Alkali enhanced biomass gasification with in situ S capture and novel syngas cleaning. Part 1: Gasifier performance

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ABSTRACT

Previous research shows that alkali addition in entrained flow biomass gasification can increase char conversion and decrease tar and soot formation through catalysis. This paper investigates two other potential benefits of alkali addition: increased slag fluidity and in situ sulfur capture.

Thermodynamic equilibrium calculations show that addition of 2–8% alkali catalyst to biomass completely changes the chemical domain of the gasifier slag phase to an alkali carbonate melt with low viscosity. This can increase feedstock flexibility and improve the operability of an entrained flow biomass gasification process. The alkali carbonate melt also leads to up to 90% sulfur capture through the formation of alkali sulfides. The resulting reduced syngas sulfur content can potentially simplify gas cleaning required for catalytic biofuel production.

Alkali catalyst recovery and recycling is a precondition for the economic feasibility of the proposed process and is effected through a wet quench. It is shown that the addition of Zn for sulfur precipitation in the alkali recovery loop enables the separation of S, Ca and Mg from the recycle. For high Si and Cl biomass feedstocks, an alternative separation technology for these elements may be required to avoid build-up.

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1. Introduction

Sustainable production of biofuels is one component required for a transition towards a low carbon transportation system. Biomass gasification is one of the most promising technologies for efficient production of biofuels, in particular when considering lignocellulosic biomass feedstock. Different biomass gasification technologies have different advantages. Entrained flow gasification (EFG) is known to be highly scalable, feasible to pressurize and generally produce a clean syngas with low concentrations of methane and tars. Pressurized pilot scale biomass EFG has been successfully demonstrated for pyrolysis liquids [1,2], black liquor (BL) [3–5], BL/pyrolysis liquid mixtures [6,7] as well as various solid biomass fuels [8–10]. The latter has been denoted pressurized entrained flow biomass gasification (PEBG) and that nomenclature is used for solid biomass EFG in this paper.

Ash components in coal and biomass have been shown to influence char gasification rates, with alkali metals and alkaline earth metals being the most active constituents [11–14]. BL gasification (BLG) is an extreme example of this with large effects from the high BL sodium content [15–19]. Adding alkali salts to PEBG has been shown experimentally to give a number of positive effects on individual sub-processes, including increased char gasification rate, improved tar decomposition and decreased soot formation (gas phase condensation reactions) [13,20–22]. Alkali enhanced PEBG can thus have the potential to improve efficiency and decrease investment costs compared to normal PEBG, leading to decreased production costs for biofuels and biochemicals.

A conceptual process for alkali enhanced PEBG including catalyst recovery and recycling has been proposed previously (see Fig. 1 of Umeki et al. [22]). A recent techno-economic study of this concept applied for methanol production showed improved gasification efficiency but no distinct economic advantage [23]. The study, however, did not include effects of potentially simplified syngas cooling and cleaning attributable to decreased tar and soot
formation. The study also pointed at alkali addition leading to a decreased slag viscosity. While this was not quantified or supported by results from the study, it can be important since slag flowability has been shown to be a problem in pilot scale PEBG.

It is known from BLG that gas-slag equilibria lead to a distribution of sulfur between the phases. For BLG at 30 bar pressure, typically two thirds of the sulfur is captured in the slag with one third in the gas phase in pilot scale experiments [7], although equilibrium calculations indicate that a somewhat higher fraction should end up in the gas phase [24]. Most biomass gasification feedstocks have much lower sulfur content than BL but sulfur removal from syngas is still a critical process to enable catalytic gas upgrading. Hence, any capture of sulfur in the gasifier slag can be important in the design of the syngas cleaning process and can potentially decrease costs associated with it. An analogy with BLG indicates that in situ gasifier sulfur capture could also occur in an alkali enhanced PEBG process. To the best of our knowledge, such an effect has however not been quantified or even mentioned previously.

As noted in previous work [22,23], alkali catalyst recycling is a prerequisite for the economic feasibility of the proposed process concept. Such recycling is facilitated by a wet quench design similar to the one used for BLG, which dissolves soluble slag components, including alkali, in water that can be recycled. However, in order to avoid build-up of sulfur and other biomass ash constituents that are captured in the slag phase, they would have to be purged from the alkali recycling loop. This important aspect of alkali enhanced PEBG has not been studied previously.

The main objective of this work is to quantify the effects of alkali addition on gasifier slag chemistry, including heterogeneous equilibria such as sulfur distribution, slagging, slag composition and slag properties. A second objective is to use predicted slag composition to assess the possibility to recycle the alkali catalyst, including verifying the speciation of the alkali catalyst itself as well as investigating possibilities to handle other ash components in the alkali recycle. The primary tool used to achieve these objectives is thermodynamic equilibrium calculations, since laboratory experimental set-ups do not easily allow for study of heterogeneous equilibria representative for oxygen-blown PEBG. Data for non-equilibrium processes, such as char conversion are based on previous experimental work.

