



Full Length Article

Co-gasification of black liquor and pyrolysis oil at high temperature: Part 1. Fate of alkali elements



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HIGHLIGHTS

- Blends of black liquor (BL) and pyrolysis oil (PO) were gasified in a drop tube.
- Equilibrium modelling qualitatively captured the fate of alkali species.
- Experimental vaporization of alkali exceeded the prediction by equilibrium.
- Diluting the alkali by blending PO in BL did not lead to alkali depletion in the char.

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ABSTRACT

The catalytic activity of alkali compounds in black liquor (BL) enables gasification at low temperatures with high carbon conversion and low tar and soot formation. The efficiency and flexibility of the BL gasification process may be improved by mixing BL with fuels with higher energy content such as pyrolysis oil (PO). The fate of alkali elements in blends of BL and PO was investigated, paying special attention to the amount of alkali remaining in the particles after experiments at high temperatures. Experiments were conducted in a drop tube furnace under different environments (5% and 0% vol. CO₂ balanced with N₂), varying temperature (800–1400 °C), particle size (90–200 μm, 500–630 μm) and blending ratio (0%, 20% and 40% of pyrolysis oil in black liquor). Thermodynamic analysis of the experimental cases was also performed.

The thermodynamic results qualitatively agreed with experimental measurements but in absolute values equilibrium under predicted alkali release. Alkali release to the gas phase was more severe under inert conditions than in the presence of CO₂, but also in 5% CO₂ most of the alkali was found in the gas phase at T = 1200 °C and above. However, the concentration of alkali in the gasification residue remained above 30% wt. and was insensitive to temperature variations and the amount of PO in the blend. Thermodynamic analysis and experimental mass balances indicated that elemental alkali strongly interacted with the reactor's walls (Al₂O₃) by forming alkali aluminates. The experience indicated that adding PO into BL does not lead to alkali depletion during high temperature gasification.

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1. Introduction

Gasification is attractive for upgrading biomass into green transportation fuels and chemicals. However, most gasification technologies results in a gas with significant amounts of tars,

Abbreviations: BL, black liquor; BLG, black liquor gasification; BPx, mixture of pyrolysis oil (x wt%) and black liquor (100 – x wt%); DTF, drop tube furnace; EFG, entrained flow gasifier; FID, flame ionization detector; GC, gas chromatography; PO, pyrolysis oil; MS, mass spectra; SEM, scanning electronic microscope; TOC, total organic carbon.

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requiring complex and expensive gas cleaning. In contrast, entrained flow gasifiers (EFG) generate a relatively clean gas, reducing to great extent the complexity of gas cleaning. The main differences from other types of gasifiers are short residence times, high temperatures and the presence of a flame within the reactor. Additionally, they are compact and can be scaled up to larger sizes more easily than other technologies. The higher syngas quality comes at the price of having to feed the fuel in a pulverized or liquid form.

Black liquor (BL) is a residual liquid product from Kraft pulping consisting of dissolved wood constituents (mainly lignin), pulping chemicals (Na and S compounds) and water. BL combustion in

Tomlinson recovery boilers is a well-established process to recycle pulping chemicals and generate process steam and power in pulp mills. Black liquor gasification (BLG) is an alternative technology to recover chemicals and energy from BL that has attracted significant research interest through laboratory experiments [1–6], pilot plant demonstration [7–9] and techno-economic analysis [10–12]. Indeed, BLG has demonstrated to be suitable for syngas upgrading to transportation fuels [13]. The liquid form of BL is advantageous in pressurized EFG, since it allows straightforward feeding and atomization. The catalytic activity of alkali in BL allows low process temperatures (around 1000 °C) with high carbon conversion as demonstrated in a 3 MW_{th} oxygen blown pressurized pilot scale gasifier in Piteå (Sweden) [7]. This can be compared to the 1200–1500 °C which is typically required for EFG of other types of biomass [14–18].

The presence of alkali in the fuel has long been associated with high char gasification rates along with more recent reports of strong effect on tar and soot reduction [19–21]. Taylor and Neville [22] provided in 1921 one of the first explanation of the catalytic activity of alkali compounds. They attributed the catalytic activity in C + CO₂ and C + H₂O reactions to and enhanced adsorption of CO₂ onto the fuel particle due to alkali carbonates. Fox and White [23] later proposed a reduction-oxidation (RedOx) cycle of alkali carbonate as the engine for oxygen transfer to carbon. Several studies were carried out on the RedOx cycle, most notably McKee [24,25], Kapteijn et al. [26] and Sams and Shadman [27]. Some authors also suggested other types of mechanisms. For example, Franke and Meraikib [28] proposed that sodium acted as an electron donor to the graphite lattice, Mims and Pabst [29] proposed that alkali species increased the number of carbon active sites by forming surface-salt complexes and Mejer et al. [30] proposed a model with active sites, oxidized sites and chemisorbed CO₂.

