

## THERMODYNAMIC ANALYSIS OF BLACK LIQUOR STEAM GASIFICATION

Hua-Jiang Huang and Shri Ramaswamy \*

Pulp and paper mills represent a major platform for the use of abundant, renewable forest-based biomass as raw material. The pulping processes produce a large amount of black liquor solids, which is currently burnt in a conventional Tomlinson recovery boiler for recovery of energy and inorganic chemicals. This combustion technology can recover chemicals with good efficiency, and steam and power can be produced for the mills. However, Black Liquor Gasification (BLG) can be used to substitute for the combustion process for potential higher energy efficiency, lower greenhouse gas emissions, and more safety. With BLG technology, current pulp and paper mills can be extended into future biorefineries. In this work, a thermodynamic equilibrium model using Gibbs free energy minimization approach and the software FactSage are utilized to analyze the thermodynamic equilibrium constraints of the complex multiple phase reactions and the effects of different operating conditions during black liquor gasification. The modeling results can help better understand the black liquor gasification process and be useful in process modeling and analysis of the future BLG-based biorefinery.

*Keywords:* Thermodynamic equilibrium; Black liquor; Gasification; Steam gasification; Syngas composition

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### INTRODUCTION

Biomass conversion to renewable and green fuels and energy, biomaterials, and chemicals has become more and more important due to the limited availability of fossil fuel, the need for of greenhouse gas emissions reduction, energy independence, and improving rural economics (Huang et al. 2010). Pulp mill black liquor is a large biomass resource. The total global potential of black liquor conversion to renewable transportation fuels and energy is equivalent to over 45 million cubic meters of gasoline per year, i.e. 2% of global fuel demand. This also implies a potential annual reduction in fossil CO<sub>2</sub> emission of more than 100 million tonnes (ChemREC 2008).

Black liquor from pulp and paper mills mainly consists of lignin, inorganic chemicals (spent pulping chemicals), other organics such as hemicellulose and short chain cellulose, and water. The dissolved inorganics need to be recovered and regenerated as the active pulping chemicals, NaOH and Na<sub>2</sub>S, for reuse in the pulping process. Currently, black liquor is burned in a recovery boiler for recovery of energy and inorganic chemicals. The recovery boiler is an established piece of technology, working well to meet the demands for energy and chemicals recovery in the kraft process.

However, this technology is difficult to be further improved. Also, it has high emission of greenhouse gases such as CO<sub>2</sub>, and the steam turbine after combustion has a lower energy efficiency than a gas turbine. In addition, black liquor recovery boilers are known to be a serious safety concern with periodic explosions due to the interaction between molten inorganic smelt and water from the boiler system. It is also known that recovery boilers are one of the major capital investments in a pulp and paper mill, with costs exceeding over 50% of the total capital costs (~\$0.5 billion) in a modern kraft mill. Also, due to the very high capital costs, and economies of scale, they are not amenable to smaller scales and hence not suitable for smaller scale capacity expansions. For these reasons, many researchers have been exploring gasification as a better alternative. Biomass gasification has already been identified as a core technology in the thermochemical conversion of biomass to syngas, which can then be used directly in combined heat and power (CHP) system for producing steam and electricity, separated into hydrogen for fuel cell vehicles, or utilized for synthesis into transportation liquid fuels including methanol, dimethyl ether (DME), gasoline and diesel fuel, etc. Compared to combustion, gasification of black liquor solids has the following advantages (Larson et al. 2006; Rezaie et al. 2006; Naqvi et al. 2010):

- Higher process efficiency;
- Reduction in greenhouse gas emissions (compared to combustion, the amount of CO<sub>2</sub> significantly decreases in gasification as it is partly converted to other components such as CO);
- Safer;
- More suitable for incremental capacity expansion;
- Can produce high-value revenue streams and increase overall profitability, with multiple-products including methanol, dimethyl ether or DME, gasoline and diesel fuel, biomaterials, and chemicals.

The pulp and paper industry has a huge potential to modify the pulp and paper mills to integrated forest biorefineries (IFBR) that can produce multiple products in addition to paper, by more fully utilizing the woody material and additional forest residues. The additional incremental costs for realizing a commercial pulp mill-based biorefinery can be minimized by leveraging the existing infrastructure (Huang et al. 2010). The modifications of a current pulp mill into IFBR include hemicellulose pre-extraction prior to pulping and further conversion to biofuels, replacement of the Tomlinson recovery boiler system by a biomass-based integrated gasification combined-cycle (BIGCC) to produce syngas and combined heat and power (CHP) with greater energy efficiency using both gas turbine and steam turbine, and further conversion of syngas into different products such as methanol and DME as well as Fischer-Tropsch (F-T) liquid transportation fuels (Agenda 2006; IEA 2007). Production of liquid fuels and chemicals via gasification of kraft black liquor has the potential to provide significant economic returns for the pulp mills (Larson et al. 2007).

In general, there are two large categories of biomass gasification for producing syngas: partial oxidation using air/oxygen as gasifying agent and steam gasification using water vapor. The first process is an overall exothermic reaction, so energy for partial oxidation is obtained from the biomass itself. The other process, steam gasification, is

endothermic, and requires an external heat source to produce a better quality and hydrogen-rich fuel gas (Baratieri et al. 2008).

Two major black liquor gasification technologies have been tested successfully (Babu 2005). One is the Manufacturing and Technology Conversion International (MTCI<sup>®</sup>) steam reforming process operating at a low temperature of about 600°C. This process produces synthesis gas rich in hydrogen (>65 vol%) with a higher heating value of about 10.4 MJ/dry Nm<sup>3</sup>. Two MTCI BLG plants with capacities of 115 ton/d and 120 ton/d respectively have been commissioned at the Norampac mill in Trenton, Ontario, Canada and the Georgia Pacific paper mill in Big Island, Virginia, USA. The other major type of BLG is the ChemRec<sup>®</sup> process operating at a high temperature of about 950°C and either a low pressure (air blown, ~2bar) or a high pressure (oxygen blown, ~30bar). A low pressure ChemRec gasifier with a capacity of 300 t BLS/day was constructed in a Weyerhaeuser mill in New Bern, North Carolina, USA. The pressurized oxygen-blown ChemRec gasifier (30bar) with a capacity of 20 ton BLS/day was constructed in 2001 and successfully operated in Piteå, Sweden in conjunction with a pulp and paper mill (Burciaga 2005).

Thermodynamic equilibrium analysis is often used to determine the thermodynamic constraints on biomass gasification. The resulting equilibrium compositions can be used for process modeling and techno-economic analysis in the research and development of a new gasification technology for biomass conversion. Unlike the common biomass resources such as wood, corn stover, and switchgrass etc., black liquor contains not only the three common elemental components of biomass – carbon, hydrogen, and oxygen, but also significant amounts of inorganic components such as sulfur and sodium. Thus, black liquor gasification (BLG) involves multiple phases of inorganic solids and solution (e.g., Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>S), in addition to the gas phase (mainly H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub>), small amounts of condensed hydrocarbon (tar), and simple solid phase matter (char, mainly carbon) similar to the common biomass gasification. In addition, during BLG the distributions of sulfur and sodium between gas and condensable (inorganic solids/ solution) phases need to be considered and are important, as sulfur and sodium are the two major elements of the pulping chemicals (Na<sub>2</sub>S, NaOH). So far, there have been a large number of studies on thermodynamic modeling of biomass gasification presented in the literature (Baratieri et al. 2008; Jayah et al. 2003; Li et al. 2004; Mountouris et al. 2006; Melgar et al. 2007; Guan et al 2007; Mahishi and Goswami 2007; Lu et al. 2007; Huang and Ramaswamy 2009; Cohce et al. 2009; Weerachanchai et al. 2009), including combination of biomass with other fossil fuels such as coal and natural gas. Even though black liquor from pulp and paper mills is one of the largest renewable fuels contributing to bioenergy, there has been very limited published literature on black liquor gasification, especially in thermodynamic equilibrium modeling. This could be potentially due to the fact that combustion is the predominant commercial process for burning black liquor as well as due to black liquor gasification being in its infancy and due to the enormous complexities associated with it. It is to be noted that, even though there are number of pilot-scale black liquor gasification installations in the world, full-scale commercial BL gasification is yet to be realized. Results presented here can help advance this important technology. Backman et al. (1993) studied the effects of different operating conditions (gasification temperature, pressure, and the air to black liquor solids ratio) on carbon

