

## Research article

# Evaluation of black liquor gasification intended for synthetic fuel or power production



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## ABSTRACT

The performance of a high-temperature pressurized black liquor gasifier intended for fuel or power production was evaluated both by thermochemical equilibrium calculations and with experiments performed in a development plant with a maximum capacity corresponding to 3 MWth. The aim of this paper was to investigate how the energy efficiency and the performance of the gasifier change with desired use of the syngas and to provide an accurate process analysis which can be used in future work for process optimization and understanding. Experiments in the plant were performed for an oxygen equivalence ratio ( $\lambda$ ) between 0.414–0.462 at two system pressures, 24.6 and 28.7 bar, respectively. The thermal load on the gasifier was 2.7 MWth during the experiments. The experimentally verified cold gas efficiency taking into account all gaseous species varied between 59.0–62.4%. However, if only CO and H<sub>2</sub> (which are the effective molecules for synthetic fuel production) were taken into account; the cold gas efficiency decreased considerably to 53.7–55.4% due to the presence of CH<sub>4</sub> in the gas. The results indicate that optimal performance for synthetic fuel production occurs at a higher  $\lambda$  compared to power production. There is also a potential to further improve the performance for an optimal operated commercial plant in the future since the theoretical results indicate that the cold gas efficiency could be as high as 68.8% ( $\lambda = 0.35$ ) for fuel production and 81.7% ( $\lambda = 0.27$ ) for power production.

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## 1. Introduction

Black liquor gasification (BLG) combined with either a gas turbine or a catalytic synthesis fuel process can be one way to produce renewable electricity or motor fuels, thereby reducing greenhouse gas emissions and the fossil resource usage [1–3]. It can be one possible contribution to reach the European Union renewable energy directive from 2009 which states a 20% reduction of greenhouse gases compared to the 1990's level and a 10% share of biofuels for inland transports by 2020 [4]. Black liquor (BL) is an intermediate product in the chemical Kraft pulping process and after the concentration step it consists roughly of 30 wt-% water, 30 wt-% inorganic cooking chemicals and 40 wt-% lignin and other organic substances separated from the wood during chemical pulping in the digester (i.e., a solid content of 70 wt-%) [5].

BLG can either be performed well above (high temperature gasification) or well below (low temperature gasification) the melting point of the inorganic salts to avoid difficulties, i.e., sticky or poor flowing salt characteristics. Since 2005 a development plant (DP1) for high temperature black liquor gasification (HT-BLG), developed by Chemrec AB, has been

in operation for over 20,000 h, in Piteå, Sweden [6]. The gasifier is typically operated under reducing conditions at 28 bar(g), at a process temperature of  $\approx 1000$  °C and a fuel capacity of 20 tons dry solids of BL per 24 h which corresponds to a thermal power of  $\sim 3$  MW. The main components of the HT-BLG process (see Fig. 1) are a refractory lined oxygen blown entrained down-flow gasification reactor, a quench and a counter-current condenser (CCC). Gasification takes place in the reactor and synthesis gas and smelt are formed [7]. The gas is cooled and separated from the inorganic smelt (cooking chemicals) and ash (from the original biomass) in the quench [8]. In the quench the smelt and ash are also dissolved in water forming green liquor that is recovered in the pulp mill. The gas is further cooled in the CCC where condensable hydrocarbons, particles and water vapor are further separated from the synthesis gas [9]. The typical composition of the synthesis gas after the condenser (dry and nitrogen free) is: 29 vol-% CO, 35 vol-% H<sub>2</sub>, 34 vol-% CO<sub>2</sub>, 1.7 vol-% H<sub>2</sub>S, 1.4 vol-% CH<sub>4</sub> and traces of COS, C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> [7,9].

Depending on the specific application of the produced synthesis gas (power or fuel production) the preferable operating conditions of the gasifier may vary significantly which means that the thermal efficiency of the process alone is not of importance. Synthesis gas intended for power production should have a high heating value and low levels of contaminants. Contaminants can be particles, alkali metals (Na, K), liquids and sulfur, which can cause process problems and/or problems

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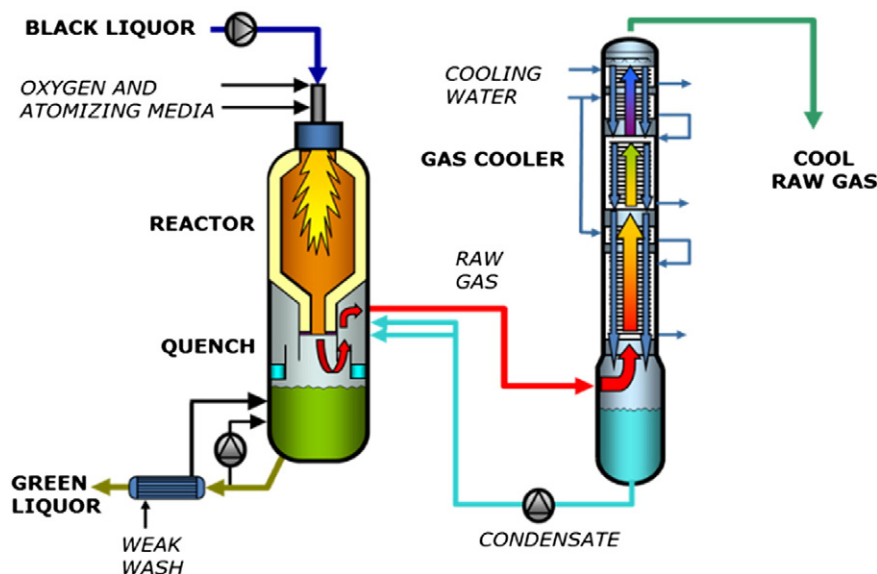


