FUEL CONVERSION CHARACTERISTICS OF BLACK LIQUOR AND PYROLYSIS OIL MIXTURE FOR EFFICIENT GASIFICATION WITH INHERENT CATALYST

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ABSTRACT: This paper describes the technical feasibility of a catalytic co-gasification process using a mixture of black liquor (BL) and pyrolysis oil (PO). A technical concern is if gasifiers can be operated at low temperature (~1000 ºC) without problems of tar, soot or char, as is the case for pure BL due to the catalytic effect of fuel alkali. Hence, we investigated fuel conversion characteristics of BL/PO mixture: conversion of single droplet in flame, and char gasification reactivity. 20wt.% (BP20) and 30wt.% (BP30) were selected for weight fraction of PO because of lignin precipitation in BP30. Single droplet was devolatilized and gasified in a methane flame with a flat flame burner at various droplet sizes. Conversion time and swelling ratio were investigated with imaging. They were more sensitive to initial droplet size and reaction atmosphere than the mixing of BL and PO. Char gasification reactivity was measured in an isothermal thermogravimeter (iTG) at T=880–940 ºC and P_{CO2}=1 bar. Both BP20 and BP30 showed complete char conversion and there was no statistically significant difference in char reactivity among BP20, BP30 and BL. These results show that PO can be co-gasified in BL gasification process without major changes in the operation.
Keywords: black liquor, pyrolysis oil, gasification, swelling, char gasification

1 INTRODUCTION

Black liquor (BL) is a liquid by-product from the Kraft pulping process, mainly consisting of dissolved lignin, pulping chemicals (primarily Na_2S, NaOH, Na_2CO_3, and Na_2SO_4) and water. Most current pulp mills recover the energy and chemicals in BL by combustion in Tomlinson type recovery boilers to generate heat and electric power [1]. Alternatively, the BL could be upgraded by converting its organic fraction into syngas [2]. Catalytic activity of inorganic content in BL enables an outlet temperature of entrained flow gasification as low as 1273–1373 K with very close to full carbon conversion [3,4]. In Piteå, Sweden, a pilot BL gasification (BLG) plant has been operating for more than 20,000 hours (from 2008 to September 2013), and syngas is further refined into bio-dimethyl ether (BioDME) since 2011 [5].

It has been shown that an investment in a BLG plant is advantageous regarding efficiency and economic performance compared to a new recovery boiler investment for pulp mills. However, the availability of black liquor is limited and strongly connected to the pulp production. This limits the maximum production capacity. One solution is to add pyrolysis oil (PO) to the black liquor feed and co-gasify the blend. By using PO feed as a buffer, the plant can process the full BL flow from the mill also when the gasification plant capacity is temporarily decreased. Further, when the BL availability is limited due to lower pulp mill production, the full capacity of the gasification plant can still be used by feeding more PO.

Some concerns about technical feasibility are incomplete char conversion or excessive formation of soot and tar at the projected gasification temperatures (1273–1373 K). Mixing a certain quantity of PO into BL prior to gasification will result in new fuel properties, e.g. heating value and alkali content. Hence fuel conversion characteristics must be investigated. Char gasification is the rate controlling step, so it is especially important to have an efficient gasification. High char conversion is also important for an efficient recovery of the inorganic pulping chemicals.

This paper compares fuel conversion characteristics of different mixing ratios of BL to PO. First, single droplets were devolatilized and gasified in premixed methane flame with a flat flame burner at various droplet sizes and atmospheres. Conversion time and swelling ratio were investigated with image analyses. Then, char gasification reactivity was measured in an isothermal thermogravimetric analyzer, and kinetic parameters for the conversion rate of char gasification were estimated.

2 EXPERIMENTAL

2.1 Sample preparation

We used black liquor (BL), pyrolysis oil (PO) and their mixtures (with PO accounting for 20% and 30% on weight basis), denoted BP20 and BP30. BP20 and BP30 were prepared in a beaker on a heated plate (363 K) for 10 minutes with a liquid mixer. These ratios were selected to have a mixture in which lignin precipitated (PO accounting 30wt.%) and a homogenous mixture (PO accounting for 20wt.%). BL contains about a third of ash while PO contains negligible amounts of ash as shown in **Table I**.