2. Materials and methods

2.1. Feedstocks and impregnation

Four forest based feedstocks for biofuel production were considered: pine stemwood (PW), pine bark (PB), pine forest residues (PFR) and spruce forest residues (SFR). PW is a low ash reference case, while the other feedstocks are residues that are probably more relevant for biofuel production in a longer perspective, due to higher availability at lower costs. The compositions and heating values of these feedstocks are shown in Table 1. The inclusion of PB, PFR and SFR allows the study of the impact of higher ash content, and varying ash compositions. Al, Fe, Mn, P and other minor components were not included in the analysis, since they are considered to have low impact on the results due to their low concentrations. It can be of interest to include P in future work.

![Fig. 1. The black liquor gasification concept (left) and the proposed alkali enhance biomass gasification concept (right).](image)

### Table 1

Composition and heating values of the feedstocks selected on dry basis.

|          | PW | PB | PFR | SFR |
|----------|----|----|-----|-----|
| HHV [MJ/kg] | 20.41 | 20.90 | 20.61 | 20.61 |
| LHV [MJ/kg] | 19.06 | 19.65 | 19.31 | 19.31 |
| C [wt%] | 50.96 | 53.67 | 51.52 | 51.48 |
| H [wt%] | 6.11 | 5.74 | 5.95 | 5.95 |
| O [wt%] | 42.70 | 39.51 | 40.98 | 40.82 |
| N [wt%] | 0.10 | 0.26 | 0.65 | 0.65 |
| S [ppm] | 90 | 20 | 330 | 2000 |
| Ca [ppm] | 600 | 5000 | 4000 | 5000 |
| Mg [ppm] | 120 | 400 | 600 | 700 |
| Na [ppm] | 7 | 20 | 30 | 50 |
| K [ppm] | 300 | 2200 | 3200 | 2500 |
| S [ppm] | 100 | 400 | 600 | 500 |
| Cl [ppm] | 70 | 150 | 200 | 270 |
| Total [wt%] | 0.13 | 0.82 | 0.90 | 1.10 |

a PW: pine stem wood, PB: pine bark, PFR: Pine forest residues, SFR: Spruce forest residues.
b Werkelin et al. [25].
c Phyllis 2 database [26] samples with ash <0.5%.
d Phyllis 2 database [26] samples with ash <5%.
e Phyllis 2 database [26] samples with mixed pine and spruce.
f C and O adjusted to make element sum 100% assuming that any missing mass 1–2% is carbonate in ash.
g Sum of Si, Ca, Mg, Na, K, S and Cl.
studies but the currently available thermodynamic databases (see below) do not include data for P in combination with the other relevant elements.

Impregnated sample compositions were calculated by assuming that 2%, 4% or 8% Na or K was added by the wet impregnation procedure described by Kirtania et al. [21]. Any impregnation of anions or leaching of organicics from the feedstock was disregarded. The composition of a representative selection of impregnated samples can be found in Table 2. Full data for all feedstock-impregnation combinations used can be found in the Supplementary material (Table S1).

2.2. Gasification technology and operating conditions

The considered gasification technology is conceptually a modification of the pressurized oxygen-blown entrained flow gasifier, developed by Chemrec AB for the purpose of gasifying BL for biofuel production [27,28] as visualized in Fig. 1. The hot syngas and slag leaving the gasifier is cooled with water in a quench zone with slag being dissolved in a quench pool. The raw syngas is cooled further in a counter-current condenser that condenses the water vapor and other condensable species that may still be present, acting as an efficient particle scrubber and giving a very clean syngas without detectable organic components except methane and benzene [29].

A more detailed description of BLG technology can be found in numerous published studies [5,29–31]. The primary reason for adopting a modification of the BLG technology is that the technology is optimized for the high alkali content of black liquor, for example through the ceramic reactor lining and the efficient alkali particle removal in the condensing gas cooler, which are both highly relevant for the present alkali enhanced PEBG concept.

The gasification temperatures for the simulation were selected to be able to provide (essentially) full carbon conversion, which enables avoiding the use of kinetic models and makes the thermodynamic simulation approach realistic. It is also practically relevant since this represents the conditions at which a commercial gasifier would likely be operated. Previous research on lab scale using thermogravimetric analysis (TGA) [21,32] and drop tube furnace [22] has indicated that the catalytic effect from added alkali enhances char gasification so that full carbon conversion can be reached at 1100 °C for impregnated biomass. Conversely, a gasification temperature of 1400 °C can be required for non-impregnated biomass at a residence time of 5–10 s [9,32], which is typical for PEBG. These temperatures were used as base cases in the simulations of the impregnated and non-impregnated cases, respectively. Based on evaluated impregnation levels in the previous experimental studies [21,22,32], impregnation with 4% Na or K was used as base case in the present study. Na and K were assumed to have a similar catalytic activity as indicated by experimental work using TGA [21].