Fig. 1. Schematic sketch of the pilot scale gasifier.

with emission requirements [10]. Downstream processes for removal of contaminants are therefore often required. For synthetic fuel production, a synthesis gas with a given composition of CO, H<sub>2</sub> and CO<sub>2</sub> is desired together with very low levels of contaminants. The catalysts used for synthetic fuel production are sensitive for certain elements, e.g., sulfur, halogens and phosphorous, which can cause catalyst deactivation even at ppb levels [11–13]. Hence, catalyst deactivating compounds must be removed from the gas. Careful characterization of the synthesis gas is therefore necessary [9,14] when considering catalytic upgrading to synthetic fuels [15], besides the determination of the main gas components, in order to choose appropriate gas cleaning systems. Finding favorable operating conditions in the gasifier is therefore more challenging compared to the power production case. To get the full picture, an integrated optimization including both the gasifier and the downstream equipment, e.g., methane reformer, units for trapping of condensable hydrocarbons, acid gas removal units, water gas shift reactors (sour or sweet shift) and guard beds must be taken into account for the synthetic fuel production case.

To our best knowledge, there exist no theoretic or experimental investigations of optimal operating condition of a HT-BLG with respect to either power or synthetic fuel production in the open literature. The main goal with this work is therefore to investigate how the energy efficiency and the performance of the gasifier changes with considered use of the syngas and to provide an accurate process analysis which can be used in future work concerning process optimization and understanding. The results presented in this paper are therefore of particular interests for researchers and engineers that plan to construct and operate BL gasifiers. However, the results should also be interesting for the general high temperature biomass (e.g., pyrolysis oil and wood powder) entrained flow gasification community since there are many similarities between the technologies.

This study includes both a theoretical analysis of the black liquor gasification followed by an experimental verification in the DP1. The originality in this work compared to other work performed by us [7–9] is that a complete thermodynamic analysis of HT-BLG is performed for the first time. Furthermore, since the mass flow of produced syngas is measured in this work it is also the first time that the energy efficiency of the gasification process can be determined experimentally and compared to the theoretical results. Based on the experimental and theoretical results, preferable operating conditions of the gasifier are thereafter discussed and important performance parameters are presented. Despite the significance of the downstream equipment these will not be taken into consideration. Instead the focus will be on

the main gas components and key performance parameters of the gasifier since these are results that can be verified experimentally in the DP1.

## 2. Theory

### 2.1. Conversion of black liquor during gasification

Although BL originally is a liquid fuel, the conversion process in a gasifier is more similar to a solid hydrocarbon fuel and consists therefore of three stages: drying, pyrolysis and char gasification [16]. The conversion of BL has been thoroughly described by Whitty [16], Marklund [17] and Carlsson [18] and are summarized in the text below in this section (2.1) also and presented in Fig. 2. The main reactions involved are also shown in Table 1.

The morphology of the droplets changes significantly during the conversion and there is a large net mass transfer from the BL to the gas phase. During drying (R1), the water in the black liquor evaporates and the size of the droplet increases due to swelling (~1.5 times). During pyrolysis (R2), the organic matter in the liquor thermally degrades, forming various gaseous compounds (e.g., H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S, light and heavier hydrocarbons). The result of this process is a porous char particle which consists of the non-volatile matter and most of the inorganics originating from the BL droplet. Furthermore, a significant swelling of the BL occur during the pyrolysis phase, and the volume of the resulting char particle can be more than 30 times larger compared to the original droplet [16]. The final stage is char gasification, where the solid carbon reacts with CO<sub>2</sub> and H<sub>2</sub>O forming gaseous species in an endothermic process according to R3 and R4. During the char gasification process the particle shrinks and when this stage is complete only the inorganic material, the smelt, remains.

Since the inorganic part of the BL is significant, the conversion of the inorganics also needs to be considered. The alkali metals in the BL come from the inorganic salts (NaOH and Na<sub>2</sub>S) that have been used to dissolve the wood. The alkali metals are bound to organic molecules that mainly originate from the hemicellulose and the lignin in the BL [19]. During char gasification, the alkali metals are bound to functional groups on the char surface where they act as catalyst for the char gasification reactions (R3 and R4) [19]. Furthermore, most of the alkali species in the char residue are ultimately converted to carbonate species via organic and inorganic processes. In addition to organic pathways, alkali carbonates are also produced from inorganic reactions, particularly inorganic sulfur reactions where the first step mainly is a reduction of

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