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RECENT ADVANCES IN THE UNDERSTANDING OF PRESSURIZED BLACK LIQUOR GASIFICATION

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Pressurized oxygen blown black liquor gasification, a new process for the recovery of energy and spent chemicals from chemical pulp mills, enables efficient power production or the production of motor fuels. In this paper, the experimental results of a 3 MW_{th} process development plant are presented and compared with the results of a CFD model.

The key parameters with the largest effect on gas composition are: operating pressure, oxygen-to-fuel equivalence ratio, black liquor load and black liquor preheating temperature.

The experimental gas composition during normal operation of the gasifier does not agree with equilibrium calculations. However, the agreement for the main components (CO, CO_2 and H_2) becomes very good if the CH_4 and H_2S concentrations are prescribed in the equilibrium code.

The impurities present in the syngas were also investigated, the observation being made that the particle content in the gas after cooling was very low, and the only significant trace elements were Cl and N.

A theoretical model for the gasifier has been implemented in the commercial CFD code Ansys-CFX. The results of the code agree well with the experiments for the major components in the gas, while the CH_4 concentration is under-predicted. A separate analysis with an equilibrium code (Factsage) shows that the CH_4 content at equilibrium, under experimental conditions is very low, which agrees with the CFD code but disagrees with the experiments. The reason for the disagreement between the experiments and the theoretical models is assumed to be the limiting kinetics for CH_4 conversion. A first approximation of the kinetics was implemented in the CFD code, which resulted in a very good agreement with the experiments.

Keywords: Black liquor, gasification, experiments, CFD

INTRODUCTION

In chemical kraft pulping, the black liquor is formed as a by-product in a digesting process in which the cellulosic fibers are separated from the lignin in wood chips to form pulp. The black liquor mainly consists of approximately equal parts of water, inorganic digesting chemicals and organic substances with a significant heating value. A novel technique to recover the inorganic chemicals and energy in the black liquor is Pressurized Entrained Flow High Temperature Black Liquor Gasification (PEHT-BLG). Compared to the conventional recovery boiler technique, PEHT-BLG can increase the total efficiency of the recovery cycle of a pulp mill, while opening up the possibility for the production of new high value added products, *e.g.* methanol or dimethylether.[1]

The main parts of the PEHT-BLG recovery unit are (Fig. 1): an entrained-flow gasification reactor, a quench cooler and a counter current condenser (CCC). In the reactor, the black liquor is gasified with oxygen at elevated pressure (app. 30 bar) and temperature (app. 1000 °C), to produce a synthetic gas and a liquid smelt. After the reactor phase, the synthetic gas and the smelt are rapidly cooled by water sprays in a quench cooler and then separated from each other. The smelt is dissolved in a liquid solution and returned to the pulp mill as a "green liquor" that can be regenerated into a new pulping liquid ("white liquor"), while the synthetic gas is sent to the CCC, which cools it and condenses the water vapors. The heat recovered from the gas in the CCC may be employed to generate low/medium pressure steam that can be used in the pulp mill.

The present paper summarizes the results of the experiments performed in a 3 MW_{th} pilot plant (called DP-1) that gasifies the black liquor from the Smurfit-Kappa Kraftliner mill in Piteå, Sweden. The gasifier is owned by Chemrec AB and it has run more than 12000 hours since it was commissioned, at the end of 2005, until the end of 2010. In parallel with the experiments, a CFD-based computer model has been developed, the predictive performance of which is also summarized in the paper.

