Comparison and Validation of Gas Phase Reaction Schemes for Black Liquor Gasification Modeling

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Introduction

Pressurized Entrained-flow High Temperature Black Liquor Gasification (PEHT-BLG) is a potential substitute or complement to the recovery boiler traditionally used for the recovery of chemicals and energy in black liquor in the Kraft pulping process. Black liquor consists of roughly 30 % moisture, 35 % inorganic pulping chemicals and 35 % combustible material (i.e. lignin). The PEHT-BLG technology can give an increase in total energy efficiency of the mill and provide new products with high added value, such as green motor fuels. The main parts of the recovery unit in the process are (see figure 1); a slagging refractory lined entrained-flow gasification reactor, with a gas assisted burner nozzle producing small black liquor droplets, used for direct gasification of the black liquor at about 1000 °C to produce a 'raw' syngas and a liquid smelt containing mainly Na_2CO_3 and Na_2S; a quench cooler beneath the reactor where the product gas and smelt are separated and the smelt is dissolved in water forming green liquor; a counter current condenser (CCC) that cools the syngas and condenses water vapor and any volatile and tar species that may be present. The heat recovered from the gas condensation is used to generate low/medium pressure steam that can be used in the pulp and paper process. Furthermore, the chemicals in the green liquor are recovered as cooking chemicals in the downstream processing.

Due to lack of demonstration of long term operation of the technology, a development (pilot) plant for PEHT-BLG (named DP-1) with a capacity of 20 tones dry solids/24h is in operation by the technology vendor Chemrec AB at the Energy Technology Centre in Piteå, Sweden [5]. An important tool for reduction of the technical risk associated with scale up of new technology is a comprehensive CFD model for the PEHT-BLG reactor that has been developed by Marklund [8]. The model includes drying, pyrolysis, char gasification and smelt formation of black liquor droplets as well as a simplified gas phase reaction mechanism.
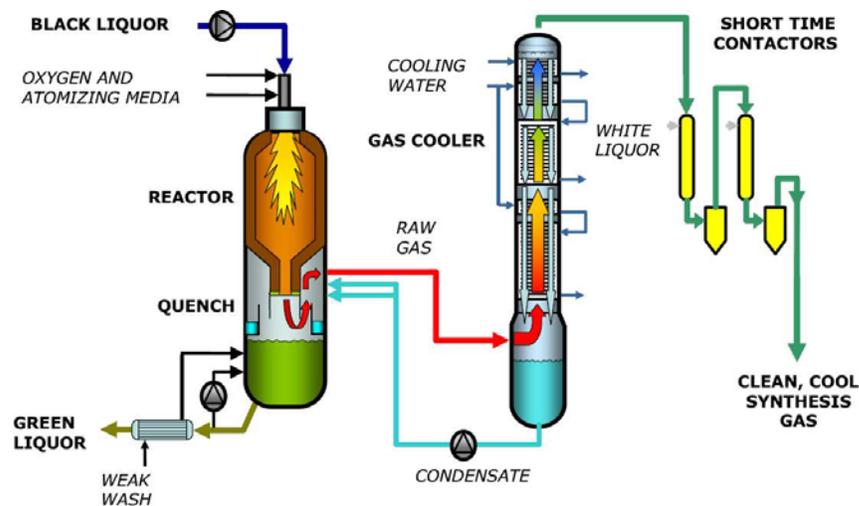
Figure 1. Schematic drawing of the PEHT-BLG process (Courtesy of Chemrec AB)

Marklund et. al [8] has made an initial validation of the model against the outlet gas composition after the Counter Current Condenser (CCC), see figure 1. The model predicted a CO / CO_2 ratio that was approximately 50% higher compared to the measurements. However, it is possible that the well known water-gas shift reaction is active in the quench and this could explain that the experimentally determined gas composition after the CCC differs from the computational results at the outlet from the hot zone.

Recently, in-situ measurements have been performed in the DP-1 reactor and a further validation of the model has been made possible. The measurements have been performed by sampling gas with a water-cooled suction probe from the lower part of the hot zone, followed by offline gas analyses. The details regarding the probe sampling equipment and procedure will be described elsewhere.