yield, and sulfur and sodium distributions at equilibrium by simulation. However, the equilibrium compositions of product gas and smelt, the gasification performance metrics such as cold gas efficiency and higher heating value, etc., were not reported. In addition, their study was focused on air gasification. Larsson et al. (2006) used the chemical equilibrium model to systematically study the influence of inaccuracies in thermodynamic data on black liquor gasification. However, black liquor steam gasification, the focus of the work presented here, was not studied in their work.

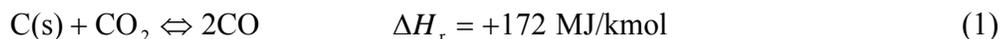
Another alternative to the conventional recovery furnace in the kraft pulping process is the black liquor steam gasification system with addition of  $\text{TiO}_2$  for direct causticization. Thermodynamic equilibrium calculations for this case have been reported in the literature (Nohlgren and Sinquefield 2004; Dahlquist and Jones 2006). This alternative causticizes  $\text{Na}_2\text{CO}_3$  to  $\text{NaOH}$  directly in the gasifier and eliminates the need for a lime kiln. However, this process has not been commercially demonstrated.

In this paper, a thermodynamic equilibrium approach and the software FactSage are utilized to analyze the thermodynamic equilibrium constraints of the complex multiple-phase reactions and the effects of different operating conditions during black liquor steam gasification. The effects of process parameters on black liquor steam gasification are systematically analyzed, including the influence of temperature, pressure, and steam to dry black liquor ratio on product gas composition, smelt composition, elemental phase distribution, cold gas efficiency, and higher heating value (HHV) of the product gas at equilibrium.

## MULTI-PHASE CHEMICAL REACTIONS

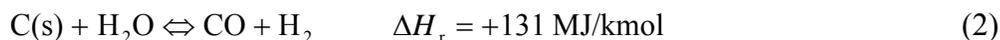
The chemical equilibrium calculations do not involve specific reactions. In order to help understand and analyze the black liquor steam gasification, however, the chemistry involved in the gasification reactions is firstly described here. Black liquor gasification is a very complex multi-phase reaction system involving dozens or even hundreds of reactions depending on operating conditions. Among these, the major reactions similar to those of coal gasification and common biomass steam gasification are as follows (Higman and Burgt 2003):

Boudouard reaction:

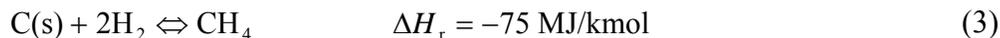


where (s) represents solid phase.

Water gas primary reaction:



Methanation reaction:



When the carbon conversion is complete, we can reduce the above three solid-gas heterogeneous reactions into the following two homogeneous gas-phase reactions:

Water-gas shift reaction (CO shift reaction) (obtained by (2) – (1)),



Methane steam reforming reaction (obtained by (2) – (3)),



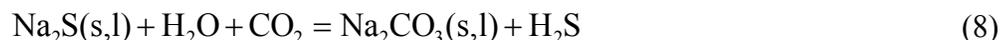
In addition to the above reactions, black liquor gasification also involves the following reactions associated with some of the inorganic compounds:

Sodium sulfate reduction and associated heats of reaction at 930°C (Grace 1985),



where (s, l) represents solid and liquid (molten solution) phases.

Sulfur solid-gas distribution reaction (Grace 1985):



Reaction (6) is the reduction of  $\text{Na}_2\text{SO}_4$  into  $\text{Na}_2\text{S}$ , which is a key chemical reactant in kraft pulping. Reactions of other inorganic substances, for example, thiosulfate in black liquor with  $\text{CO}$ ,  $\text{CO}_2$ , and water also leads to the formation of carbonate, but these are less important (Sricharoenchaikul et al. 2003). In fact, combustion or gasification is the only unit operation during which reduction of  $\text{Na}_2\text{SO}_4$  into  $\text{Na}_2\text{S}$  can be achieved. The reaction (8) is exothermic. It represents the distribution of sulfur between gas phase in the form of  $\text{H}_2\text{S}$  and smelt in the form of  $\text{Na}_2\text{S}$  (s, l).

## APPROACH FOR THERMODYNAMIC EQUILIBRIUM ANALYSIS

In this study, the thermodynamic software FactSage 6.1™, developed jointly between Thermfact/CRCT (Montreal, Canada) and GTT-Technologies (Aachen, Germany), was used as a tool to predict the equilibrium compositions of gas and solid phases and analyze the effects of operating conditions. FactSage's Equilib module for thermodynamic equilibrium analysis is based on the Gibbs free energy minimization approach. The basic principle of the Gibbs free energy minimization algorithm is as follows (Handbook 2010):

The total Gibbs free energy of the gasification system is

$$G = \sum_{\substack{\text{pure} \\ \text{ideal} \\ \text{gas}}} n_i (g_i^0 + RT \ln P_i) + \sum_{\substack{\text{pure} \\ \text{condensed} \\ \text{phases}}} n_i g_i^0 + \sum_{\text{solution 1}} n_i (g_i^0 + RT \ln X_i + RT \ln \gamma_i) \\ + \sum_{\text{solution 2}} n_i (g_i^0 + RT \ln X_i + RT \ln \gamma_i) + \dots \quad (9)$$

where  $n_i$  = moles;  $g_i^0$  = standard molar Gibbs energy;  $R$  = ideal gas constant;  $T$  = temperature;  $P_i$  = gas partial pressure;  $X_i$  = mole fraction; and  $\gamma_i$  = activity coefficient.

With the FactSage Equilib module, given the biomass elemental compositions and the mass, and operating conditions such as gasification temperature, total pressure, and the amount of water vapor input as oxidant,  $n_i$ ,  $P_i$ , and  $X_i$  are determined by minimizing the total Gibbs free energy  $G$  function (9).

Smith and Missen (1991) can be referred to for further details on the general algorithm of the Gibbs free energy minimization approach.

#### *Selection of database, species and phases*

FactSage contains the Fact53 compound database and some special databases such as FACT oxide database and FACT salt database, etc. In our modeling, we selected Fact53 and FTpulp databases.

The FTpulp database has recently been developed for thermodynamic and phase equilibrium calculations involving molten and solid alkali salts related to the black liquor combustion for heat and inorganic chemicals recovery in pulp and paper mills (Database 2010). Since gasification is actually a partial oxidation/combustion process, the FTpulp Database can be borrowed for thermodynamic modeling of black liquor gasification. After selection of databases and phases involved, all possible relevant species are automatically included in the FactSage equilibrium model. Table 1 below shows some major species in our FactSage BLG model.

