RECOVERY OF SODIUM ORGANIC SALTS FROM PARTIALLY WET OXIDIZED BLACK LIQUOR

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Partial wet oxidation is a recently proposed biorefinery concept for black liquor, generating carboxylic acids and their sodium salts. The aim of this study is to investigate the recovery of sodium organic salts and carboxylic acids from partial wet oxidation downstream by using a preliminary thermodynamic model. The paper illustrates the speciation of sodium formate-sodium acetate-water system together with formic and acetic acids in aqueous solution with respect to pH and temperature. The speciation results indicate that salt recovery requires water evaporation and high pH, whereas acid recovery requires low pH. Temperature slightly influences the salt recovery but has no major impact on acid recovery. Hence, the alternatives for the recovery process can be evaporator-crystallizer-pH reduction with acid or evaporative crystallizer-cooling crystallizer-pH reduction with acid addition.

Keywords: aqueous thermodynamics, speciation, electrolyte thermodynamics, activity coefficient, Bromley's method, crystallization, carboxylic acids, sodium organic salts, biorefinery, black liquor, acid recovery, salt recovery, partial wet oxidation

INTRODUCTION

Due to environmental issues and sustainable development aspects, the integration of biorefinery processes into chemical industry has been proposed and investigated to produce biofuel, energy and chemicals. Pulp and paper industry has an important biorefinery potential due to the lignocellulosic content of black liquor. However, commercial treatment involves the recovery boiler: the complete combustion of the organic content. This treatment does not utilize the bio-chemical potential of black liquor and does not provide the optimum energy efficiency, despite being considered as feasible for large-scale wood mills. Moreover, this commercial treatment is unfeasible for relatively small-scale non-wood mills because of the high investment cost of a recovery boiler unit. As a result, an alternative biorefinery process can be integrated in pulp mills: utilizing a part of weak black liquor in wood mills (such as 10-20%) and the whole black liquor stream in non-wood mills.
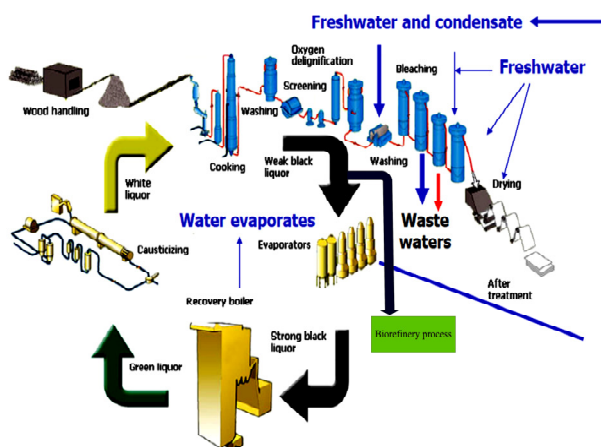

Figure 1: Commercial recovery boiler treatment and integration of an alternative biorefinery[4]

Figure 1 shows the commercial treatment of black liquor and mapping the biorefinery integration for a typical wood mill.

There is no commercialized biorefinery integration; therefore, more research and improvements are needed in the currently investigated alternatives. The most investigated biorefinery is gasification of black liquor to produce syngas. However, gasification gives low efficiency for high-moisture feedstock, thus requiring prior drying, which is energy consuming. Moreover, gasification of black liquor includes safety and economic issues.[1] An alternative treatment suggested recently involves partial wet oxidation to produce organic acids (mainly acetic, formic, lactic and glycolic acids)

and their sodium salts by neutralizing sodium carbonate.[2] Partial wet oxidation is suitable for aqueous feedstocks (such as black liquor) and can decompose lignocellulosic components in lower temperature and pressure compared with gasification.[3] Figure 2 shows this treatment option as a route.

