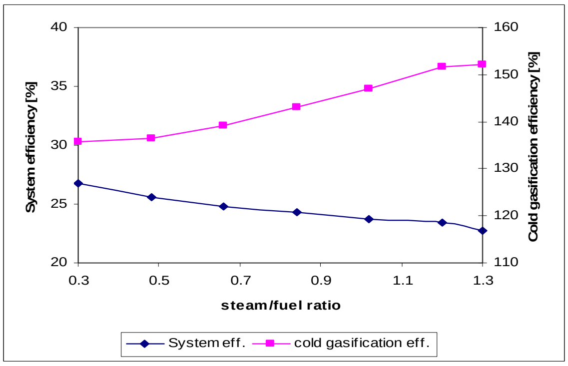

Figure 9: System efficiency and cold gasification efficiency vs. steam/fuel ratio at temperature 1100C and pressure 1 bar.

4. CONCLUSIONS

This study aimed to understand the thermodynamic limitations and advantages of a new conceptual black liquor gasification model-direct heating of black liquor vapour and steam mixture by using an additional preheating system that uses part of the syngas produced. The system has been studied both for varying steam/ fuel ratio and gasification temperature.

- Though thermodynamic equilibrium calculation does not give the full picture of the real process but it shows the trend of the results. To get the better result it should be supported with kinetic studies.
- The steam/fuel ratio and gasification temperature has a strong influence on syngas quantity and quality. Hydrogen/carbon monoxide ratio increases from 0.92 to 2.66 for the increase in steam/fuel ratio from 0.30 to 1.30 respectively.
- Hydrogen production increases with increase in steam/fuel ratio and decreases with increase in gasification temperature. For steam/fuel ratio 1.30, maximum hydrogen production is about 55.5%.
- LHV decreases from 10.52 MJ/Nm^3 to 8.20 MJ/Nm^3 with increase in steam-fuel ratio from 0.30 to 1.30 and it increases from 8.57 MJ/Nm^3 to 10.55 MJ/Nm^3 with increase in gasification temperature from 700C to 1200C respectively.
- Both the energy density and exergy density of produced gas increases with the increase in gasification temperature.
- The maximum exergy 72.5% is achieved at 1100C and steam/fuel ratio 0.30. The largest part of exergy loss occurs in the gasifier which is 23.5%.
- The net electrical power generation efficiency decreases with increasing steam/fuel ratio but it increases with increasing gasification temperature. Power generation efficiency increases from 17.30% to 19.90% with the increase in gasification temperature from 700C to 1200C.
- The Cold Gasification Efficiency (CGE) of gasifier system increases for both the increase in steam/fuel ratio and gasification temperature. The CGE increases from 135.73% to 152.24% for the increase in steam /fuel ratio from 0.30 to 1.30

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6. NOMENCLATURE

Symbol	Meaning	Unit
LHV	Lower Heating Value	Kj/Nm^3
$H_{CH,BLV}$	Chemical energy of feedstock	KW
$H_{SG,RS}$	Syngas used in reg. system	KW
$H_{CH,SG}$	Chemical energy of syngas	KW
$H_{PH,SG}$	Physical energy of syngas	KW
$\overset{o}{m}_{SG}$	Mass flow of syngas	Kg/s
x_i	Mole of different species	
R	Molar gas constant	Kj/KG-k
$h_{0,i}$	Enthalpy at standard state	KJ/kg