**Table 1.** Some Chemical Species in the FactSage Equilibrium Model

Phase	Compounds
Gas	H <sub>2</sub> O, H <sub>2</sub> , CO, CO <sub>2</sub> , CH <sub>4</sub> , COS, H <sub>2</sub> S, Na, NaOH, NaCl, NaH, (NaOH) <sub>2</sub> , (NaCl) <sub>2</sub> , K, KOH, KCl, KH, (KOH) <sub>2</sub> , (KCl) <sub>2</sub> , H, HCl, H <sub>2</sub> CO, HS, SO <sub>2</sub> , S <sub>2</sub> , H <sub>2</sub> S <sub>2</sub>
Liquid (molten solution)	Na <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> S, NaOH, NaCl, Na <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> CO <sub>3</sub> , K <sub>2</sub> S, KOH, KCl, K <sub>2</sub> SO <sub>4</sub>
Solid	Na <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> S, NaOH, NaCl, Na <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> CO <sub>3</sub> , K <sub>2</sub> S, KOH, KCl, K <sub>2</sub> SO <sub>4</sub> , C

#### *Cold gas efficiency and HHV of product gas*

The cold gas efficiency is defined as

$$\text{Cold gas efficiency [\%]} = \frac{HHV_g \times V_g}{HHV_f} \times 100 \quad (10)$$

where  $HHV_g$  is the higher heating value in product gas [MJ/Nm<sup>3</sup>],  $HHV_f$  the higher heating value in feedstock, in the unit of MJ/kg BLS (black liquor solids), and  $V_g$  the standard volume of the dry product gas (Nm<sup>3</sup>/kg BLS).

The  $HHV_g$  value of product gas represents the gas quality. It can be calculated with the following formula (Li et al. 2004),

$$HHV_g = 12.75 \times y_{H_2} + 12.63 \times y_{CO} + 39.82 \times y_{CH_4} + 25.105 \times y_{H_2S} \quad [MJ/Nm^3]$$

where  $y_{H_2}$ ,  $y_{CO}$ ,  $y_{CH_4}$ , and  $y_{H_2S}$  are the mole fractions of  $H_2$ ,  $CO$ ,  $CH_4$ , and  $H_2S$ , respectively.

$V_g$  is calculated by,

$$V_g = (n_{H_2} + n_{CO} + n_{CH_4} + n_{H_2S}) \times 22.4 \times 10^{-3} / W_{BLS} \quad [Nm^3/kg \text{ BLS}]$$

where  $n_{H_2}$ ,  $n_{CO}$ ,  $n_{CH_4}$ , and  $n_{H_2S}$  are the number of moles of  $H_2$ ,  $CO$ ,  $CH_4$ , and  $H_2S$ , respectively.  $W_{BLS}$  is the dry weight of black liquor solids.

The typical  $HHV$  of BLS is in the range of 13.4 to 15.5 MJ/kg·BLS (Frederick 1997), and the range of elemental compositions of BLS was also reported (Larsson et al. 2006). BLS having experimental  $HHV_f$  of 13.840 MJ/kg BLS, and the following elemental compositions (Table 2) is used as feedstock in this simulation based on the work of Marklund (2006).

**Table 2.** Elemental Compositions (wt% on dry basis)

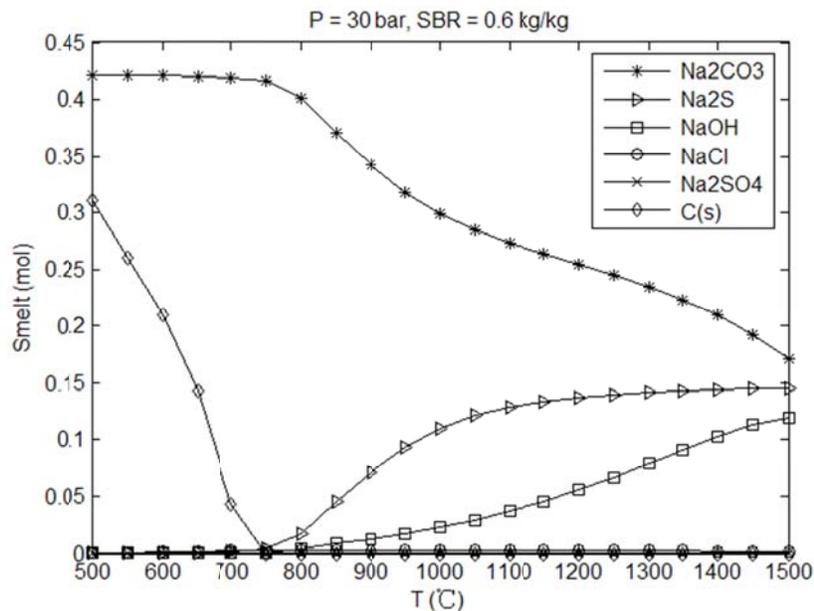
	C	H	O	S	Cl	Na	K
BLS	34.9	3.4	35.07	5	0.11	19.4	2.12

## RESULTS AND DISCUSSIONS

### Effect of Temperature

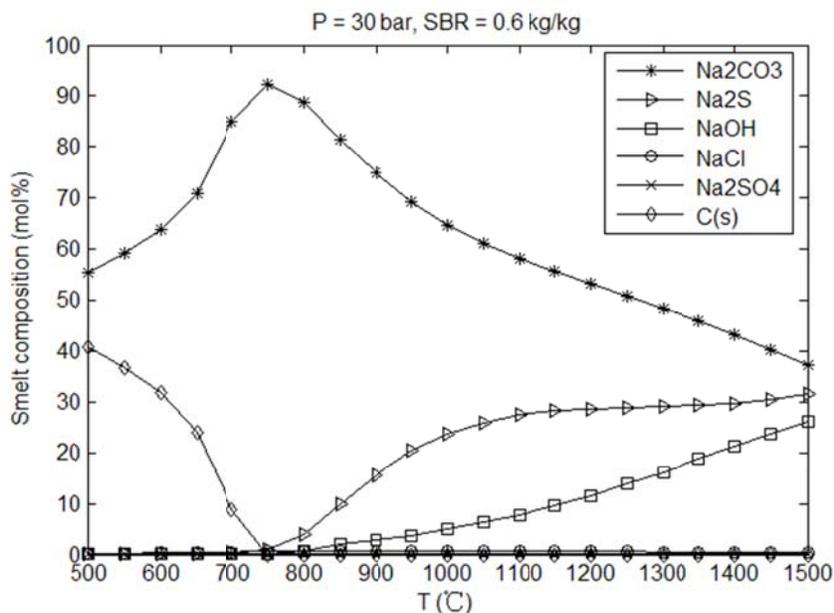
#### *Smelt equilibrium mole number and composition*

The equilibrium mole number of the major components in the non-gaseous or liquid+solid phase (smelt) as a function of temperature at a fixed pressure (P) of 30 bar and a fixed steam-to-dry black liquor ratio (SBR) of 0.6 (kg/kg) is shown in Fig. 1(a). It can be seen from this figure that the carbon content decreases with increasing temperature until it becomes zero (completely converted) at around 750°C and above. This is because the overall gasification reactions, mainly (1) and (2), are endothermic, and the increasing temperature favors the carbon conversion. Besides, at temperatures less than around 750°C, solid  $Na_2S$  is no longer stable (at a relatively high pressure), almost all of it is converted to  $Na_2CO_3$ , and the amount of  $Na_2CO_3$  hardly changes. This is because the equilibrium constant of the reversible reaction (8) at  $T < 750^\circ C$  and  $P = 30$  bar is very small. In addition,  $Na_2SO_4$  is in very small quantity in the system ( $< 1.5 \times 10^{-6}$  mol at  $P=30$  bar &  $T = 500-1500^\circ C$ ), so the production of  $Na_2S$  from the reactions (6) and (7) can be omitted. At above 750°C, from the constrained exothermic reaction (8) we can see that there is  $Na_2S$  formed and the  $Na_2S$  content increases while  $Na_2CO_3$  decreases with temperature according to the Le Chatelier's principle.