The first measurements in the hot reactor showed that; reactions in the quench vessel and following CCC did not change the gas composition significantly. The over-prediction of the CO / CO_2 ratio was therefore assumed to be caused by a mechanism not included in Marklund's model [9]. The model relies on a four step simplified gas phase reaction scheme for hydrocarbons, proposed by Jones and Lindstedt [4]. This reaction scheme does not include oxidation of CO by O_2 and was believed to be the main contributor to the over-predicted CO / CO_2 ratio.

The present paper investigates the difference between Marklund's model [9], which uses the reaction scheme by Jones and Lindstedt for the gas phase, and a modified model with the additional $CO + O_2$ reaction added to the Jones - Lindstedt reaction mechanism as proposed by several other authors [2, 11, 13]. The simulation results are compared against measurements obtained by the gas sampling probe in the DP-1 reactor.

Geometry and Mathematical Model

The DP-1 reactor is an axi-symmetric entrained-flow reactor with the spray burner centrally placed at the reactor top, see figure 1. The reactor dimensions are 2.3 m in height and 0.6 m in inner diameter. Based on the rotational symmetry, the reactor geometry was modeled as a 2D slice using periodic azimuthal boundary conditions. Heat losses were neglected in this study and the refractory lined reactor wall was modeled as adiabatic. However, rough estimates

have shown that the heat loss through the reactor wall is of the order of 100 kW or about 3% of the total thermal fuel power.

Marklund [9] implemented his model in the commercially available finite volume method based CFD program, ANSYS CFX 4. Since then, the model has been implemented in ANSYS CFX 11 by the present authors to take advantage of the improved numeric schemes in the later version of the code. The implementation of the current model into CFX 11 has been made with particle user Fortran routines in a similar manner as in [8] and should in theory yield the same results. The details of the model are described thoroughly by Marklund [9] and will therefore only be described in brief below.

The burner was modeled as a simplified spray burner with concentrical annular inlets where oxygen and discrete black liquor droplets enter the gasifier at a prescribed angle and velocity. The dispersed black liquor particles were modeled using the Euler – Lagrange formulation [1]. In the present paper the black liquor spray was represented by 1003 discrete particles having a fitted Rosin Rammler size distribution. The droplet size distribution and flow velocity are consistent with data from nozzle experiments measured by phase Doppler anemometry.

As the black liquor droplets pass through the reactor they undergo four main steps of conversion: drying, devolatilization, char gasification and finally smelt formation. During the different conversion stages there is a large mass transfer from the particles to the gas phase. During drying, water is vaporized, during devolatilization gaseous species (CO, CO_2, CH_4, H_2 and H_2S) are released and when the remaining char is gasified CO, CO_2 and H_2 are released.

In the model by Marklund [9] the simplified reaction scheme described by Jones and Lindstedt was used for the gas phase reactions, see reaction R1 to R4. Only CH_4 was considered in the model, hence n=1.

$$C_nH_{2n+2} + \frac{n}{2}O_2 \rightarrow nCO + (n+1)H_2 \qquad\qquad \text{R1}$$

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2 \qquad\qquad \text{R2}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad\qquad \text{R3}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad\qquad \text{R4}$$

Several authors [2, 11, 13] has included an additional reaction (R5) to the gas phase reaction scheme above when modeling gasification and achieved acceptable results.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad\qquad \text{R5}$$

In the present paper the simplified reaction scheme by Jones and Lindstedt (reactions R1-R4) was implemented. The influence of reaction R5 was also implemented together with reaction R1 to R4 to see the response in flame temperature and outlet gas composition.

Due to numerical difficulties, kinetics could not be included for all reactions. Reaction R1, R2 and R5 was modeled using only the Eddy Dissipation Model (EDM) [7]. Reaction R3 and R4 was modeled using a combination of Finite Rate Chemistry (FRC) and EDM using the

kinetics from Jones and Lindstedt. The EDM-FRC model calculates the turbulent and kinetic reaction rate and uses the minimum of the two. The simplified reaction scheme described by reactions R1 to R4 will be referred to as case 1, and reactions R1 to R5 to case 2.

To model turbulence the k-ε model with standard wall functions [12] was used. The radiative heat transfer was modeled using the Discrete Transfer (DT) radiation model by Lockwood and Shah [6] treating the wall as optically smooth with a radiative emissivity of 0.5. The absorption coefficient for the gas was calculated as the mass weight average of the participating species. Particles that hit the wall were assumed to lose 50% of their momentum in the perpendicular direction and none in the parallel direction in order to simulate a wall film flow. Initial calculations with deterministic particle trajectories suffered from poor convergence and a large amount of the particles became trapped in the recirculation zone. By introducing a model for turbulent dispersion as suggested by Gosman and Ioannides [3] this phenomenon was reduced.