To address the recovery for the downstream of partial wet oxidation, this study illustrates sodium formate-sodium acetate-water system together with formic acid and acetic acid by using a preliminary thermodynamic model. The speciation of the system is investigated with respect to the temperature and pH, then the results are analysed to propose a recovery process.
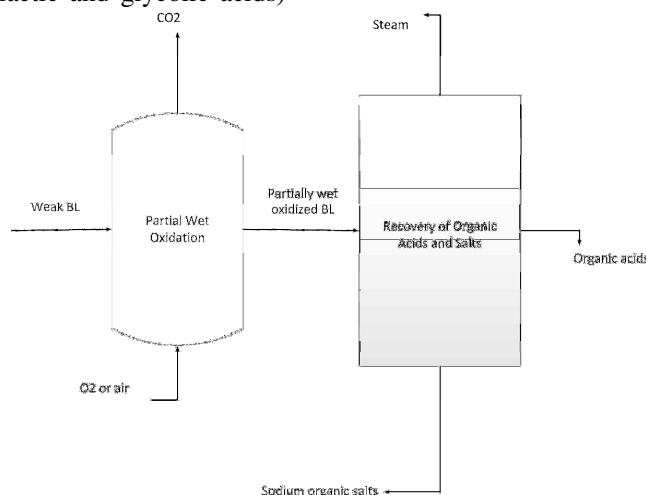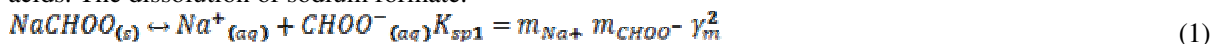

Figure 2: An alternative biorefinery process – partial wet oxidation followed by further recovery

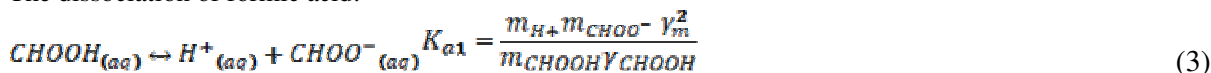## THERMODYNAMICS OF SALTS AND ACIDS DISSOCIATION

The aqueous sodium formate-acetate system has four reactions: dissolution of salts and dissociation of acids. The dissolution of sodium formate:
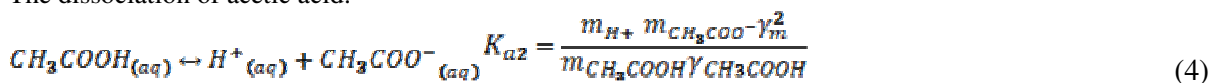
$$NaCHOO_{(s)} \leftrightarrow Na^+_{(aq)} + CHOO^-_{(aq)} \quad K_{sp1} = m_{Na+}\, m_{CHOO^-}\, \gamma_m^2 \tag{1}$$

The dissolution of sodium acetate:

$$NaCH_3COO_{(s)} \leftrightarrow Na^+_{(aq)} + CH_3COO^-_{(aq)} \quad K_{sp2} = m_{Na+}\, m_{CH_3COO^-}\, \gamma_m^2 \tag{2}$$

The dissociation of formic acid:

$$CHOOH_{(aq)} \leftrightarrow H^+_{(aq)} + CHOO^-_{(aq)} \quad K_{a1} = \frac{m_{H+}m_{CHOO^-}\gamma_m^2}{m_{CHOOH}\gamma_{CHOOH}} \tag{3}$$

The dissociation of acetic acid:

$$CH_3COOH_{(aq)} \leftrightarrow H^+_{(aq)} + CH_3COO^-_{(aq)} \quad K_{a2} = \frac{m_{H+}\, m_{CH_3COO^-}\gamma_m^2}{m_{CH_3COOH}\gamma_{CH3COOH}} \tag{4}$$

where m represents the molal concentration and γ_m represents mean molal activity coefficients of ions. Alternatively, salts can also be generated in hydrate forms, as shown in equations 5 and 6. For instance, the phase diagram of aqueous sodium acetate solution indicates that the saturation concentration of the di-hydrate solid form is much lower than that of the anhydrous solid form at temperatures below around 60 °C.[5] Thus, the complete speciation model should include equilibrium constants of hydrate solid forms as well.

$$NaCHOO.2H_2O_{(s)} \leftrightarrow Na^+_{(aq)} + CHOO^-_{(aq)} + 2H_2O \tag{5}$$

$$NaCH_3COO.3H_2O_{(s)} \leftrightarrow Na^+_{(aq)} + CH_3COO^-_{(aq)} + 3H_2O \tag{6}$$
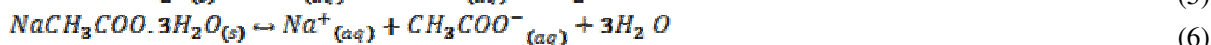
The equilibrium constants are fundamentally calculated through the standard state Gibbs free energies of formation as in equation 7:

$$K = \exp\left(-\frac{\Delta_{rxn}G^\circ(T)}{RT}\right) \text{ and } \Delta_{rxn}G^\circ(T) = \sum_i^{products} \Delta_f G_i^\circ(T) - \sum_i^{reactants} \Delta_f G_i^\circ(T) \tag{7}$$