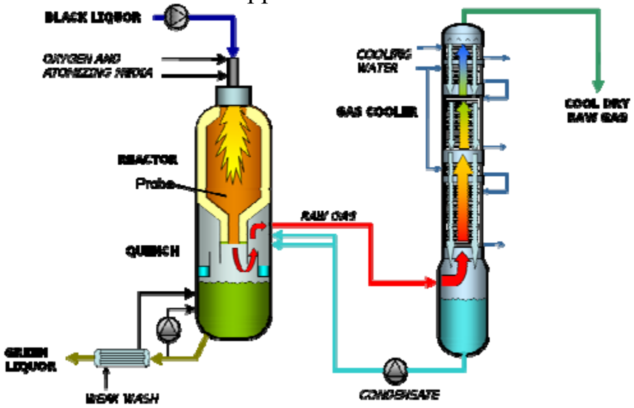

Figure 1: Schematic process diagram for Chemrec DP-1 pilot gasifier

EXPERIMENTAL AND NUMERICAL DETAILS

The DP-1 gasifier is rated for 20 ton (dry substance) black liquor per 24 h, which corresponds to about 3 MW fuel power. The DP-1 unit is an entrained flow, oxygen blown gasifier that operates [2] at a nominal pressure of 30 bar and a temperature slightly above 1000 °C. The process diagram plotted in Figure 1 shows the entrained flow gasifier, followed by a direct quench where the inorganic smelt droplets are dissolved in a liquid, to form the green liquor. After the quench, the gas is saturated with steam, and then removed by cooling in a counter current condenser before it is sent to a flare for incineration. In an industrial process, the heat will be used to produce medium pressure steam while, in the DP-1 plant, cooling is done with cold water. Samples of syngas were taken from inside the gasifier with a cooled quench probe. The probe cools the gas samples at more than 10000 °C/s through a combination of expansion and convective cooling.[3] Thus, the chemical composition at the sampling point is believed to be "frozen", so that the analysis results are representative for the state inside the gasifier. The approximate position of the sampling point is indicated in Figure 1. The samples were stored in a detachable pressure vessel for off-line analysis with a GC-instrument. The experimental conditions in the two experimental campaigns are described in Table 1, together with the ultimate analysis of the black liquor.

A detailed fluid dynamics model for the turbulent and reacting multi-phase flow in the gasification reactor has been implemented in the commercial software ANSYS CFX 12.0. In short, the model uses the Euler-Lagrange approach to particle tracking and it utilizes several sub-models describing the different steps of black liquor conversion in the reactor. Both radiative and convective heat transfer is included in the model. The heterogeneous reactions are described by a reaction model for the particle phase, while the homogeneous reactions are described with a gas phase reaction scheme based on the eddy dissipation concept with kinetic limitations. More details about the model can be found in literature.[4]

RESULTS AND DISCUSSION

The experiments were carried out according to an experimental plan with frequent replicates of a reference setting, to check the stability of the system. Table 2 shows an average of all measurements of the reference state. The low standard deviation in the experimental values shows that the process is stable and yields repeatable results. The table also compares the probe measurements with the gas composition, after cooling and depressurization of the gas. In the reference case, no significant changes occur in the gas composition, except for COS. Most likely, the reduction in COS concentration occurs through reactions with water in the quench.

When the green liquor from the process was tested in a standard sedimentation test for green liquor, it was observed that the rate of sedimentation and filterability was on par with that from the mill recovery boiler. Moreover, the amount of unconverted char in the green liquor was extremely low and, based on this, it was estimated that the char conversion of the gasifier was of at least 99.9%.

Table 1
Reactor operating parameters and black liquor ultimate analysis in the experiments[2]

Variable	May	October	Unit
Pressure	30	27	bar (g)
Black liquor mass flow rate	1250	870	kg h^{-1}
O_2 mass flow rate	375	254	kg h^{-1}
Black liquor temperature	140	140	°C
O_2 temperature	50	50	°C
λ	0.42	0.43	-
BLP	41.67	32.22	kg h^{-1} bar^{-1}
Black liquor ultimate analysis (on dry sample)			
C	33.8	31.3	%wt
H	3.6	3.4	%wt
O	35.1	37.3	%wt
N	< 0.1	< 0.1	%wt
S	5.1	5.6	%wt
Na	20.2	20.1	%wt
K	2.2	2.3	%wt
HHV	13.37	12.57	MJ/kg
Dry substance	72.4	75.2	%wt

Table 2
Average dry gas composition ±1 standard deviation for the reference operating conditions (p = 27 bar, T = 1050 °C, and λ = 0.4)[3]

Species	Probe measurements	After CCC
CO_2 (% mole)	33.9 ± 0.3	33.6 ± 0.2
CO (% mole)	28.7 ± 0.2	28.5 ± 0.2
H_2 (% mole)	34.3 ± 0.2	34.8 ± 0.1
CH_4 (% mole)	1.36 ± 0.07	1.44 ± 0.07
H_2S (% mole)	1.65 ± 0.04	1.71 ± 0.02
COS (ppm mole)	468 ± 22	122 ± 5

Two independent experimental campaigns were carried out, at 5 month intervals. The nominal operating parameters and the black liquor ultimate analysis for both cases are shown in Table 1. The present paper discusses only the results of the first campaign (denoted May in Table 1), but the conclusions are valid for both campaigns. A full discussion of all results is also available.[2,4] Figure 2 illustrates the effect of variation in the reactor pressure. Both the H_2 and CO concentrations increase with pressure, while the CH_4 concentration is approximately constant. The H_2S concentration is significantly lower than at equilibrium (typically, only about 40 instead of 60% sulfur in gas phase), which indicates that the characteristic time scale for sulfur reactions is longer than the residence time for fuel particles in the reactor. A similar conclusion can be drawn for the CH_4 content in the syngas. According to equilibrium calculations, there should be negligible amounts of methane in the syngas at the measured process temperature, while the experiments show that methane concentration is of the order 1.5%.