In order to study the influence of different process conditions, a number of simulations were carried out with varying feedstock type, feedstock dryness (90–99% dry solids), impregnation (0–8% Na/K), temperature (1000–1400 °C, up to 1500 °C for non-impregnated PW) and pressure (5–60 bar). The simulations are summarized in Table 3. Cases 2 and 15 in the table constitute the base cases for Na and K impregnation, respectively. Case 26 is the base case for standard, non-impregnated, PEBG.

2.3. Gasification simulation

Important aspects of this study are slag phases formed, slag properties and the equilibrium between sulfur in the slag and in the gas phases. As noted above, laboratory experimental set-ups do not easily allow for study of heterogeneous equilibria representative for oxygen-blown pressurized PEBG. An important reason is that the partial pressure of gas phase components, primarily CO2 and H2S, are of major importance for the heterogeneous equilibria controlling slag composition and sulfur capture. Laboratory experiments using a drop tube furnace [22] often use lower pressures and more diluted gas atmosphere than a commercial oxygen-blown pressurized PEBG process. This means that such experiments are not representative for the aspects of the process studied in this work, which is why thermodynamic equilibrium modelling is used.

In order to enable proper and quantitative consideration of slag properties and slag-gas equilibria, it is important to use an appropriate thermodynamic representation of the slag phase. The Matlab based thermodynamic equilibrium tool SIMGAS [24] has been applied in previous work [33], was not suitable for this study, since it lacks detailed descriptions of the slag phases, which are crucial for the current investigation.

The oxygen blown gasification process was modelled by thermodynamic equilibrium in ChemSheet [34] using thermodynamic databases and models from the Equilib module of FactSage 6.4 [35]. Data from the databases FToxid and FTPulp were used to represent liquid and solid inorganic solution phases according to Table 4. Simulations of the auto-thermal process were executed for a determined temperature and pressure by iteratively estimating the oxygen addition required to reach this equilibrium temperature. This means that more oxygen is added for higher gasification temperatures, everything else being equal. A heat loss of 0.7% of the thermal input was assumed, which is realistic for a commercial scale process [24].

2.4. Alkali recovery and recycling simulation

In order to assess the possibility to recycle the alkali catalyst, the commercial software OLı Stream Analyzer (OLı Systems, Cedar Knolls, NJ, USA) was used to study the equilibrium composition of aqueous solutions and slurries of ash components, based on the database of phase and electrolyte equilibria embedded in the software. The degree of dissolution for each element was estimated based on gasifier slag composition as calculated by ChemSheet/FactSage. In the calculation, water was added corresponding to the dry sludge. The water in the wet quench, as described above. The feasibility of S removal by precipitation using a Zn-based additive was studied after initial consideration of both Fe- and Zn-based additives. The condition used in this work was set to be 80 °C and 1 bar,
The effects of gasification temperature and pressure on the fraction of sulfur captured in the gasifier slag are shown in Fig. 2 for 4% Na and K impregnation, respectively. These results show that in situ S capture rates of up to >90% can be obtained with 4% Na impregnation, although at base case conditions (1100 °C and 30 bar), the capture rate is 77% and 54%, respectively, for 4% Na and K impregnation. These levels can be compared to approximately 70% S capture for BLG, which contains around 5% S and 20% Na in the gas phase and needs to be removed from the syngas, for the non-impregnated cases.

Since those are conditions that are relevant for the biomass impregnation process, following the S removal step [21].

3. Results and discussion

3.1. In situ sulfur capture

The equilibrium reaction is shifted to the right (i.e. higher capture of S in the slag) with increasing temperature and decreasing pressure, which is in general agreement with the results in Fig. 2, although they are influenced by a much more complex network of reactions. The only deviation from this trend is the decreasing S capture with K impregnation at temperatures >1200 °C. This is explained by the higher volatility of K in the gasifier environment (left side of Fig. 2), which is related to the lower stability of K2CO3 compared to Na2CO3. At temperatures >1200 °C, a significant fraction of the K is found in gas phase, primarily as KOH(g) and K(g). At 1400 °C, there is no K at all in condensed phase, which means that no liquid inorganic phase is present, as discussed further below. This consequently also results in zero S capture. The high volatility of K, in combination with the fact that Na shows a higher S capture rate even in the absence of alkali volatilization, indicates that Na can be a better choice as additive/catalyst from the S capture perspective.