**Fig. 1(a).** Smelt equilibrium mole number as a function of temperature

The equilibrium mole percent of the major components in the solid phase as a function of temperature at  $P = 30$  bar and  $SBR = 0.6$  (kg/kg) is shown in Fig. 1(b). The equilibrium composition of  $\text{Na}_2\text{CO}_3(\text{s})$  increases with temperature, reaches a maximum at around  $750^\circ\text{C}$ , and then decreases with further increasing temperature. Though the equilibrium mole number of  $\text{Na}_2\text{CO}_3$  does not change significantly (Fig. 1(a)), the total moles of the solid phase decrease significantly with temperature because solid carbon is



**Fig. 1(b).** Smelt equilibrium composition as a function of temperature

gasified and decreases with  $T$  significantly until it is completely converted at around  $750^{\circ}\text{C}$ . Thus, the equilibrium mole percent of  $\text{Na}_2\text{CO}_3$  over the total solid moles increases quickly with  $T$  for  $T < 750^{\circ}\text{C}$ , which is different from the equilibrium mole profile in Fig. 1(a). The distribution profile of other components with temperature is similar to that in Fig. 1(a). Note that the critical temperature of  $750^{\circ}\text{C}$  mentioned here is for the current system at  $P = 30$  bar and  $\text{SBR} = 0.6$  (kg/kg) and it is dependent on  $P$  and  $\text{SBR}$ . It is worth noting that even though there have been some published studies on black liquor steam gasification (Li and Heiningen 1994; Wei et al. 2006; Preto et al. 2008), the equilibrium mole concentrations and/or compositions of solid phase of the steam gasification system have not yet been reported in the literature.

#### *Effect of temperature on product gas composition*

The equilibrium mole concentration of the gas components as a function of temperature at  $P = 30$  bar and  $\text{SBR} = 0.6$  (kg/kg) is shown in Fig. 2(a). From this figure we can see that the equilibrium moles of  $\text{H}_2$  increases with temperature, reaches a maximum value, and then decreases slightly with further increase in temperature. The moles of  $\text{CO}$  increases while the equilibrium moles of  $\text{CH}_4$ , and  $\text{H}_2\text{S}$  decrease with temperature for the whole temperature range. In addition,  $\text{CO}_2$  increases slightly, and then decreases with temperature. This follows the Le Chatelier's principle. For  $T < 750^{\circ}\text{C}$ , solid carbon  $\text{C(s)}$  is not converted completely, the analysis of the temperature effects should be based on the reactions (1)-(3) and (8) (exothermic) as follows:

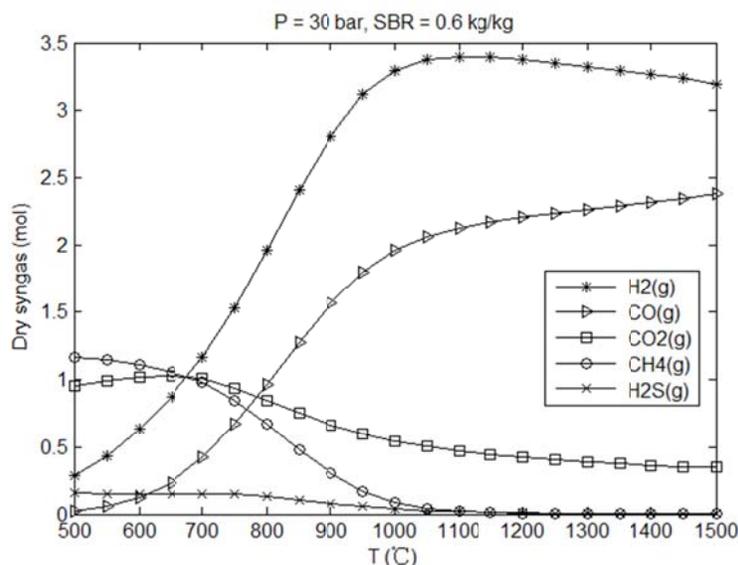
- (1)  $T \uparrow, \text{CO} \uparrow, \text{CO}_2 \downarrow$  (meaning that the moles of  $\text{CO}$  increases while the moles of  $\text{CO}_2$  decreases with increasing  $T$ )
- (2)  $T \uparrow, \text{CO} \uparrow, \text{H}_2 \uparrow$
- (3)  $T \uparrow, \text{CH}_4 \downarrow, \text{H}_2 \uparrow$
- (8)  $T \uparrow, \text{H}_2\text{S} \downarrow, \text{CO}_2 \uparrow$

So, as  $T \uparrow, \text{CO} \uparrow, \text{CH}_4 \downarrow, \text{H}_2\text{S} \downarrow, \text{H}_2 \uparrow$ , since the overall  $\text{CO}_2$  is dependent on the competitive effects of reactions (1) and (8), thus leading to slight increase with temperature, reaching a peak and then decreasing due to the different effect of temperature on their respective equilibrium constants. For  $T \geq 750^{\circ}\text{C}$ , solid carbon  $\text{C(s)}$  is converted completely, and the analysis of the temperature effects is based on reactions (4), (5) and (8).

- From (4) (exothermic):  $T \uparrow, \text{CO} \uparrow, \text{CO}_2 \downarrow, \text{H}_2 \downarrow$ ,  
 From (5) (endothermic):  $T \uparrow, \text{CO} \uparrow, \text{CH}_4 \downarrow, \text{H}_2 \uparrow$ ,  
 From (8) (exothermic):  $T \uparrow, \text{H}_2\text{S} \downarrow, \text{CO}_2 \uparrow$

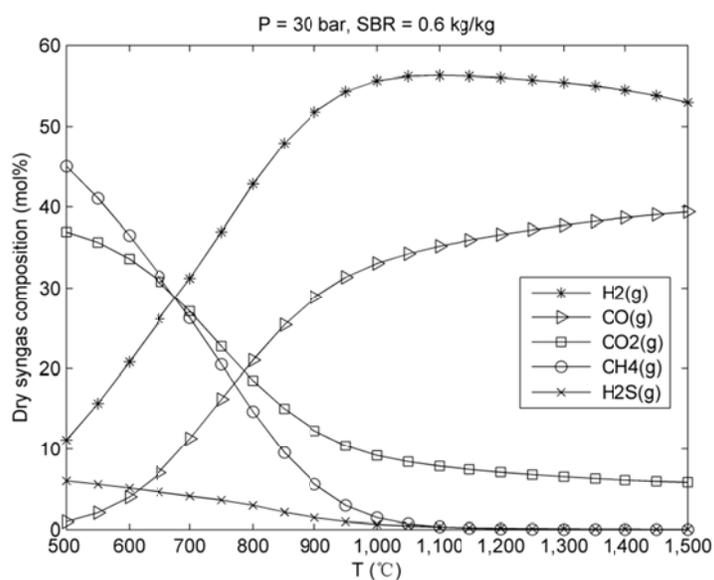
Thus, it can be directly seen that the overall temperature effects are: as  $T \uparrow, \text{CO} \uparrow, \text{CH}_4 \downarrow, \text{H}_2\text{S} \downarrow$ . The overall  $\text{CO}_2$  is dependent on the combined effects of reactions (4) and (8). As the temperature effect on  $\text{CO}_2$  in the reaction (4) is dominant over that of the reaction (5), thus overall, the moles of  $\text{CO}_2$  decrease with increasing temperature. Besides, the overall moles of  $\text{H}_2$  are dependent on the competitive effects of reactions (4)

and (5), hence, leading to increasing with temperature, reaching a peak and then decreasing in the equilibrium mole profiles of  $H_2$ , as seen in Fig. 2(a). In addition, the effects of temperature on the equilibrium moles of dry syngas are similar to those of the conventional (non-black liquor) biomass steam gasification (Mahishi and Goswami 2007) for the same temperature range excluding  $H_2S$  for comparison.