In the current model the proximate analysis done by Marklund [9] was used with some modification based on more recent elementary and heating value data. The proximate analysis results are presented in table 1, the composition of the volatile matter in table 2 and initial smelt composition in table 3.

Table 1. Proximate analysis result, the weight fractions are consistent with elemental analysis.

Proximate matter	%wt
Moisture	30.00
Volatile matter	27.67
Char in smelt	9.38
Smelt (ash)	32.95

Table 2. Volatile matter composition as released during devolatilization.

	Specie	%wt
	H_2S	7.66
	CO	53.13
Volatile matter	CO_2	10.44
	H_2	2.26
	CH_4	26.51

Table 3. Initial smelt composition present in the virgin black liquor.

	Specie	%wt
	Na_2SO_4	13.13
Smelt	Na_2S	1.03
	Na_2CO_3	85.84

Results

Experimental

Four measurements were made in the DP-1 reactor with the gas sampling probe placed close to the outlet but still inside the hot zone. The oxygen / dry black liquor mass flow ratio (kg/kg) and pressure were held constant at 0.42 and 27 bar respectively. The synthesis gas samples that were withdrawn from the reactor were analyzed for: CO, CO_2, CH_4, H_2 and H_2S using a Varian CP-3800 gas chromatograph. The resulting dry average gas composition from the measurements in DP-1 is presented in table 4 together with the average LHV.

Table 4. Average molar gas composition ± one standard deviation, CO / CO$_2$ ratio and average LHV. The measurements were made with the probe in the DP-1 reactor at 0.42 oxygen / dry black liquor ratio (kg/kg) and 27 bar pressure.

Specie	Gas composition (%mole)
CO	27.6 ± 0.83
CO_2	33.7 ± 0.46
CH_4	1.2 ± 0.05
H_2	36.2 ± 0.71
H_2S	1.3 ± 0.05
CO / CO_2	0.82
LHV	7.62 MJ/kg

During the measurements all relevant process parameters, e.g. mass flow rates, temperatures and operating pressure, were logged using the process monitoring system available in DP-1.

Computational

The computed gas composition was sampled at a point that corresponds to the position of the hot probe tip used in the measurements. The results are presented in table 5 with the H_2O excluded so a comparison can be made between the calculated and measured values.

Table 5. Molar gas composition, CO / CO$_2$ ratio and LHV from the PEHT-BLG-CFD model with reaction R1-R4 implemented (left) and with extended reaction scheme R1-R5 (right).

Specie	Case 1 R1-R4 Outlet gas composition (%mole)	Case 2 R1-R5 Outlet gas composition (%mole)
CO	33.11	33.49
CO_2	26.01	26.36
CH_4	0.00	0.00
H_2	38.87	38.12
H_2S	2.01	2.03
CO / CO_2	1.27	1.27
LHV	7.85 MJ/kg	7.77 MJ/kg

The volume average gas temperature was calculated over the complete modeled reactor. The difference between the volume average gas temperature, the sampling point gas temperature and the reactor outlet gas temperature was minimal for each case, see table 6. The peak gas temperature was significantly higher in case 2 compared to case 1.

Table 6. Calculated gas temperatures from the PEHT-BLG-CFD model with reaction R1-R4 implemented (left) and with extended reaction scheme R1-R5 (right).

	Case 1 R1-R4 Temperature (K)	Case 2 R1-R5 Temperature (K)
Peak gas temperature	2866	3576
Volume average gas temperature	1322	1366
Sampling point gas temperature	1331	1372
Reactor outlet gas temperature	1330	1372

Discussion

The peak temperatures in the simulations are noticeably high. However, an estimate of the peak temperature, assuming that hot CO is recirculated from the lower part to the top of the gasifier where it reacts with O_2 from the burner nozzle, shows that the temperatures are thermodynamically possible. Figure 2 shows a vector plot from the simulations and the flow pattern is consistent with the assumption that hot CO can be convected to the top of the reactor. Assuming that CO is entrained into the shear layer created by the oxygen jet that is used for atomization of the black liquor and the resulting CO / O_2 mixture has a temperature of about 900K results in an adiabatic flame temperature of about 3570K at 27 bar which is close to the computed values. The calculation of the adiabatic flame temperature was done with the chemical equilibrium program Gaseq [10] using thermodynamic data from the database in this program.