Generally, it is often advantageous to operate a gasifier at lower temperature, which leads to higher efficiency provided that sufficient fuel conversion can be obtained, and higher pressure to avoid syngas compression costs. Hence, the results in Fig. 2 indicate that there may be a trade-off between the S removal and other techno-economic factors. This trade-off is important and is further investigated in part 2 of this paper [36].

Table 3
Summary of simulated cases. Case names formed from feedstock (Table 2), impregnation (Table S1), dry solids content, gasification temperature and gasification pressure. Boldface cases (2, 15, 26) represent the base cases for Na impregnation, K impregnation and no impregnation, respectively.

| No | Name       | Feedstock | Impregnation | Feedstock dry solids | Temperature [°C] | Pressure [bar] |
|----|------------|-----------|--------------|----------------------|------------------|---------------|
| 1  | PW4Na-98-1000-30 | PW        | 4% Na        | 98%                  | 1000             | 30            |
| 2  | PW4Na-98-1100-30 | PW        | 4% Na        | 98%                  | 1100             | 30            |
| 3  | PW4Na-98-1200-30 | PW        | 4% Na        | 98%                  | 1100             | 30            |
| 4  | PW4Na-98-1300-30 | PW        | 4% Na        | 98%                  | 1100             | 30            |
| 5  | PW4Na-98-1400-30 | PW        | 4% Na        | 98%                  | 1100             | 30            |
| 6  | PW4Na-98-1100-30 | PW        | 4% Na        | 90%                  | 1100             | 30            |
| 7  | PW4Na-98-1100-30 | PW        | 4% Na        | 90%                  | 1100             | 30            |
| 8  | PW4Na-98-1100-30 | PW        | 4% Na        | 90%                  | 1100             | 30            |
| 9  | PW4Na-98-1100-30 | PW        | 4% Na        | 90%                  | 1100             | 30            |
| 10 | PW4Na-98-1100-30 | PW        | 4% Na        | 90%                  | 1100             | 10            |
| 11 | PW4Na-98-1100-30 | PW        | 4% Na        | 90%                  | 1100             | 30            |
| 12 | PW2Na-98-1100-30 | PW        | 2% Na        | 98%                  | 1100             | 30            |
| 13 | PW2Na-98-1100-30 | PW        | 2% Na        | 98%                  | 1100             | 30            |
| 14 | PW2K-98-1100-30  | PW        | 2% K         | 98%                  | 1100             | 30            |
| 15 | PW4K-98-1100-30  | PW        | 4% K         | 98%                  | 1100             | 30            |
| 16 | PW8K-98-1100-30  | PW        | 8% K         | 98%                  | 1100             | 30            |
| 17 | PW2K-98-1100-30  | PW        | 2% K         | 98%                  | 1100             | 30            |
| 18 | PW2K-98-1100-30  | PW        | 2% K         | 98%                  | 1100             | 30            |
| 19 | PW4K-98-1100-30  | PW        | 4% K         | 98%                  | 1100             | 30            |
| 20 | PW4K-98-1100-30  | PW        | 4% K         | 98%                  | 1100             | 30            |
| 21 | PW4K-98-1100-30  | PW        | 4% K         | 98%                  | 1100             | 30            |
| 22 | PW4K-98-1100-30  | PW        | 4% K         | 98%                  | 1100             | 30            |
| 23 | PW4K-98-1100-30  | PW        | 4% K         | 98%                  | 1100             | 30            |
| 24 | PW8K-98-1100-30  | PW        | 8% K         | 98%                  | 1100             | 30            |
| 25 | PW8-1300-30      | PW        | -            | 98%                  | 1300             | 30            |
| 26 | PW/98-1400-30    | PW        | -            | 98%                  | 1400             | 30            |
| 27 | PW/98-1500-30    | PW        | -            | 98%                  | 1500             | 30            |
| 28 | PFR/98-1400-30   | PFR       | -            | 98%                  | 1400             | 30            |
| 29 | PFR4Na-98-1100-30| PFR       | 4% Na        | 98%                  | 1100             | 30            |
| 30 | PFR4Na-98-1300-30| PFR       | 4% Na        | 98%                  | 1300             | 30            |
| 31 | PFR8Na-98-1100-30| PFR       | 8% Na        | 98%                  | 1100             | 30            |

Table 4
FactSage database used for thermodynamic equilibrium calculations.

| Database          | Phase description                                                                 |
|-------------------|------------------------------------------------------------------------------------|
| FT pulp           | MeltA: Na+·(K+/Co2+)·(OH-)·(Cl-)·SO42-·S2- melt                                     |
| FT pulp           | Gort: Solid solution of (Na2SO4)x in K2Na(SO4)x                                     |
| FT pulp           | OrtA: Na+·(K+/Co2+)·SO42-·solid solution                                            |
| FT oxid           | SlagA: Oxide melt (e.g. Na, K, Mg, Ca, Si)                                         |
| FactPS            | Pure stoichiometric gas and solid phases                                           |