Table I: Fuel properties of raw samples.

	Pyrolysis oil	Black liquor
Moisture, wt%	26.3	27.2
Combustible, wt%	n.a.	33.3
Ash, wt%	n.a.	39.5
HHV, MJ/kg-w.b.	16.7	9.2
C, wt%-d.b.	39.7	30.6
H, wt%-d.b.	7.70	3.40
N, wt%-d.b.	0.10	0.08
S, wt%-d.b.	<0.01	5.10
Cl, wt%-d.b.	<50 ppm	0.16
K, wt%-d.b.	n.a.	3.24
Na, wt%-d.b.	n.a.	21.6
O (diff.) , wt%-d.b.	52.5	35.8

2.2 Procedure of single droplet conversion experiments

Single droplet conversion experiments were carried out in premixed methane flame with a McKenna flat

flame burner (FFB) as shown in **Figure 1(a)**. To avoid the radial diffusion, the stream of combustion gas was guided by a quartz cylinder. Methane and air were premixed at three air-fuel equivalence ratio (i.e. excess air ratio), λ=0.833, 1, and 1.25, to generate fuel-rich/lean conditions and temperature variation. Gas temperatures measured by thin-wire thermocouple (diameter: 100 µm) are shown in **Table II** with equilibrium gas composition.

Table II: Measured gas temperature and calculated equilibrium composition at FFB

λ	0.833	1	1.25
T_{gas} [K]	1441±15	1348±11	1334±10
N_2 [vol.%]	67.6	71.5	72.9
O_2 [vol.%]	0	0	3.9
H_2 [vol.%]	3.7	0	0
CO [vol.%]	3.5	0	0
CO_2 [vol.%]	7.3	9.5	7.8
H_2O [vol.%]	17.9	19.0	15.5

The methane flame was located at a few millimeters away from the exit of premixed methane-air mixture. After the methane flame became stable, a single droplet of BL, BP20 or BP30 was inserted on the centerline of the combustion gas stream 21 mm away from the exit of premixed methane-air mixture using an actuator driven by a pneumatic air cylinder. The reaction behaviour of single droplet was recorded at 30 frames per second by a 3 CCD camera (JAI CV-M9 GE) for further analyses.
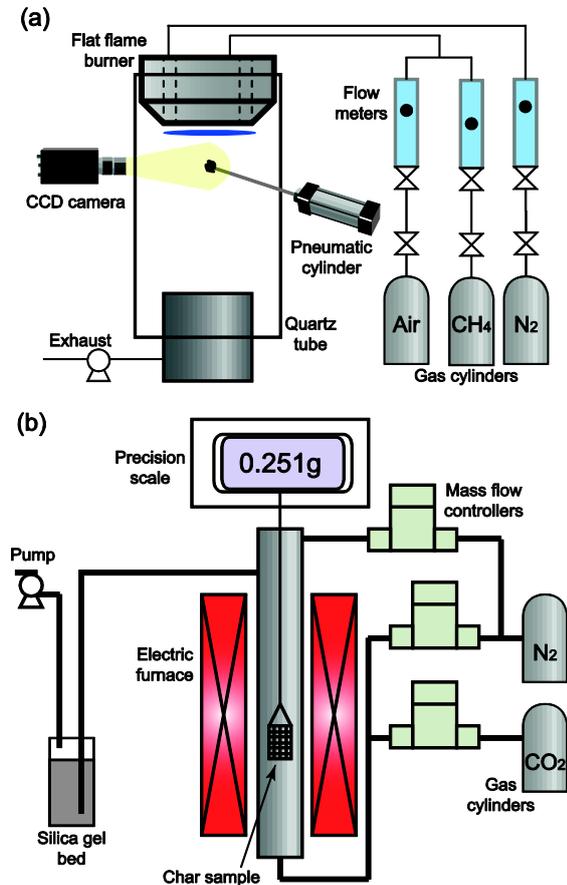

Figure 1: Experimental apparatus. (a) Single droplet conversion experiments with a flat flame burner (FFB). (b) Isothermal thermogravimetric analyzer (iTG).