When the oxygen mass flow rate was varied at constant fuel mass flow rate, the most significant effect obtained was that methane concentration was reduced by a factor of 3 (Fig. 3b). The variation in the oxygen flow rate corresponds to an oxygen equivalence ratio variation of 0.40-0.44, which results in an increased temperature inside the reactor and in a corresponding increase of the rate of reaction for all species. It is believed that this is the main reason for the reduction of the methane content with increasing the equivalence ratio. In this case, there is an approximate balance, for the total carbon content in the gas, between the reduction in methane concentration and an increase in CO and CO_2 concentration (Fig. 3). For the other experimental variations here discussed (Figs. 2 and 4), it becomes difficult to draw similar conclusions about the total carbon in the syngas, since they are not possible without a change in several other state parameters.

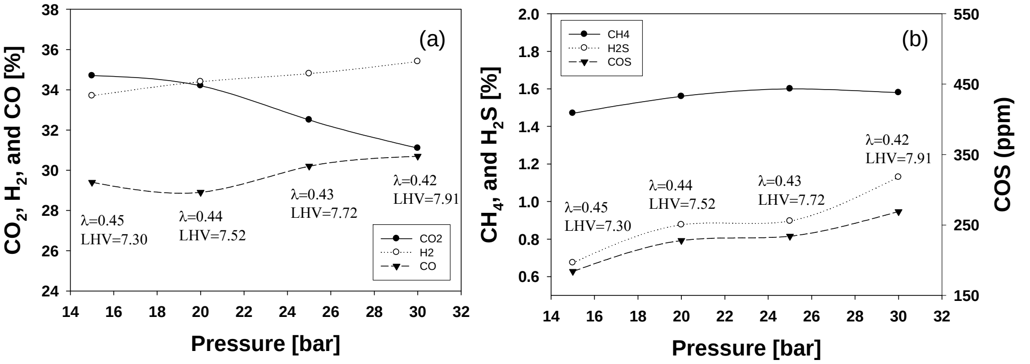

Figure 2: Effect of reactor pressure variation on syngas composition

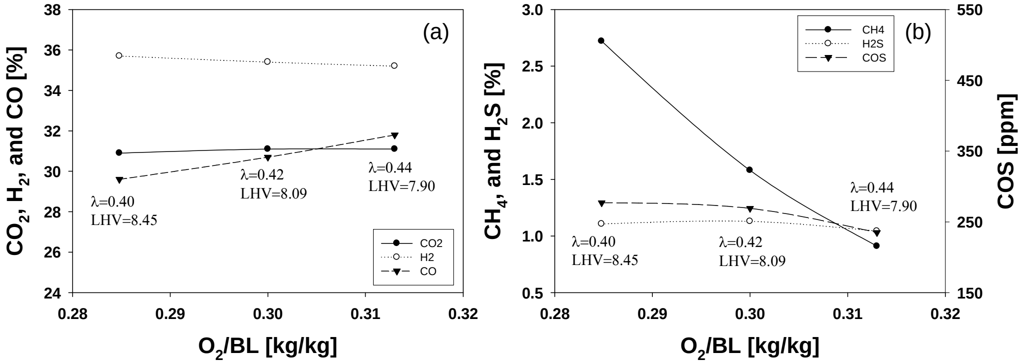

Figure 3: Effect of oxygen-to-fuel ratio variation on syngas composition

When the preheating temperature of the black liquor was increased from 120 to 145 °C, it was observed that the methane content was significantly reduced, with about 25% (Fig. 4). For the other species, the change in concentration was modest. The increased preheating temperature corresponds to a significant reduction in viscosity and surface tension which, in turn, should result in reduced droplet size distribution and modified spray shape. An independent experiment confirmed that the droplet size distribution decreased significantly when the preheating temperature was increased.[5] Qualitatively, this should result in a faster heating of droplets entering the reactor and a release of pyrolysis products higher up in the reactor which, in turn, will give the pyrolysis products and the remaining char particles a longer residence time inside the hot reactor.

Most importantly, there will be more time available for the conversion of gaseous products past the "methane bottle neck", which seems to agree with the experimental result.

In the numerical simulations of experiments, the agreement with the actual experiments was at first very poor, similar to the results from equilibrium calculations for the measured temperature, the main reason of this being considered the slow kinetics of methane conversion. As a first approximation of the real kinetics, a fraction of the methane released from the particles was treated as inert in the CFD model. The fixed fraction was fine-tuned until the concentration at the sampling point agreed with the experiments for one experimental condition. Therefore, the resulting predictions of the computer model agreed well with all experiments (Fig. 5). In the current version of the computer model, which eliminates the need for adjusting the fraction of "inert" methane, a more realistic kinetic model has been implemented. The advantage with the CFD model, compared to equilibrium-based models, is that it yields additional information about heat loads on containment materials, temperatures and dependence on the reactor geometry, so that arbitrary scale gasifiers can be designed without the need for "calibration experiments" apart from the pilot scale tests.