Several studies have indicated that the catalytic activity in char gasification increases with the alkali-to-carbon ratio, but saturates around 0.04–0.12 mol mol⁻¹ [20,22,29,31,32]. Verill et al. [33] reported a saturation threshold of 0.1 mol mol⁻¹ of Na/C in synthetic BL char. A typical BL contains much more alkali than needed to catalyse carbon gasification; e.g. BL used in this study has an alkali-to-carbon ratio of (Na + K)/C = 0.38 mol mol⁻¹. Above the saturation limit additional alkali can also be disadvantageous due to pore blocking by inorganics deposits. Furthermore, in a full scale gasifier, an excess of alkali content also leads to an energy penalty in the form of thermal ballast. Therefore, one focus of current BLG research, including the work presented in this paper, is increasing the organic fraction of the fuel, i.e. decreasing thermal ballast while maintaining catalytic activity. Co-gasification of BL with coal [34,35], petroleum coke [35], pulp sludge [36] and solid types of biomass [37] have been studied. The results showed catalytic activity in all cases but the degree varied depending on the fraction of BL and the quality of the contact between fuels. From an operational point of view, homogenous liquid blends are preferable in EFG. More recently, a techno economic study [38] showed that co-gasification of BL and pyrolysis oil (PO) might be beneficial. And a TGA study [39] concluded that char reactivity of BL/PO mixtures remained as high as that of pure BL up to 30% of PO addition. However, this study was based on experiments at low temperatures (720–860 °C). At higher temperatures, the vaporization of alkali components can reduce the amount of alkali available as a catalyst in the char [2,27,40,41]. Some studies have investigated sodium release in BL [2,40,42–44]. The results reported vary between less than 1% to as much as 30–40%. The disparity in results is mainly due to the variety of environments studied. Generally, high temperature, low pressure and strongly reducing environments enhance sodium vaporization. In EFG, local temperature in the flame region can be well above 1400 °C. The effect of such high temperature on alkali retention in the gasifying particles is

unclear, especially for alkali-diluted fuels such as BL and PO mixtures.

The research in this paper and its companion paper aims to increase the fundamental understanding of PO/BL gasification at high temperature, complementing experiments carried out in pilot plant scale [45]. The work is based on pyrolysis and gasification of BL and PO/BL mixtures in a laminar drop tube furnace (DTF) using temperatures relevant for commercial EFG. In part I (current paper), we investigate if thermodynamic equilibrium modelling could be useful to explain the fate of alkali. This work also studies a hypothetical and undesirable depletion of alkali in the char particles at high temperature. In particular, we present how the release of sodium and potassium are affected by temperature, gas atmosphere, particle size and the amount of PO in the fuel blend. Part II [46] addresses fuel conversion with special focus on undesired by-products from gasification, i.e. CH₄, tar and unconverted carbon.

2. Methods

2.1. Sample preparation

We prepared blends of PO and BL with different mixing ratios: namely BL (0% of PO on weight basis, i.e. pure BL), BP20 (20% of PO) and BP40 (40% of PO), BL was received from Smurfit Kappa Kraftliner mill (Piteå, Sweden). PO was received from VTT pyrolysis pilot plant (Espoo, Finland).

BP20 was prepared by adding 80 g of PO into 320 g of BL, followed by 20 min of mixing (model: VELP Scientifica Overhead Stirrer LS). The fuels were pre-heated to 60 °C to ease mixing. Given that PO is acidic; BP40 would have reached a pH below what is needed to keep lignin dissolved. Hence, to avoid lignin precipitation, sodium hydroxide was added to BL; 240 g of BL were first blended with a NaOH solution (12.5 g of NaOH and 12.5 g of H₂O) and subsequently blended with 160 g of PO. Mixing was performed analogously to BP20. To expedite feeding in the drop tube, the fuel was converted in dry solid particles as follows: The different fuel blends were spread on a thin surface (1 mm) to avoid local enrichments of inorganics during drying. Drying was carried out at T = 105 °C for 16 h. Eventually, the dried fuels were grinded and sieved into 2 different sieve sizes: one between 90 and 200 µm and the other between 500 and 630 µm. Table 1 shows the properties of the prepared solids.

2.2. Experimental setup and procedure

The experiments were conducted in two separate campaigns: one in oxidizing environment (5% of CO₂ on volume basis, balanced with N₂) and the other in inert conditions. As one of the main objectives was to investigate differences regarding alkali release between pure BL and BL/PO mixtures the gas environments were selected to have moderate vaporization of alkali compounds. Feeding rate was kept low enough to minimize the disturbance of the reactor's environment by the release of products gases while high enough to quantify minor gases. Volume fraction of CO₂ at the reactor exit was around 4.5% for the experiments in oxidizing environment. All the experiments were conducted in an atmospheric laminar drop tube furnace (DTF) shown in Fig. 1. The reactor consists of an alumina tube (internal diameter: 54 mm, heated length: 2.3 m) heated by 6 heating elements with independent temperature control. Gas flow rate into the reactor is regulated by mass flow controllers (Bronkhorst: EL-FLOW series). The feeding system is based on a syringe pump that displaces upwards a bed of fuel which eventually falls into the reactor through a hole in its middle, the design is thoroughly described in this publication [47]. In our setup vibration was applied to the feeding unit to improve the

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