2.3 Procedure of char gasification experiments

Both char preparation (pyrolysis) and char gasification experiments were carried out with an isothermal thermogravimetric analyser (iTG) as shown in **Figure 1(b)**. The iTG is a vertical cylindrical reactor with a diameter of 100 mm. The length of the electrically heated reaction zone is 450 mm. Sample can be kept in the reaction zone hanging from a precision scale with a nickel-chromium wire. The atmosphere of the reaction zone can be controlled by a continuous gas flow from the bottom of the reactor. Biomass sample can be kept in a cooling zone with nitrogen flow after the experiment to avoid further oxidation.

Char preparation methods largely affect the gasification reactivity [6]. We prepared char with CO_2 flow because the presence of CO_2 is known to affect the reactivity of char significantly. To avoid partial char conversion with CO_2, a moderately low pyrolysis temperature (813 K) was chosen. Since the resulted char had a diameter larger than 10 mm, it was impossible to carry out gasification test under chemically controlled regime *in-situ*. To minimize the effect of mass transfer on the apparent char reactivity, char sample was ground and sieved to particle size from 200 to 300 µm. Char morphology and alkali distribution were investigated by scanning electron microscope (SEM), model: JSM-6460LV by JEOL, with energy-dispersive X-ray spectroscopy (EDS), model: 7574 by Oxford Instruments.

Char gasification experiments were carried out at the temperature of 993-1133 K with various reaction atmosphere (from 10 to 100 vol.% of CO_2 with N_2 balance at total pressure of 1 bar). Char sample (~100 mg) was held in a platinum wire-mesh basket with a diameter of 15 mm. The sample basket was moved to the reaction zone by lowering the wire. Temporal mass of the sample basket was recorded in a PC every two seconds during the experiments. After the sample stopped losing its mass (i.e. sample completed char gasification), the sample basket was extracted from the reaction zone and then quenched in the cooling zone. Each experiment was repeated between 2 and 5 times in order to estimate reproducibility.

3 RESULTS AND DISCUSSION

3.1 Effect of BL/PO mixing on the fuel conversion characteristics of single droplet

The FFB experiments were employed for investigating the effect of BL/PO mixing on fuel conversion, especially devolatilization time, swelling ratio, and char gasification/oxidation times. **Figure 2** shows the example of the images during the fuel conversion of single droplet. The droplet was heated and swelled while emitting wake flame. The flame disappeared 2-3 frames (<0.1 s) before or after the droplet showed the maximum area (t=0.267 s for **Figure 2**). Then, char particles shrank or lost their surface by char gasification and/or combustion dependent on the reaction conditions. The char particles had a cenosphere structure (empty core with thin film-like solid surface).
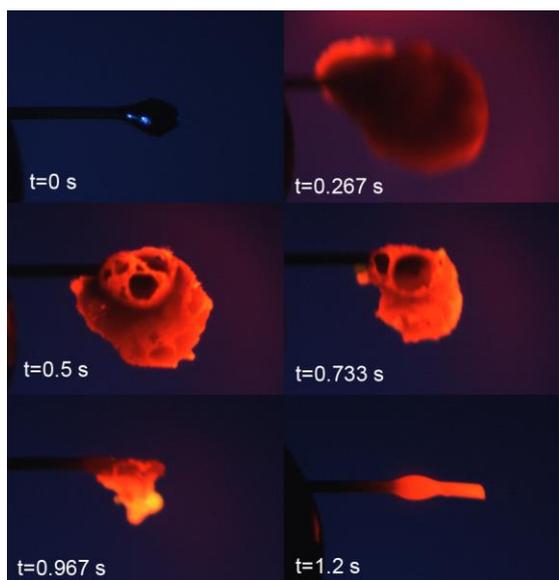
Figure 2: Fuel conversion of black liquor droplet under the presence of oxygen (λ=1.25). Horizontal field of view: 4.5 mm.
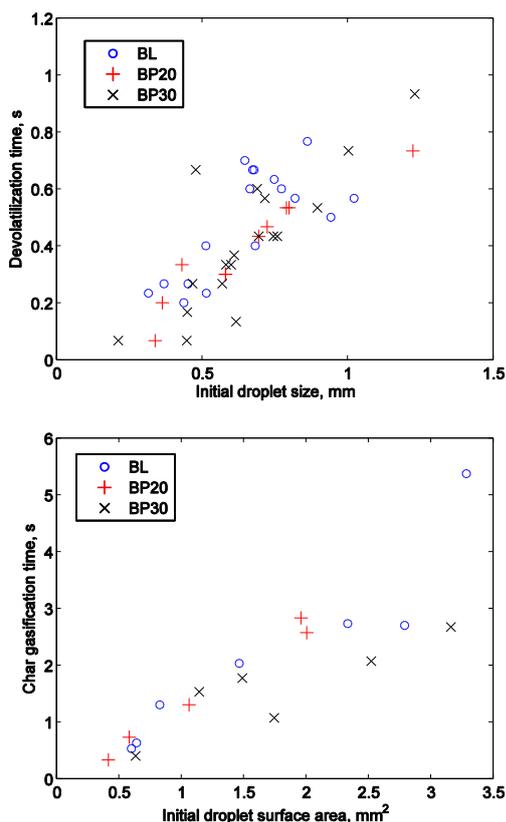