This equilibrium reaction is shifted to the right (i.e. higher capture of S in the slag) with increasing temperature and decreasing pressure, which is in general agreement with the results in Fig. 2, although they are influenced by a much more complex network of reactions. The only deviation from this trend is the decreasing S capture with K impregnation at temperatures >1200 °C. This is explained by the higher volatility of K in the gasifier environment (left side of Fig. 2), which is related to the lower stability of K2CO3 compared to Na2CO3. At temperatures >1200 °C, a significant fraction of the K is found in gas phase, primarily as KOH(g) and K(g). At 1400 °C, there is no K at all in condensed phase, which means that no liquid inorganic phase is present, as discussed further below. This consequently also results in zero S capture. The high volatility of K, in combination with the fact that Na shows a higher S capture rate even in the absence of significant alkali volatilization, indicates that Na can be a better choice as additive/catalyst from the S capture perspective.
the biomass to be oxidized in order to provide the required heat for the auto-thermal process. As shown in Fig. 3 (left), this effect is very small. Increasing impregnation from 0% to 8% at 1100°C only decreases the cold gas efficiency (CGE) from 85% to 83%. It should be emphasized that, as noted above, the non-impregnated case is not relevant at 1100°C since the char conversion would be poor, leaving high amounts of unconverted particles, and the tar production high in the absence of the catalytic effect of the alkali impregnation. Hence, the relevant comparison for 0% alkali impregnation is 1400°C, at which the CGE is 78%. This means that in total, alkali impregnation improves the CGE, as shown in the earlier techno-economic study of alkali enhanced PEBG [23].

The effect of increasing the feedstock dryness is quite straightforward. As is well known, increasing feedstock dryness improves the CGE due to decreased thermal ballast from water, which means that less oxygen needs to be added. This fact is also responsible for the increased S capture with dryer feedstock, since less added oxygen means less water vapor and CO₂ in the gas phase, shifting Eq. (1) to the right according to Le Chatelier’s principle. In all cases, gas phase sulfur is dominated by H₂S and COS. Any presence of other S species is determined mainly by the process temperature. At 1100°C or below, more than 99.9% of gas phase sulfur is present as H₂S or COS while at 1400–1500°C, 0.6–1.2% of the total gas phase S is in other forms.

Fig. 4 shows the effect of varying the feedstock, and thereby ash content and composition as shown in Table 1, by comparing S capture for all feedstocks, at the same conditions. It is clear that the feedstock type has a relatively limited influence, which means that the analysis presented above, which was carried out for PW, is also valid for other feedstock types in the domain studied.
3.2. Slag composition and properties

Table 5 shows data for the phases leaving the gasification reactor. More than 97% of the flow exits the reactor as a gas, since the feedstock consists mostly of organic material that is gasified. As noted above, and as shown in Table 5, a few cases result in significant amounts of alkali in gas phase. This occurs for non-impregnated PW and PFR (cases 24–28) and for K impregnated PW at the highest temperatures (≥1300 °C, cases 19–20).

The condensed phases leaving the reactor are always purely inorganic according to the equilibrium calculations, since full carbon conversion is obtained at equilibrium. As noted above, based on experimental data this is considered to be realistic for impregnated feedstocks at ≥1100 °C and for non-impregnated feedstock at ≥1400 °C. Cases with temperatures below these thresholds (cases 1, 17, 25) would risk incomplete carbon conversion, which would cause the presence of char/carbon in the condensed material exiting the reactor. The composition of the inorganic condensed phase, however, is still considered to be realistically predicted by equilibrium.

For the properties of the slag, especially viscosity, it is of fundamental importance whether the slag is an alkali carbonate dominated melt, or an oxide melt. Oxide dominated slags have been shown to have high viscosity [37], and slag/ash accumulation has been shown to cause operational problems for pilot scale non-catalytic PEBG [38,39]. From Table 5 it is very clear that for alkali enhanced PEBG, the carbonate melt phase completely dominates the condensed phases formed in the reactor; more than 85% of the condensed phase is the carbonate melt except for the single high temperature case where the alkali volatilization is close to 100%.