where R represents the gas constant, $\Delta_{rxn}G^\circ$ represents the Gibbs free energy of a reaction and $\Delta_f G_i^\circ$ represents the Gibbs free energy of formation of the component i at the standard state. The values of $\Delta_f G_i^\circ$ and specific heats at 25 °C are provided in NBS Tables.[6] On the other hand, fundamental calculations require temperature dependence of specific heat as well. Moreover, the specific heat data of hydrate solid forms are unavailable in NBS Tables. Therefore, this study used experimental measurements from the literature or some simplifications, and the equilibrium constants were fitted to the empirical relation in equation 8 with respect to the temperature:

$$lnK \text{ or } pK = A + \frac{B}{T} + ClnT + DT \tag{8}$$

where A, B, C and D are parameters fitted to the data.

The equilibrium constants of sodium acetate and acetic acid were experimentally determined as the multiplication of ion activities at the temperature range of 20-240 °C and the corresponding saturation pressures.[7] Assuming that pressure has no major impact on the dissociation constants of solid salts, the data was fitted to the empirical relation by the minimization of relative squared error of lnK. The equilibrium constant of sodium formate was calculated based on the dissociation of anhydrous solid form as in equation 9 (assuming constant specific heat) from 273.15 K to 373.15 K with 5 K increments and fitted to the empirical relation in equation 8.

$$lnK = \left(-\frac{\Delta_{rxn}G^\circ(T^\circ)}{RT^\circ}\right) - \frac{\Delta_{rxn}H^\circ(T^\circ)}{R}\left(\frac{1}{T} - \frac{1}{T^\circ}\right) - \frac{\Delta_{rxn}Cp^\circ(T^\circ)}{R}\left(\frac{lnT}{T^\circ} - \frac{T^\circ}{T} + 1\right) \tag{9}$$

where T is in Kelvin and T° is 298.15 K.[8] The equilibrium constant of formic acid was expressed as a function of temperature.[9] Table 1 shows the fitted parameters for empirical temperature dependence of equilibrium constants and Figure 3 shows sodium acetate and acetic acid as fitted and measured.
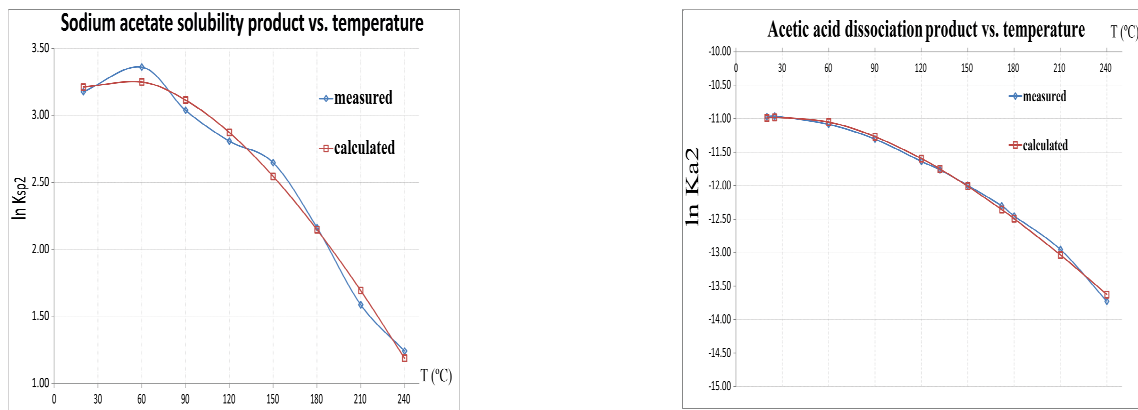

Figure 3: Fitted and measured equilibrium constants for sodium acetate and acetic acid