Figure 3: Comparison of fuel conversion times among different fuel mixtures (BL, BP20 and BP30). Top: initial drop size vs. devolatilization time. Bottom: initial droplet surface area vs. char gasification time.

These images were used to further analyze the characteristic times of fuel conversion processes (i.e. devolatilization and char gasification). Since we cannot observe the change in temporal mass in this setup, we regarded that devolatilization lasted from the insertion of

droplet (i.e. first frame with the droplet inside the image) until the droplet/char area showed maximum value. Then, we assumed that char gasification/oxidation started when devolatilization completed and completed when the change in char area became negligible. We should note that the characteristic times in this section contain the effect of both chemical reactions and transport phenomena.

Figure 3 shows the comparison of devolatilization and char gasification times among three samples (BL, BP20 and BP30). Devolatilization time contain the experimental data of all examined equivalence ratios because air-to-fuel equivalence ratio of the methane flame had negligible effect on devolatilization time. On the other hand, char gasification time is shown only for λ=0.833 because the reaction conditions (gas composition and temperature) are quite similar to that of entrained flow BL gasifier. Both devolatilization and char gasification times had strong correlation with initial droplet size. On the other hand, there was no significant difference in fuel conversion times among three samples (BL, BP20 and BP 30).

In general, devolatilization proceeds while droplets (or particle for solid fuels) are being heated. Therefore, the devolatilization time is decided as a result of competition among chemical reaction and external and internal heat transfer. **Table III** shows the characteristic times of these processes. Characteristic time of chemical reaction is independent of droplet size while those of external and internal heat transfer are proportional to initial droplet size and the square of initial droplet size, respectively. As shown in **Figure 3**, the devolatilization time had linear correlation to the initial droplet size, showing that the process was governed by the external heat transfer. Similarly, we can observe that the char gasification was controlled by internal mass transfer under the examined conditions.

Table III: Characteristic times of physical and chemical processes related to the fuel conversion [7].

Processes	Characteristic time
Devolatilization, τ_{dev}	$1/k_{dev}$
Char gasification, τ_{cg}	$1/k_{cg}$
External heat transfer, τ_{eh}	$\rho c_p d/6h_{eff}$
Internal heat transfer, τ_{ih}	$\rho c_p d^2/36\lambda$
External mass transfer, τ_{em}	$1/h_m$
Internal mass transfer, τ_{im}	d^2/D_{eff}