### Table 5

| No | Name | Gas phase | Condensed phase | No of phases |
|----|------|-----------|----------------|-------------|
|    |      | Overall *a* | Alkalib | Oxide melt | Carbonate melt | K2Ca(CO3)2(s) | MgO(s) | CaO(s) | Ca2SiO4(s) | Ca3SiO5(s) | Na2CaSiO4(s) | Ca3MgSi2O8(s) |
| 1  | PW4Na-98-1000-30 | 98.7% | 0.0% | 98.2% | 0.5% | 0.9% | 0.4% | 5 |
| 2  | PW4Na-98-1100-30 | 98.8% | 0.3% | 98.2% | 0.5% | 0.9% | 0.4% | 5 |
| 3  | PW4Na-98-1200-30 | 98.8% | 1.4% | 98.2% | 0.5% | 0.9% | 0.3% | 5 |
| 4  | PW4Na-98-1300-30 | 98.8% | 5.4% | 1.1% | 97.3% | 0.5% | 1.1% | 5 |
| 5  | PW4Na-98-1400-30 | 98.9% | 17.4% | 1.2% | 97.0% | 0.6% | 1.3% | 5 |
| 6  | PW4Na-90-1100-30 | 98.8% | 0.3% | 98.2% | 0.5% | 0.9% | 0.3% | 5 |
| 7  | PW4Na-95-1100-30 | 98.8% | 0.3% | 98.2% | 0.5% | 0.9% | 0.3% | 5 |
| 8  | PW4Na-99-1100-30 | 98.7% | 0.3% | 98.2% | 0.5% | 0.9% | 0.4% | 5 |
| 9  | PW4Na-98-1100-5  | 98.8% | 2.7% | 97.8% | 0.6% | 1.3% | 0.4% | 5 |
| 10 | PW4Na-98-1100-10 | 98.8% | 1.1% | 98.2% | 0.5% | 0.9% | 0.4% | 5 |
| 11 | PW4Na-98-1100-60 | 98.8% | 1.1% | 98.2% | 0.5% | 0.9% | 0.3% | 5 |
| 12 | PW2Na-98-1100-30 | 99.4% | 0.6% | 96.4% | 1.1% | 1.8% | 0.7% | 5 |
| 13 | PW8Na-98-1100-30 | 97.5% | 0.1% | 99.1% | 0.3% | 0.5% | 0.2% | 5 |
| 14 | PW2K-98-1100-30 | 99.6% | 7.0% | 93.8% | 1.8% | 3.2% | 1.2% | 5 |
| 15 | PW4K-98-1100-30 | 99.3% | 3.5% | 96.9% | 0.9% | 1.6% | 0.6% | 5 |
| 16 | PW8K-98-1100-30 | 98.6% | 1.8% | 98.4% | 0.5% | 0.8% | 0.3% | 5 |
| 17 | PW4K-98-1000-30 | 99.3% | 0.6% | 97.1% | 0.6% | 1.9% | 0.3% | 5 |
| 18 | PW4K-98-1200-30 | 99.3% | 14.2% | 96.6% | 1.0% | 1.8% | 0.7% | 5 |
| 19 | PW4K-98-1300-30 | 99.6% | 46.4% | 95.7% | 1.6% | 1.7% | 1.0% | 5 |
| 20 | PW4K-98-1400-30 | 99.9% | 100.0% | 36.6% | 39.5% | 23.9% | 4 |
| 21 | PB4Na-98-1100-30 | 98.6% | 0.3% | 86.8% | 1.5% | 11.6% | 0.1% | 5 |
| 22 | PFR4Na-98-1100-30 | 98.6% | 0.3% | 89.3% | 2.3% | 7.3% | 1.1% | 5 |
| 23 | SFR4Na-98-1100-30 | 98.6% | 0.3% | 93.5% | 1.1% | 3.6% | 1.8% | 5 |
| 24 | PW-98-1100-30 | 99.9% | 99.3% | 29.6% | 51.3% | 19.2% | 4 |
| 25 | PW-98-1300-30 | 99.9% | 99.4% | 36.6% | 39.6% | 23.8% | 4 |
| 26 | PW-98-1400-30 | 99.9% | 99.5% | 36.6% | 39.5% | 23.9% | 4 |
| 27 | PW-98-1500-30 | 99.9% | 99.6% | 36.8% | 39.1% | 24.2% | 4 |
| 28 | PFR-98-1400-30 | 99.9% | 99.9% | 24.4% | 63.9% | 11.6% | 4 |
| 29 | PFR4Na-98-1100-10 | 98.6% | 1.3% | 89.2% | 2.4% | 7.3% | 1.1% | 5 |
| 30 | PFR4Na-98-1300-30 | 98.6% | 5.9% | 3.4% | 86.6% | 2.3% | 7.7% | 5 |
| 31 | PFR8Na-98-1100-30 | 97.3% | 0.2% | 94.2% | 1.3% | 3.9% | 0.6% | 5 |

* a Fraction of total flow exiting the reactor that is in gas phase.
* b Fraction of total alkali (Na+K) exiting the reactor that is in gas phase.
* c Flow of each phase as fraction of total condensed phases flow exiting the reactor.
Compared to oxide slags [37], a carbonate melt has significantly lower melting point and very low viscosity [40]. For the forest residue based feedstocks (PB, PFR and SFR), the fraction of solid phases is higher than for stem wood (PW) but it is still <15%. This can be compared to 30% solid material, which is usually considered the limit for a flowing slag with a composition in the relevant domain [41,42]. For the non-impregnated cases (and the impregnated case with 100% K volatilization, case 20), there is no liquid phase predicted at all. Only small amounts of solid oxides and silicates are formed, which means a severe risk for ash accumulation in the gasification reactor. Hence, these results strongly support the previous hypothesis [23] stating that alkali impregnation of the feedstock does indeed facilitate the flow of inorganic components out of the gasification reactor and thus can improve the operability.