**Fig. 2(a).** Dry product gas equilibrium mole number as a function of temperature

Fig. 2(b) shows the equilibrium compositions of the product gas as a function of temperature at  $P = 30$  bar and  $SBR = 0.6$  kg/kg. It is found that the equilibrium composition of  $H_2$  (g) increases with temperature, reaches a maximum value, and then decreases slightly with further increasing temperature.



**Fig. 2(b).** Dry product gas equilibrium composition as a function of temperature

The composition of CO (g) increases while the equilibrium compositions of CO<sub>2</sub> (g) and CH<sub>4</sub> (g) decrease with temperature for the whole temperature range. Besides, the effects of temperature on the gas (excluding H<sub>2</sub>S) equilibrium composition are similar to those of non-black liquor biomass steam gasification (Schuster et al. 2001).

#### Cold gas efficiency and HHV

Figure 3 shows the cold gas efficiency and higher heating value (HHV) as a function of temperature under the condition of P = 30 bar and SBR = 0.6 kg/kg. It can be seen that with increasing temperature the cold gas efficiency increases while the HHV of the gas product decreases significantly at T < 1000°C. When T is over 1000°C, the cold gas efficiency is close to 1 and the HHV of the gas product stays almost constant at around 11.8 MJ/Nm<sup>3</sup>. This is in agreement with the literature (Umeki et al. 2010), where it has been reported that the higher heating value of syngas from steam gasification is greater than 10 MJ/Nm<sup>3</sup>.

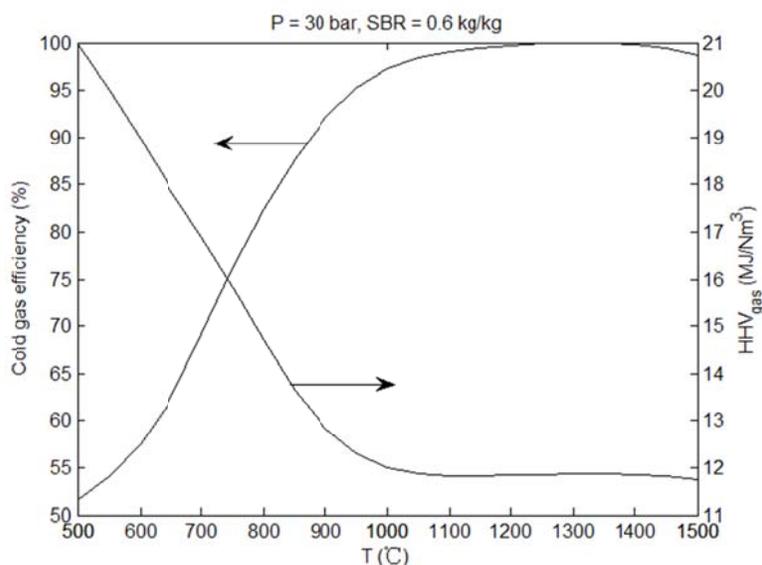


Fig. 3. Effect of temperature on cold gas efficiency and HHV

#### Effect of Pressure

##### Smelt equilibrium composition

Figure 4 shows the impact of pressure on smelt composition. It is shown that with increasing pressure the Na<sub>2</sub>CO<sub>3</sub> composition increases while the Na<sub>2</sub>S composition decreases. This is in agreement with the reaction (8) and the Le Chatelier's principle: P↑, Na<sub>2</sub>CO<sub>3</sub>↑, Na<sub>2</sub>S↓.

##### Product gas composition

Fig. 5 shows the influence of pressure on the product gas equilibrium compositions at T = 1000 °C and SBR = 0.6 kg/kg. From Fig. 5 we can see that the equilibrium compositions of H<sub>2</sub> and CO slightly decrease with pressure, or the impact of pressure is not significant.

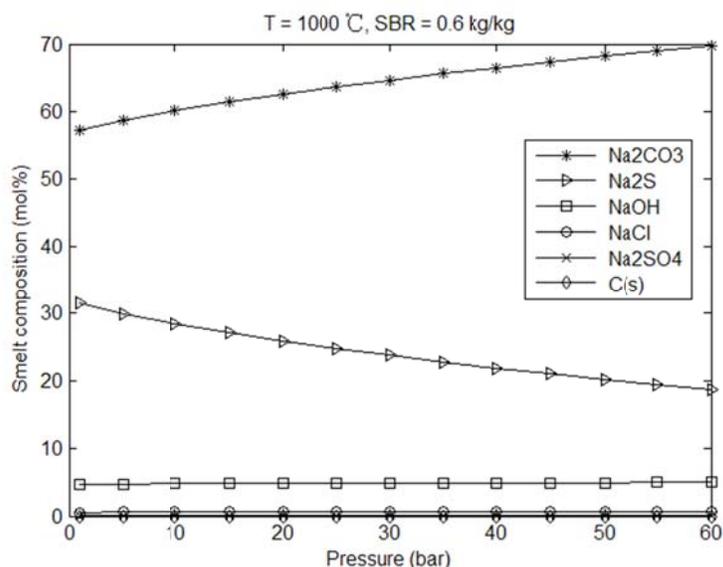


Fig. 4. Smelt equilibrium composition as a function of pressure

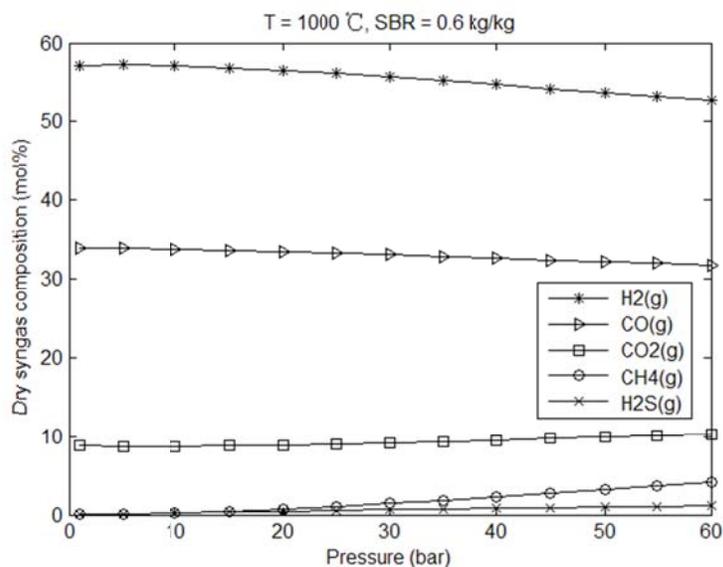


Fig. 5. Dry product gas equilibrium composition as a function of pressure

As the solid carbon is completely converted at 1000 °C (Fig. 4), the effect of pressure on the product gas composition can be explained by the Le Chatelier's principle, based on reactions (4), (5), and (8).

From (4): there is no direct effect of pressure on the equilibrium compositions.

From (5):  $P \uparrow$ ,  $[CO] \downarrow$ ,  $[H_2] \downarrow$ ,  $[CH_4] \uparrow$

From (8):  $P \uparrow$ ,  $[H_2S] \uparrow$ ,  $[CO_2] \downarrow$ .

Thus, the trends of CO, H<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>S are in agreement with Fig. 4.