3.2 Effect of fuel mixing on char gasification reactivity

Figure 4 shows char and ash yields for different samples at 1133K in 100% CO_2. The ash yield increased almost linearly with the fraction of BL as expected. Char yield was approximately same for BL, BP20 and BP30. PO itself showed a high volatility resulting in a very low char yield. This is reasonable since PO was derived from the condensed volatiles released by the thermal decomposition of forestry biomass.
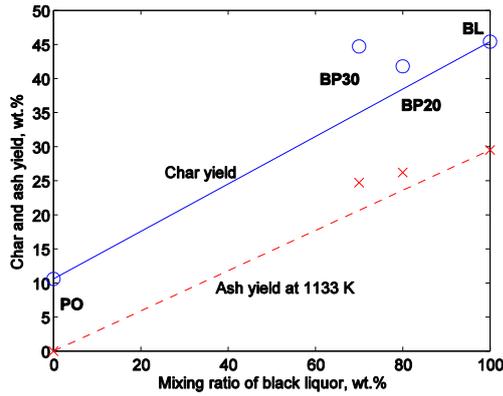
Figure 4: Char and ash yields (wet basis) as a function of black liquor fraction at 1133 K and $P_{CO2} = 1$ bar.

Each mass loss curve was standardized to char conversion, X, according to Equation 1.

$$X = \frac{m_o - m}{m_o - m_*} .\qquad(1)$$

Here, m, m_0 and m_* represent temporal, initial and final mass of sample. **Figure 5** shows the effect of black liquor fraction in the raw sample on initial char conversion rate at various reaction temperatures. Char reactivity showed no statistically significant difference among BL, BP20 and BP30 despite different concentrations of alkali metals. BP20 and BP30 reactivities were much higher than those expected from a linear interpolation between BL and PO, indicating that the catalytic effect of alkali in BL acted also on the PO derived part of the char. A possible explanation to this observation is that the molar ratio of Na/C is over the threshold of catalyst saturation. For synthetic BL this value was reported to be 0.1 mol-Na/mol-C in the original fuel [8]. The ratios of Na to C in the original fuels were 0.37, 0.29 and 0.25 for BL, BP20 and BP30, respectively.
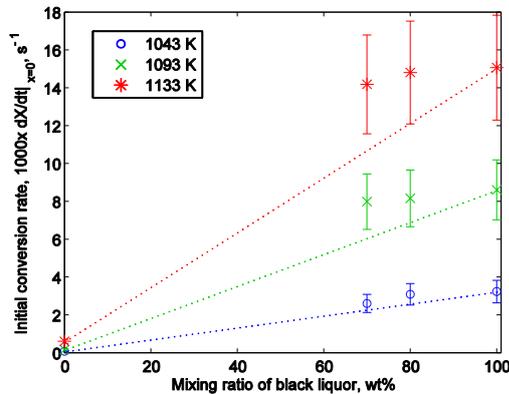

Figure 5: The effect of black liquor fraction on the initial conversion rate at T=1043, 1093 and 1133 K and P_{CO2}=1 bar. Error bars show a range of ±1 standard deviation. The line illustrates the interpolation between BL and PO.

SEM was used to study both morphology and element distribution in char samples as **Figure 6** shows

the example of char morphology for BP20. Images indicate that BL, BP20 and BP30 have similar porosities and structure. Elementary mapping of Na by SEM/EDS also showed that alkali elements were homogenously distributed for all char samples, which probably contributes to high catalytic activity.
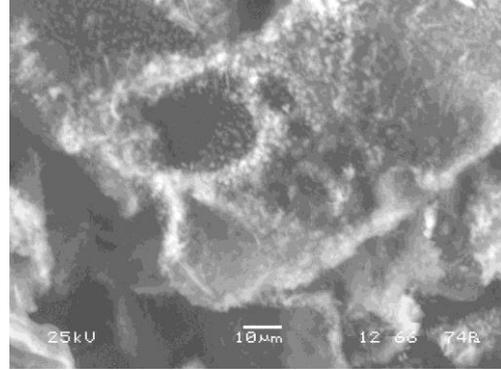

Figure 6: SEM image of BP20 char at 1000 times magnification.