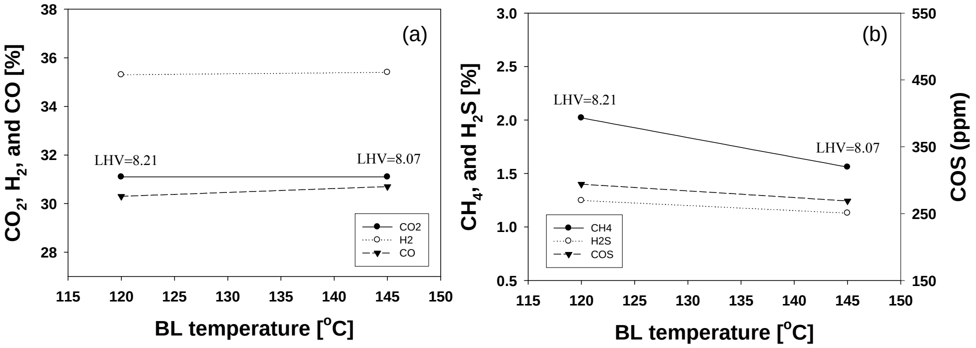

Figure 4: Effect of variation of black liquor preheating temperature

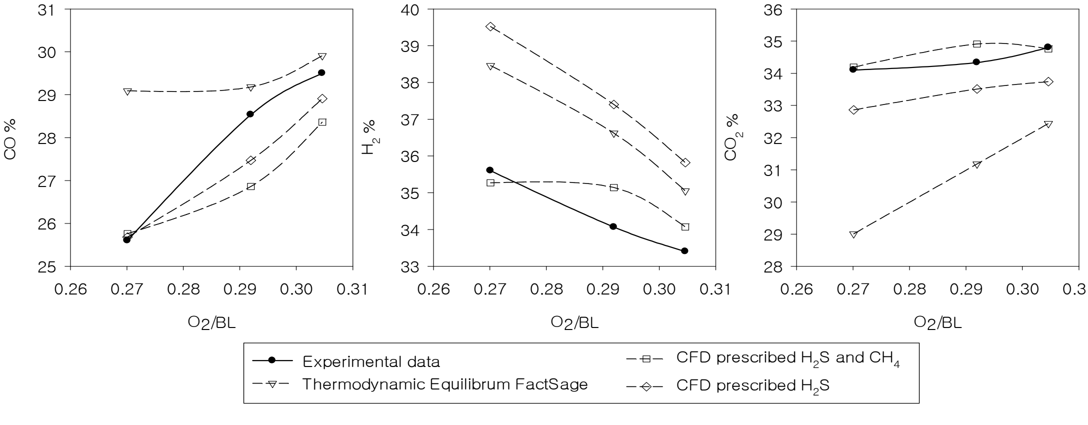

Figure 5: Molar concentration for CO, H_2 and CO_2 obtained from experiments, predicted assuming thermodynamic equilibrium and with CFD; with and without a zero order kinetic model for CH_4

CONCLUSIONS

A detailed experimental investigation of the syngas composition from a 3 MW_{th} black liquor gasifier has been carried out. The process has been shown to be stable, to exhibit a char conversion better than 99.9% and to produce a repeatable syngas composition when the same operating conditions are applied.

The syngas composition deviates from the one predicted by thermodynamic equilibrium calculations, non-equilibrium being due to the relatively short residence time in the gasification reactor. In particular, the sulfur content in the syngas is lower than predicted by the equilibrium corresponding to a sulfur split with about 40% sulfur in the gas phase and the rest in the green liquor, at 30 bar reactor pressure. Also, the methane content deviates from equilibrium with a typical methane concentration in syngas of about 1.5%.

Typically, the concentrations of H_2, CO and CO_2 in syngas are of 34, 29 and 34%, respectively, at 27 bar, 1050 °C and an oxygen equivalence ratio of 0.4. When the reactor pressure is increased, the higher heating value of the gas increases together with H_2 and CO, while CO_2 is reduced and H_2S is simultaneously increased.

When the oxygen equivalence ratio is increased, the reactor temperature increases together with the CO level. The CH_4 molar concentration is reduced with about the same amount as the CO level is increased, indicating that the main effect of an increased oxygen equivalence ratio is to convert methane into CO.

Another way to reduce methane concentration is to increase the black liquor preheating temperature. When temperature increased from 115 to 145 °C, the methane content dropped by about 0.5% units.

The CFD model had to be modified with a kinetic limitation for the reactions involving CH_4. In this paper, a model with a zero order approximation of methane kinetics predicted concentrations of H_2, CO, CO_2 and CH_4, with a relative error of about 5%. Moreover, the model also agrees excellently with the trends in the experiments, *e.g.* the dependence on the oxygen equivalence ratio, which means that the model can be used for scaling up to arbitrary size.

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