The volume average gas temperature and outlet gas temperature are much lower and are reasonably close to the temperatures measured with wall mounted and shielded thermocouples in the DP1 gasifier. It is well known that measurements in high temperature environments are difficult due to the large radiative heat flux to the temperature sensor. It is therefore likely that the experimental temperatures also differ from the true gas temperature and the validation of the computed gas temperature is therefore not possible based on the current experimental set-up.

Validation of the temperatures and especially the peak temperature are extremely difficult due to the highly corrosive atmosphere inside the reactor. However, more detailed temperature measurements with a different sensor technology are planned.
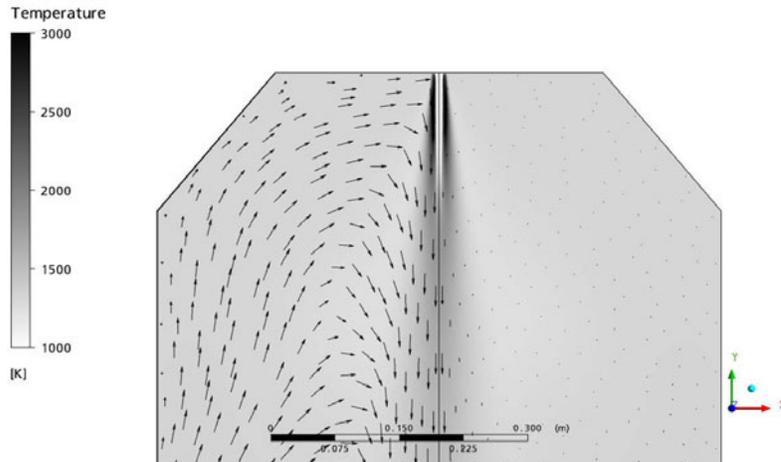
Figure 2. Velocity vectors and temperature field at the top of the reactor from the PEHT-BLG-CFD model.

Since wall heat losses are neglected in the model it can be assumed that the simulated gas temperatures are higher than in the DP-1 reactor. The elevated temperature will shift the chemical equilibrium of the water gas shift reaction (R4) towards the left i.e. a larger concentration of CO. Implementation of wall heat losses in the model would lower the gas temperature which would yield a gas composition closer to the one measured in the DP-1 reactor.

H_2S is currently implemented as an inert gas species in the model; the concentration of H_2S in the outlet gas is therefore determined already when specifying devolatilization species and mass fractions.

CH_4 is not present in the outlet gas composition from either of the models. This is consistent with thermodynamic equilibrium but differs from the experiments where the CH4 concentration is about 1.2%. The most likely reason for this is that tars are not included in the models. In the real gasifier, lignin is decomposed into heavy volatile compounds (tars) which in turn are decomposed further until equilibrium is achieved. It is possible that the kinetics of this chain of reactions is such that a significant fraction of CH_4 is still unreacted when the gas exits the gasifier. In the models; the CH_4 released during devolatilization will immediately be oxidized to CO and H_2 (reaction R1 and R2) limited only by the rate of mixing. If tars were included into the model, it would be possible to implement mechanisms for the thermal decomposition of tars to CH_4. However, validation of the mechanisms are difficult and the implementation would have to be made more or less *ad hoc*.

Conclusions

It has been showed that by implementing reaction 5 into the PEHT-BLG CFD model developed by Marklund [8] the local flame temperature was increased significantly. The effect on volume average and outlet gas temperature was minimal. It has also been showed that reaction 5 has very little effect on outlet gas composition when used with the Jones – Lindstedt simplified reaction scheme.

The peak temperatures in both models are very high while the volume average and outlet temperatures are consistent with measurements. However, it was shown that the computed temperatures are thermodynamically possible if one assumes that hot CO is entrained into the shear layer of the oxygen jet that is used for atomization of black liquor.

For the improvement of the model, heat losses through the reactor wall should be investigated further. It is also of interest to investigate chemical reaction models that can predict the experimentally determined levels of CH_4 at the outlet of the gasifier,

Acknowledgments

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