3.3 Modelling of char gasification rate

Char gasification reactivities (conversion rate) of BL, BP20 and BP30 were modelled with a random pore model (RPM) and a re-parameterized Arrhenius expression as:

$$\frac{dX}{dt} = k(p,T) \cdot f(X),\qquad(2)$$

$$f(X) = (1-X)\sqrt{1 - \psi \ln(1-X)}, \text{ and}\qquad(3)$$

$$k(T) = A\exp\left[-E/R \cdot \left(1/T - 1/T_{ref}\right)\right],\qquad(4)$$

where $k(p,T)$ is rate constant, $f(X)$ is structural function (random pore model in this case), Ψ is a structural parameter according to a pore structure, A is pre-exponential factor, E is activation energy, R is gas constant, and T_{ref} is reference temperature. All parameters in RPM and Arrhenius equations were estimated simultaneously by weighed least-square method. The estimated parameters are shown in **Table IV**.

Table IV: Kinetic parameters of char gasification model

	A (s^{-1})	E (kJ/mol)	T_{ref} (K)	Ψ	R_{adj}
BL	5.32×10^{-3}	154	1063	1.7	0.985
BP20	5.31×10^{-3}	142	1063	1.2	0.993
BP30	4.97×10^{-3}	140	1063	1.8	0.979

Estimated activation energies are 154, 142 and 140 kJ/mol for BL, BP20 and BP30, respectively. These values are not significantly different considering experimental uncertainty. Activation energies determined in this work are lower than previous work on BL [9] and are within the range normally seen for other types of biomass and coal chars that have lower reactivity [9–13]. This fact does not discard catalytic activity of alkali metals as the explanation for the higher reactivity because activation energy estimated in this study is the apparent value of the overall reaction. Higher reactivities of alkali metal containing fuels are related to an increased pre-exponential term rather than a reduced energy of

activation [14].

Figure 7 shows an Arrhenius plot for several types of biomass and coal chars in 100% CO_2 atmosphere, including the experiments carried out in this study. Since there is no significant difference in reactivities among BL, BP20 and BP30 chars, reactivity of BL char is plotted as a representative of these three samples. Initial conversion rate of the plotted species was coal<forestry biomass<BL. Initial conversion rate of BL from this work was around 300 times higher than that of high rank coal and approximately 15 times higher than that of wood. They were slightly higher than the previous work on BL at lower temperatures. This is mainly because of the difference in char preparation methods. We prepared the char under CO_2 flow, which is more close to the conditions in industrial gasifiers and tends to produce more reactive char than conventional char preparation methods [6] (low heating rate under N_2 flow).
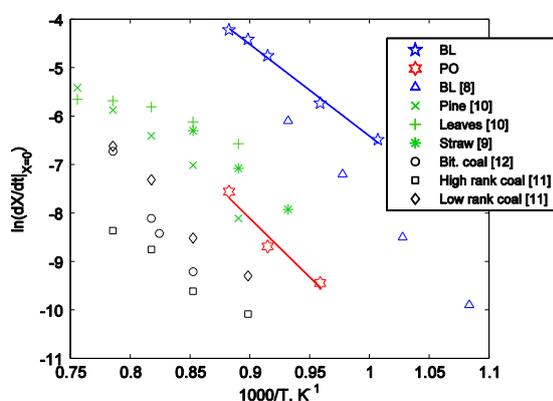

Figure 7: Arrhenius plots of the samples studied in this study using rate coefficient at X=0. Literature data for BL (blue), solid biomass (green) and coal (black) are based on references [9–13].

4   CONCLUSIONS

Both devolatilization and char gasification time of a single droplet was largely affected by the initial droplet size while fuel composition (i.e. mixing ratio of black liquor and pyrolysis oil) had negligible effect. The devolatilization time was proportional to the initial diameter, indicating the process was controlled by external heat transfer. The char gasification time was proportional to the square of the initial diameter, showing that process was controlled by internal mass diffusion.

Both mixed samples, BP20 and BP30, showed high intrinsic char reactivity, not significantly different from that of BL, implying strong catalytic activity of alkali from BL in the mixtures. Char reactivities of BL, BP20 and BP30 were significantly higher than those for other types of biomass. The random pore model with Arrhenius equation was found to fit the dynamics of char conversion in CO_2 well.

In summary, the results indicate that the black liquor gasification process may also be used for mixture of pyrolysis oil and black liquor without major modification.

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