Full Length Article

Co-gasification of black liquor and pyrolysis oil at high temperature: Part 2. Fuel conversion

Albert Bach-Oller *, Kawnish Kirtania, Erik Furusjö, Kentaro Umeki

Division of Energy Science, Luleå University of Technology, Universitetsområdet Porsön, SE-971 87 Luleå, Sweden

HIGHLIGHTS

- Blends of black liquor (BL) and pyrolysis oil (PO) were studied in a drop tube.
- Blending PO into BL increased the gas yield and carbon conversion of the char.
- BL generated much less tar than a pine reference.
- Blending PO into BL strongly reduced the amount of tar.
- The combined results encourage co-gasification of BL and PO.

ARTICLE INFO

ABSTRACT

The efficiency and flexibility of the BL gasification process may improve by mixing BL with more energy-rich fuels such as pyrolysis oil (PO). To improve understanding of the fuel conversion process, blends of BL and PO were studied in an atmospheric drop tube furnace. Experiments were performed in varying atmosphere (5% and 0% CO_2, balanced by N_2), temperature (800–1400 °C), particle size (90–200 μm and 500–630 μm) and blending ratio (0%, 20% and 40% of PO in BL on weight basis). Additionally, pine wood was used as a reference fuel containing little alkali. The addition of PO to BL significantly increased the combined yield of CO and H_2 and that of CH_4. BL/based fuels showed much lower concentration of tar in syngas than pine wood. Remarkably, the addition of PO in BL further promoted tar reforming in presence of CO_2. Unconverted carbon in the gasification residue decreased with increasing fractions of PO. Small fuel particles showed complete conversion at 1000 °C but larger particles did not reach complete conversion even at T = 1400 °C.

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1. Introduction

Black liquor gasification (BLG) is an alternative to combustion to recover chemicals and energy from BL which has attracted significant research interest [1–7]. BLG has been demonstrated in a 3 MW$_{th}$ oxygen blown pressurized pilot scale gasifier in Piteå (Sweden) [8,9]. A major appeal of BLG (beyond logistic advantages) is the abundance of alkali compounds with catalytic activity, which enable relatively low process temperatures (around 1000 °C) with high carbon conversion. Some studies have identified the role of alkali elements in catalysing char gasification [7,10–13], reducing tar [14–17], and enhancing soot oxidation [18,19]. Yet, most of the existing work on BLG has been limited to low temperatures and/or low heating rates. At high temperatures different phenomena may take place, for example molten ashes may coat the char thereby isolating the carbon from the oxidizing gases [20].

A focus of current BLG research, including the work presented in this paper, is increasing the organic fraction of the fuel thereby reducing the thermal ballast of inorganic species [21–24]. More recently, co-gasification of BL and pyrolysis oil (PO) has been evaluated economically, showing potential benefit for small plants [25,26]. However, an essential requirement for co-gasification is that the fuel blend maintains the catalytic activity of alkali. This was shown to be the case for blends of BL with up to 30% of PO based on char gasification experiments [27] albeit at lower temperatures than is realistic for EFG. The study presented in this series of

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two publication aims to extend the experimental research on co-gasification of BL and PO but at higher temperatures and heating rates. In part 1 of the series [28], we presented how the fate of alkali elements are affected by temperature, gas atmosphere, particle size and the amount of PO in the fuel blend. This second part will address the consequences of fuel mixing on fuel conversion with special focus on undesired products from gasification, i.e. tar, unconverted carbon, and soot.

2. Experimental

2.1. Experimental procedure

Experiments were carried out in a laminar drop tube furnace (DTF) at T = 800–1400 °C in two separate campaigns, one with presence of oxidizing gas (5% CO_2 balanced by N_2 on volume basis) and the other with inert gas flow (100% N_2), i.e. pyrolysis condition. Three fuel samples, BL (100% BL), BP20 (20% PO; 80% BL w/w) and BP40 (40% PO; 60% BL w/w), were prepared in the form of dry solid particles in two sizes (90–200 and 500–630 μm). Pine wood was also used as a reference fuel. The fuel analysis of the samples is shown in Table 1. Details of sample preparation methods, and experimental procedures are provided in the part 1 [28].