For carbon dioxide, from (8),  $[\text{CO}_2]$  decreases with increasing pressure. However, from (5) we can see  $[\text{H}_2]$  decreases more than  $[\text{CO}]$  with increasing  $P$  since 3 moles of  $\text{H}_2$  reacts with 1 mole of  $\text{CO}$  in the reaction, and considering the concentration effect from reaction (4), with  $[\text{H}_2]$  decreasing more than  $[\text{CO}]$ ,  $[\text{CO}_2] \uparrow$ . The small increase in  $\text{CO}_2$  concentration with increasing pressure is attributable to the overall influence of  $P$  (from (8)) and concentration effects as shown above.

Briefly, as  $P \uparrow$ ,  $[\text{H}_2] \downarrow$ ,  $[\text{CO}] \downarrow$ ,  $[\text{CH}_4] \uparrow$ ,  $[\text{H}_2\text{S}] \uparrow$ , total  $[\text{CO}_2] \uparrow$ . Overall, however, the effects of pressure on syngas equilibrium composition are not very strong.

#### Cold gas efficiency and HHV

Figure 6 shows the cold gas efficiency and HHV as a function of temperature under the condition of  $T = 1000 \text{ }^\circ\text{C}$  and  $\text{SBR} = 0.6 \text{ kg/kg}$ . It can be seen that both the cold gas efficiency and the HHV of the gas product do not change significantly with pressure.

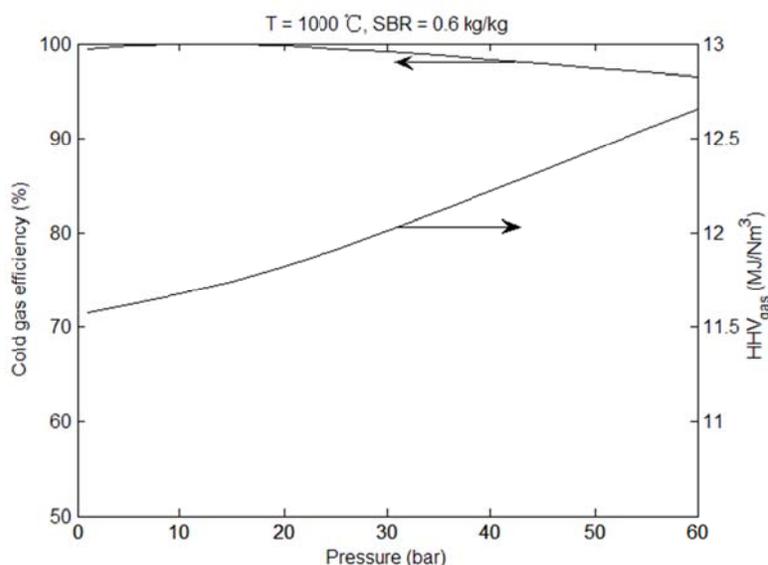


Fig. 6. Influence of pressure on higher heating value and cold gas efficiency

### Effect of Steam to Black Liquor Ratio (SBR)

#### Smelt equilibrium composition

Figure 7 shows the smelt equilibrium compositions as a function of SBR at  $T = 1000 \text{ }^\circ\text{C}$  and  $P = 30 \text{ bar}$ . It can be seen that the carbon composition decreases with SBR until it becomes zero (completely converted) at around  $\text{SBR} = 0.3$ . At low values of SBR or amount of  $\text{H}_2\text{O}$  (about  $\text{SBR} < 0.3$ ), both the  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{S}$  compositions increase with SBR. For  $\text{SBR} > 0.3$ , the  $\text{Na}_2\text{CO}_3$  composition increases, while the  $\text{Na}_2\text{S}$  composition decreases with increasing SBR. These results can also be explained by Le Chatelier's principle: for  $\text{SBR} < 0.3$ , based on reaction (2), solid carbon  $\text{C}(\text{s})$  decreases with SBR. From (8),  $\text{SBR} \uparrow$ ,  $\text{Na}_2\text{CO}_3$  (in mole number)  $\uparrow$ ,  $\text{Na}_2\text{S} \downarrow$ . As  $\text{C}(\text{s})$  decreases quickly with SBR at  $\text{SBR} < 0.3$ , the total moles of solid phase decreases significantly with SBR. Therefore, though the equilibrium moles of  $\text{Na}_2\text{S}$  decreases with SBR based on Le

Chatelier's principle, its equilibrium mole percent over the total moles of solid phase,  $[\text{Na}_2\text{S}]$ , increases with SBR. For  $\text{SBR} > 0.3$ , solid carbon converted completely, and the total moles of solid phase do not change significantly. Thus, from the reaction (8), as  $\text{SBR} \uparrow$ ,  $[\text{Na}_2\text{CO}_3] \uparrow$ ,  $[\text{Na}_2\text{S}] \downarrow$ .

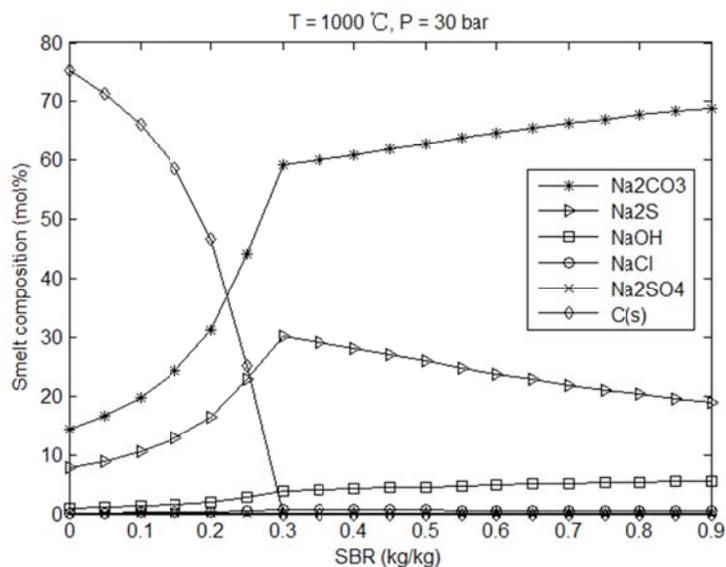


Fig. 7. Influence of SBR on smelt equilibrium

#### Product gas composition

The equilibrium mole concentrations of various components in the gas phase as a function of SBR at  $T = 1000\text{ °C}$  and  $P = 30\text{ bar}$  is shown in Fig. 8(a).

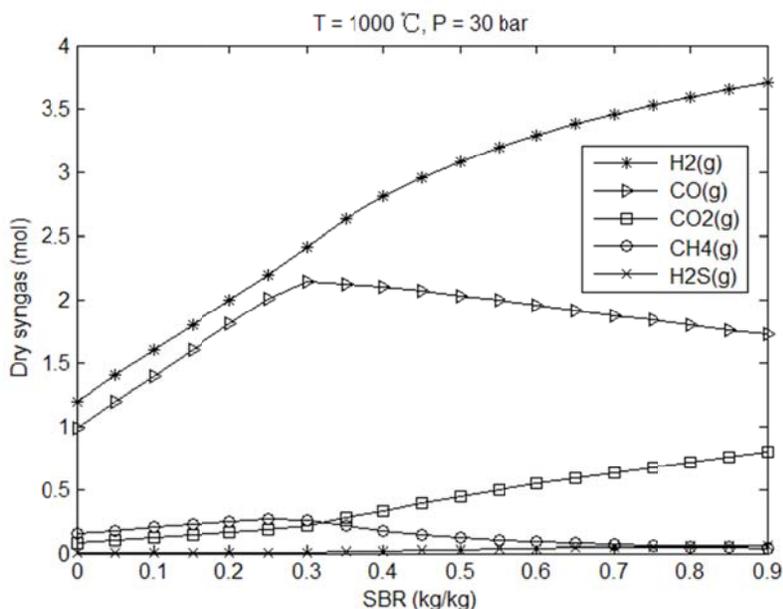


Fig. 8(a). Influence of SBR on dry product gas equilibrium mole number

For  $SBR < 0.3$ , as solid carbon is not converted completely as stated above, the analysis of syngas profiles should be based on reactions (1) - (3): with  $SBR$  or  $H_2O \uparrow$ ,  $CO \uparrow$ ,  $H_2 \uparrow$ ,  $CH_4 \uparrow$ ,  $CO_2 \uparrow$  (In fact, the moles of  $CH_4$  and  $CO_2$  do not increase significantly). For  $SBR > 0.3$ , solid carbon is converted completely, and therefore, the syngas profiles can be analyzed with reactions (4) & (5):