Fig. 5 shows the composition of the carbonate melt phase for selected cases. The main conclusions to be drawn from this data are that increased temperature promotes the formation of hydroxide, in agreement with earlier results for BLG [24], and that the amount of sulfur in the slag increases with increasing feedstock sulfur content. The latter is a direct consequence of the in situ sulfur capture discussed above and of that sulfur is indeed captured in the form of alkali sulfates, as shown in Eq. (1). In addition, >99% of chloride is captured in the carbonate melt phase as alkali chlorides, which decreases the formation of HCl in the gas phase.

### 3.3. Alkali recycle loop

The slag compositions of ten selected cases from different biomass gasification conditions were chosen to study the removal efficiency for S and other ash elements, as shown in Table 6, in order to assess the possibility to recycle the alkali catalyst. If ash elements are not removed, there is a risk of accumulation in the alkali recycle loop. The cases studied correspond to cases listed in Table 3 but were given new more descriptive brief names, as shown in Table 6. It was assumed that any gaseous alkali, primarily in the forms of KOH/NaOH(g) and K/Na(g) was transformed to K2CO3 and Na2CO3 by reaction with CO2(g) during quenching, which is known to happen in BLG [5]. Furthermore, Ca silicates were converted to CaO and silicic acid to enable the OLI calculation while still maintaining element balances.

The reference cases (cases 26 and 28), without alkali impregnation, have less Na2CO3 and Na2S, but otherwise the composition of the slag that is mixed with water is quite similar as shown in Table 6. In addition, no S is included in the slag phases for the non-impregnated cases. Thus, the slags from these cases are not of
interest for either S removal or alkali catalyst recycle and they are not discussed further in this section.

The amount of water being added in the quench section of the gasifier can be adjusted to a certain extent, giving different concentrations of the aqueous alkali solution for catalyst recycle. As the concentration of Na$^+$ is directly related to the amount of water that is added to form aqueous solutions, the concentration of Na$^+$ was in this work used as reference for discussing the effect of adding varying amounts of water.

The degree of dissolution of each slag element at 1–4 mol/L Na$^+$ was investigated based on the composition of the slag for the cases in Table 6. Fig. 6 (left) shows this for Ca for the two base impregnation cases PW Imp and PFR Imp base (cases 2 and 22). For these, more than 98% and 99.8%, respectively, of elemental Ca is converted into solid phases, for the relevant Na$^+$ concentration interval. The precipitated Ca is found as a mixture of CaCO$_3$(s) and Ca(OH)$_2$(s). Of other important slag elements, Mg is always 100% transferred into the solid phase as Mg(OH)$_2$(s), while S, Si and Cl are always found fully in dissolved form, with the speciation for Si exemplified in Fig. 6 (right).

These results show that Ca and Mg can be removed with very high efficiency by filtration of the water-slag mixture. Based on this and on the knowledge that S can be precipitated as metal sulfides (as discussed below), we propose a general process for the recycling of alkali catalyst and removal of Ca, Mg and S from slags as shown in Fig. 7. The process consists of three steps; (1) dissolving the slag, (2) filtering Ca/Mg, and (3) removing S by adding additive followed by filtration. The results above for Ca precipitation, in combination with the fact that around 1 mol/L of Na$^+$ is a suitable concentration for impregnating biomass with Na$_2$[21], made 1.2–1.4 mol/L of Na$^+$ being selected for further study of S removal.

ZnS and FeS are both well-known as useful byproducts, and thus the Fe- or Zn-based S precipitation agents are promising. However, a preliminarily survey showed that it is difficult to find inexpensive Fe-based precipitation agents, and Fe$^{2+}$ can also easily be oxidized to Fe$^{3+}$. Therefore, Zn-based agents were investigated in this work. To study the effect of different anions on the S removal efficiency, ZnCO$_3$ and Zn(OH)$_2$ were chosen as feasible additives.