2.2. Tar collection and analyses methods

Tar was collected in two serially connected gas washing bottles, each of which was filled with 50 ml of solvent. The temperature of the solvent was kept at T = −50 °C to collect as much tar as possible while avoiding condensation of H_2S. The solvent was isopropanol for the gasification campaign (5% CO_2). In the pyrolysis campaign (100% N_2) methanol was used instead of isopropanol to avoid the co-elution between benzene and isopropanol in GC-FID. The change of solvent did not affect the measurements. These solutions were kept refrigerated at the temperature of −18 °C until the analyses. Isopropanol based solutions were analysed in a commercial lab with a dual detector system GC/FID + GC/MS (Agilent 7890 GC, Supelcowax capillary column, 5975 MS detector). FID was used to quantify the tar species except for benzene due to the above mentioned co-elution with the solvent. Benzene was quantified by single ion monitoring MS (ion 78). A 10:1 split ratio was used in those samples with expected high concentrations of tar (experiments at T = 800 °C) and splitless injection was performed for the rest. In both cases the injection volume was 1 μl. The temperature program run from 35 °C to 280 °C with a constant heating rate of 5 °C/s. Methanol based solutions were analysed in our lab with

GC/FID (Agilent 7820A with DB-EUPAH column, length: 60 m; internal diameter: 0.25 mm; film thickness: 0.25 μm). The temperatures of both the injector and the detector were kept at 280 °C. The temperature program run from 57 °C to 280 °C, to optimize signal resolution the heating rate was set to 4 °C/s for the first 10 min and then to 10 °C/s until the final temperature.

2.3. Char collection and analyses methods

Ultimate analysis (C/H/N/S/O) and total organic carbon (TOC) analysis of the – gasification residues collected in the char bin were carried out for each experimental condition (except at 1400 °C due to insufficient amount of product) at Mikroanalytisches Laboratorium, University of Vienna. Details concerning CHNS analysis are available at Part I [28]. For TOC analysis, the inorganic carbon was digested using two doses of 20 μl 0.2 M HCl for 2 h. Finally, V_2O_5 was added to the sample to ensure complete mineralization. Both ultimate and TOC analyses were performed using Eurovector EA 3000 by flash combustion (at 25 kPa and T = 1000 °C under the flow of oxygen) with the sample loaded in a tin vial. The typical accuracy of this method is ±0.3 wt.%.

Unconverted carbon (UC) was calculated from the collected gasification residue as:

$$UC = 100\left(\frac{m_{residue}TOC_{residue}}{m_{fuel}TOC_{fuel}}\right)$$

where TOC is the total organic carbon in wt.%. The particle size of both the fuel and the gasification residues was calculated by static image analyses methods through the following procedure. Images containing about 200 particles each on plain surface were captured and then transformed into b/w images that distinguished the particles from the background. Thereafter the Matlab function, 'bwconncomp', was used to identify the particles and calculate the area of each particle. Despite we have a device specially designed to calculate the shape and the size of solid particles it could not be used for the gasification residues due to the tendency of these particles to break. Scanning electron microscopy on the both fuel samples and residues was performed using FEI Magellan 400 XHR-SEM (FEI Company, USA).

3. Results and discussion

3.1. Syngas

One of the objectives of blending BL with PO was to increase the cold gas efficiency (CGE) of BLG. CGE in a commercial gasification

Table 1
Fuel properties and composition of the dry solids samples and their original fuels. All the results have been expressed on the dry basis.

Sample Sieve size	BL liquid	PO liquid	BL 90–200	BL 500–630	BP20 90–200	BP20 500–630	BP40 90–200	BP40 500–630	Pine 90–200
Volatiles wt.%[a]	n.a.	n.a.	30.0	30.0[d]	37.0	37.0[d]	41.0	41.0[d]	77.9
Ash content, wt.%[b]	52.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.5
HHV, MJ/kg	12.9	23.4	13.2	13.3	15.3	15.6	17.1	17.2	19.3
C, wt.%	30.7	55.4	30.9	31.5	35.7	38.5	42.1	41.6	49.3
H, wt.%	3.70	6.60	3.73	3.73	4.10	4.19	4.20	4.30	6.40
N, wt.%	0.07	0.14	0.12	0.12	0.15	0.17	0.14	0.15	0.08
S, wt.%	4.30	n.a.	5.84	5.91	4.10	3.89	3.38	3.29	< 0.02
Cl, wt.%	0.19	0	0.19[c]	0.19[c]	0.15[c]	0.15[c]	0.11[c]	0.11[c]	n.a.
K, wt.%	3.12	n.a.	2.66	3.11	2.36	2.17	1.64	1.77	0.05
Na, wt.%	20.6	n.a.	17.5	17.8	14.7	15.0	13.1	13.3	0.00
O (diff.), wt.%	35.9	37.9	39.1	37.7	38.8	36.0	35.3	35.5	44.2

wt.% refers to weight basis.
[a] The volatile content was measured at 540 °C under 100% CO_2 for 8 min to avoid alkali vaporization.
[b] Ash content was measured at 550 °C in pure O_2.
[c] Calculated based on a linear interpolation between BL and PO.
[d] Volatile matter for the 500–630 μm particles is assumed to be the same than that of 90–200 μm particles.