So, as  $SBR \uparrow$ ,  $H_2 \uparrow$ ,  $CO_2 \uparrow$ ,  $CH_4 \downarrow$  and as (4) is dominant over (5), the overall  $CO \downarrow$ . In addition, the effect of  $SBR$  on the equilibrium moles of dry syngas is similar to that of conventional (non-black liquor) biomass steam gasification (Mahishi and Goswami 2007) for the same  $SBR$  range excluding  $H_2S$  for comparison.

The influence of  $SBR$  on product gas composition at  $T = 1000 \text{ }^\circ\text{C}$  and  $P = 30 \text{ bar}$  is shown in Fig. 8(b). From the figure we can see that when  $SBR$  is below 0.30, the gas equilibrium compositions do not change significantly; when  $SBR > 0.30$ , the compositions of  $H_2$  and  $CO_2$  increase and the compositions of  $CO$  and  $CH_4$  decrease with increase in temperature.

Note that for  $SBR < 0.3$ , as the total moles of gas phase increases significantly with  $SBR$ , the mole percent of  $H_2$  does not change in the same way as its number of moles. By comparing with non-black liquor steam gasification in the literature (Schuster et al. 2001; Gao et al. 2008; Umeki et al. 2010), the trends of the gas ( $H_2$ ,  $CO$ ,  $CO_2$ ) equilibrium composition as a function of  $SBR$  at  $SBR > 0.3$  are similar to those of non-black liquor steam gasification.

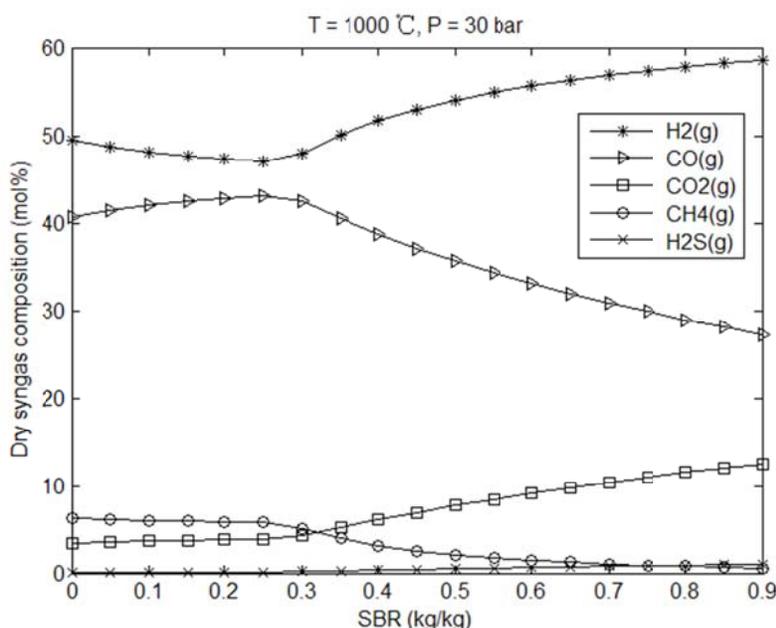


Fig. 8(b). Influence of  $SBR$  on dry product gas equilibrium composition

### Cold gas efficiency and HHV

Figure 9 shows the cold gas efficiency and HHV as a function of SBR under the condition of  $T = 1000\text{ }^{\circ}\text{C}$  and  $P = 30\text{ bar}$ . It can be seen that with increasing SBR the cold gas efficiency increases rapidly until it reaches the maximum value of 1.0 and then slightly decreases with SBR. On the other hand, the HHV of the gas product decreases slightly when  $\text{SBR} < 0.3\text{ kg/kg}$  and quickly when  $\text{SBR} > 0.3$  with increasing SBR.

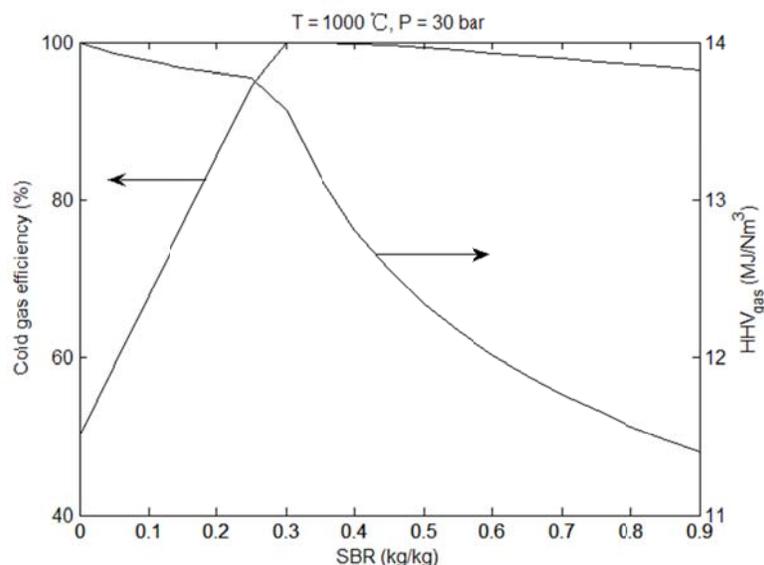


Fig. 9. Effect of SBR on higher heating value and cold gas efficiency

### Effect of Operating Conditions on Elemental Phase Distribution

Figure 10 shows the equilibrium distribution of sulfur between gas (mainly in the form of  $\text{H}_2\text{S}$ ) and condensed phase or smelt (mainly in the form of  $\text{Na}_2\text{S}$ ) as a function of temperature in black liquor solids gasification at two total pressures (1 and 30 bars) and three steam to black liquor solid ratios (0.0, 0.3, and 0.6). At fixed  $P = 30\text{ bar}$  and  $\text{SBR} = 0.3\text{ kg/kg}$ , almost all the equilibrium sulfur remains in gas phase at temperature below  $700\text{ }^{\circ}\text{C}$ . And, above  $700\text{ }^{\circ}\text{C}$  with increasing temperature, the sulfur percent in the gas phase decreases (or the sulfur percent in smelt increases) with increasing temperature until no sulfur exists in the gas at around  $1200\text{ }^{\circ}\text{C}$ , and then the sulfur percent in the gas increases with temperature. Similar trends are observed for other  $P$  and SBR conditions. The gasification pressure also influences the sulfur distribution. The higher pressure favors the formation of  $\text{H}_2\text{S}$  in the gas. Moreover, higher SBR favors the formation of  $\text{H}_2\text{S}$  in the gas phase under the conditions of fixed pressure and temperature. At  $P = 1\text{ bar}$  and around  $T = 750\text{ }^{\circ}\text{C}$ , or  $P = 30\text{ bar}$  and around  $T = 1000\text{ }^{\circ}\text{C}$ , the sulfur will mostly remain in the smelt in the form of  $\text{Na}_2\text{S}$ . This is an important operating point for retaining  $\text{Na}_2\text{S}$  in the smelt phase and recovering all the  $\text{Na}_2\text{S}$  for the kraft process. In addition, the effect of operating conditions on sulfur distribution at equilibrium during steam gasification of black liquor has similar trends compared to black liquor gasification with air as oxidant (Backman et al. 1993).