In the simulations, precipitated Ca and Mg was separated by filtering, after which the S precipitation agents (Zn(OH)$_2$ or ZnCO$_3$) were added into the aqueous solution in different amounts, and the resulting equilibrium mixture composition calculated. As shown in Fig. 8 (left), increasing the amount of added precipitation agent results in a gradual increase of the S removal efficiency, and at a mole ratio of Zn- or Cd-based additive to S of around 1:1, all S is found as ZnS(s). Zn(OH)$_2$ and ZnCO$_3$ showed no significant difference as precipitation agents. Fig. 8 (right) shows the concentration of the remaining Zn$^{2+}$ in the liquid phase as a function of the S removal efficiency. The results show that it is possible to remove very close to 100% of S in the aqueous phase with the addition of Zn(OH)$_2$ or ZnCO$_3$. However, the concentration of Zn$^{2+}$ in the aqueous phase increases drastically when the S removal efficiency increases from 95% to 100%. Zn$^{2+}$ should be avoided in the alkali recycle, since it is an undesired element in the gasification process. Hence, process conditions giving around 98% of S removal efficiency were then selected for all the eight impregnation cases.

In order to assess the potential to recycle the alkali catalyst, the eight cases were simulated according to the full process as shown in Fig. 7. The final results, as given in Table 7, indicate that Ca, Mg, and S can be removed with very high efficiency and that very low concentrations of these elements, as well as of Zn, would end up in the alkali recycle. However, Si and Cl are not removed by the proposed process and will have concentrations in the alkali recycle depending on their abundance in the biomass feedstock. For high Si and Cl biomass feedstocks, an alternative separation technology for these elements may thus be required in order to avoid build-up or catalyst losses through purging. In particular, Si separation is a priority in further work, due to the potential formation of alkali

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**Fig. 6.** The pH and percentage of elements Ca transferred into solid phase with the change of alkali ion concentration (left) as well as the existing forms of Si in aqueous solution at water addition corresponding to 1.25 mol/L Na$^+$ (right), for the base impregnation cases (cases 2 and 22).

**Fig. 7.** The general process of the removal of S, Ca, Mg from slags in order to facilitate alkali catalyst recycle.
alkali addition, both in terms of char gasification efficiency and slag viscosity decrease. This can be a problem primarily for feedstocks with higher Si content than the feedstocks studied in this work, or if Si is enriched in the alkali recirculation stream.

Improved feedstock flexibility since the original ash composition is no longer determining the slag properties. The analysis presented in this article indicates that there is no substantial difference regarding S capture between stem wood and various types of forest residues investigated, and that satisfactory slag flowability is obtained for both feedstock categories.

Even for low sulfur biomass, the syngas sulfur levels resulting from normal PEBG are too high for catalytic gas upgrading. Hence, some type of sulfur removal is always required. The up to 90% in situ sulfur capture resulting from alkali addition in the PEBG can potentially simplify the sulfur removal and decrease the costs associated with it, which is further investigated in Part 2 of this article [36].

Alkali catalyst recovery is a precondition for the economic feasibility of the proposed process. It is facilitated by a wet quench design similar to the one used for black liquor gasification (BLG), which partly dissolves the slag phase in water. The addition of Zn for sulfur precipitation in the alkali recovery loop enables the separation of for example S, Ca and Mg, but some soluble ash elements are not removed by the proposed solution. Work is in progress to experimentally study the effects of Si on the gasification process in laboratory scale.

Improved feedstock flexibility and associated lower gas cleaning requirements can lead to decreased production costs. Furthermore, silicates in the gasifier, which can decrease the positive effects of alkali addition, both in terms of char gasification reactivity improvement and slag viscosity decrease. This can be a problem primarily for feedstocks with higher Si content than the feedstocks studied in this work, or if Si is enriched in the alkali recirculation loop.

### 4. Conclusions

Addition of an alkali catalyst to biomass can completely change the chemical domain of the pressurized entrained flow biomass gasification (PEBG) slag phase, from oxide/silicate slags to an alkali carbonate dominated slag phase. In addition to the positive effects on char gasification and tar and soot formation, alkali impregnation can give improved slag flowability and in situ sulfur capture, the latter through the formation of alkali sulfides in the carbonate melt. The low melting point and low viscosity of the slag phase can greatly enhance practical operability of a PEBG process. It can also lead to improved feedstock flexibility since the original ash composition is no longer determining the slag properties. The analysis presented in this article indicates that there is no substantial difference regarding S capture between stem wood and various types of forest residues investigated, and that satisfactory slag flowability is obtained for both feedstock categories.

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Improved feedstock flexibility and associated lower gas cleaning requirements can lead to decreased production costs. Furthermore,
the possibility to decrease the process temperature can lead to improved energy efficiency. To quantify these effects, a techno-economic analysis is presented in part 2 of this study [36]. Experimental verification of the results presented in this paper should be undertaken as a next step, but would likely require pilot scale experiments in order to be representative for a commercial process for production of biofuels or bio-chemicals.

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Appendix A: Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.energy.2018.05.097.

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