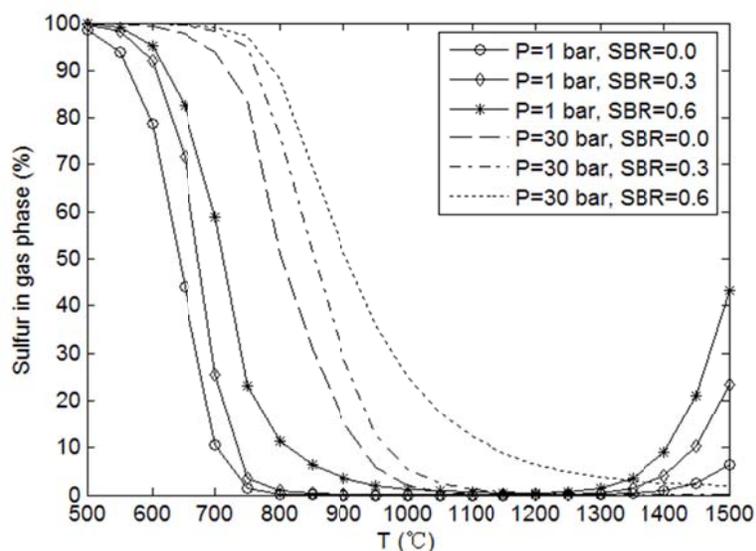


Fig. 10. Effect of operating conditions on sulfur distribution at equilibrium

The amount of Na-compounds in the gas phase, in the form of Na(g) and NaOH(g), is dependent on temperature, pressure, and the ratio of steam to black liquor solids (see Fig. 11). For  $P=1$  bar, these gaseous Na-compounds form in significant amounts when  $T>900^{\circ}\text{C}$ , while for  $P=30$  bar, they form in significant amounts when  $T>1200^{\circ}\text{C}$ , and the percent of Na-compounds in the gas phase increases with increasing temperature. The gasification pressure is also an important factor influencing the equilibrium sodium distribution in the gas phase, with higher pressure leading to lower percentage of Na-compounds in the gas phase. In addition, higher SBR results in lower equilibrium release of sodium to the gas. These results are important in retaining the Na in the smelt phase and are similar to those of black liquor oxygen gasification published in the literature (Backman et al. 1993).

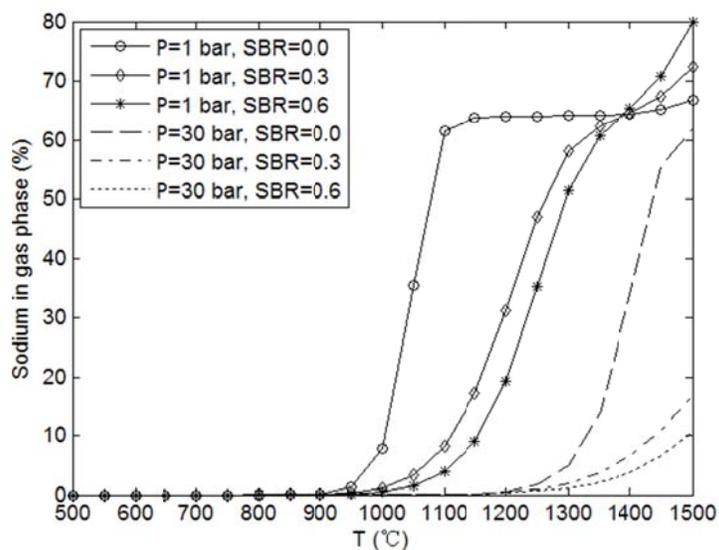


Fig. 11. Effect of operating conditions on sodium distribution at equilibrium

It is clear that for black liquor gasification since Na is the major element of the pulping chemicals ( $\text{Na}_2\text{S}$ ,  $\text{NaOH}$ ) the amount of gaseous Na-compounds formed in the gas phase should be minimized. The results here can help select suitable conditions avoiding the formation of gaseous Na-compounds. For example, the conditions of  $T = 1000$  and  $P = 30$  bar can avoid distribution of Na in gas phase.

## CONCLUSIONS

1. A thermodynamic equilibrium model using Gibbs free energy minimization approach and the software FactSage are utilized to analyze the thermodynamic equilibrium constraints of the complex multiple phase reactions and the effects of different operating conditions during black liquor steam gasification. The modeling results can help understand the black liquor gasification process and be useful in process modeling and analysis of the future BLG-based biorefinery. Unlike conventional biomass gasification, there is very limited work presented in the literature on black liquor gasification, and the present work attempts to address the same. In addition to gasification of the organic components of black liquor, the role of inorganics and their constituent reactions during gasification and multiple phases are also considered, for the first time.
2. The model showed important results with regard to compositions of the product gas as well as the solid and liquid phases.
3. At temperature below  $750^\circ\text{C}$ , solid carbon  $\text{C(s)}$  decreases with increasing temperature until it becomes zero at around  $750^\circ\text{C}$ , indicating a full carbon conversion at and above this temperature.
4. With increasing  $T$ ,  $\text{H}_2\%$  increases, reaches a maximum, and then decreases;  $\text{CO}$  increases while  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{S}$  decrease;  $\text{Na}_2\text{CO}_3$  % increases, reaches a maximum, and then decreases. This provides important equilibrium data for maximizing the syngas proportion (i.e.  $\text{H}_2$  and  $\text{CO}$ ) for further F-T type conversion. At  $T < 750^\circ\text{C}$ , no  $\text{Na}_2\text{S}$  is formed; above  $750^\circ\text{C}$ ,  $\text{Na}_2\text{S}$  increase with temperature; the cold gas efficiency increases, while HHV decreases with temperature. This is important for maximizing the  $\text{Na}_2\text{S}$  recovery for re-use in the pulping process.
5. With increasing pressure,  $\text{H}_2$  and  $\text{CO}$  slightly decrease. In addition,  $\text{Na}_2\text{S}$  decreases while  $\text{Na}_2\text{CO}_3$  increases. Besides, the cold gas efficiency decreases with pressure while HHV does not significantly change.
6. The more steam, the more  $\text{H}_2$  fraction in the gas phase, but the less  $\text{CO}$ ; the more steam, the more  $\text{Na}_2\text{CO}_3$ , but the less  $\text{Na}_2\text{S}$ . For  $\text{SBR} \leq 0.3$ , with increasing SBR, cold gas efficiency increases while HHV decreases slightly. For  $\text{SBR} > 0.3$ , with increasing SBR, cold gas efficiency remains unchanged while HHV decreases.
7. The thermodynamic model provides a simple tool to simulate equilibrium compositions during black liquor gasification. It can be applied for process modeling, techno-economic and environmental analysis of IFBR. The thermodynamic equilibrium model presented here in conjunction with local fluid flow, heat and mass transfer model of a specific gasifier type can be used in the design and development and optimum operation of future black liquor gasifiers.

8. Operating with a  $0.3 < SBR < 0.6$  in combination with high  $P$  (30 bar) and high  $T$  ( $\sim 1000^{\circ}\text{C}$ ) appears most beneficial for obtaining a smelt with no C(s) and maximizing Na and S capture in the smelt.

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