The activity coefficients of undissociated molecules were assumed as one in this study and the mean molal activity coefficient of ions was calculated by using Bromley's method.[8,10] This method considers the dissolved ions as one complex salt. This activity coefficient model involves Debye-Hückel term for long range electrostatic interactions and additional term F_i for short range interactions of opposite-charged ions, ignoring the short range interactions of the same-kind-charged ions. The advantage of this model over local composition models (such as Pitzer, extended UNIQUAC and e-NRTL) is its simplicity: fewer parameters to fit and binary data of each salt being sufficient.[8,11] The individual activity coefficient is calculated as:

$$log\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+\sqrt{I}} + F_i \tag{10}$$

$$F_i = \sum_j B_{ij}Z_{ij}m_j \quad (j \text{ refers to the ions having opposite charge of } i) \tag{11}$$

$$Z_{ij} = \frac{z_i + z_j}{2}$$

$$\dot{B}_{ij} = \frac{0.06 + 0.6B_{ij}}{\left(1+\frac{1.5}{|z_iz_j|}I\right)^2} + B_{ij} \quad \left(B_{ij} \text{ value is listed for each salt at } 25\,^{\circ}C\right) \tag{12}$$

$$I = \frac{1}{2}\sum_i^{ions} m_i z_i^2 \tag{13}$$

where z_i represents the number of charge of i, B_{ij} represents the interaction parameter between oppositely charged ions, I represents the ionic strength and A is Debye-Hückel constant.[8,10] The system in this study includes four ions: Na^+ (1), CH_3COO^- (2), H^+ (3) and $CHOO^-$ (4). Accordingly, F_i values are calculated as: (Z_{ij} is equal to one for this system)

$$F_1 = \dot{B}_{12}m_2 + \dot{B}_{14}m_4 \tag{14}$$
$$F_2 = \dot{B}_{12}m_1 + \dot{B}_{32}m_3 \tag{15}$$
$$F_3 = \dot{B}_{32}m_2 + \dot{B}_{34}m_4 \tag{16}$$
$$F_4 = \dot{B}_{14}m_1 + \dot{B}_{34}m_3 \tag{17}$$

where A and B_{ij} are temperature-dependent parameters.

Table 1
Fitted parameters for the dependence of empirical temperature on the equilibrium constants

	A	B	C	D
lnK_{sp1}	3.4005	-6397.7	3.1071	0.018783
lnK_{sp2}	-1.4454	-2131.0	3.8048	-0.033043
pK_{a1}	-57.528	2773.9	9.1232	0
lnK_{a2}	-1.5042	-2607.8	1.6222	-0.033444

Table 2
B parameter of Bromley activity coefficient model at 25 °C[8,10]

Salt or acid	B_{ij}
CH_3COONa	0.0519
$HCOONa$	0.1048
CH_3COOH	0.0874
$HCOOH$	0.11631

In this study, B_{ij} was assumed to be constant as a simplification due to limited concentration-activity coefficient data at various temperatures for these salts. Table 2 shows the calculation of B and the related values at 25 °C. Equation 18 gives the temperature dependence of A in natural logarithm scale.[12] Then, it is converted to logarithm of 10 base by equation 19.

$$A_{ln} = 1.131 + 1.335 * 10^{-3} * (T - 273.15) + 1.164 * 10^{-5} * (T - 273.15)^2 \tag{18}$$
$$A = log(exp(A_{ln})) \tag{19}$$

The mean molal activity coefficient is calculated based on individual coefficients as:

$$log\gamma_m = \frac{\sum_i^{ions} m_i log\gamma_i}{\sum_i^{ions} m_i} \tag{20}$$

THE RECOVERY PROCESS CONCEPT ON THE BASIS OF SPECIATION RESULTS

The feed concentrations are selected based on the analysis of partially wet oxidized wheat straw black liquor:[2] 1.26 m of sodium, 0.42 m of formate and 0.84 m of acetate contents. The partial wet oxidation downstream is a liquid at high temperature, pressure and pH (e.g. 20 bars, 200 ºC and pH 9). Thus, the stream can be concentrated by water evaporation before applying acid or salt recovery. The concentrations after water evaporation are:

$$m_{i\,total} = \frac{m_{i\,feed}}{100 - percent\,water\,evaporation\,rate} \quad (21)$$

Then, the species distribution was solved by using Solver in Excel to maximize the ionic strength in the constraints of the equilibrium constants (equations 1 to 4) and component mass balances (equations 22 to 24), assuming that the acid dissociation reactions are always in equilibrium. The species distribution was investigated with respect to measurable process conditions, temperature and pH (a measure of the activity of hydrogen ion: the mean activity coefficient multiplied by the molality of hydrogen ion) with two different water evaporation rates. Figure 4 and Figure 5 show the speciation results. Acid recovery refers to acid concentration in aqueous phase and solid recovery refers to the formation of sodium salt.

$$Na\ balance:\ m_{Na\,total} - m_{Na+(aq)} - m_{NaFormate\,(s)} - m_{NaAcetate\,(s)} = 0 \quad (22)$$

$$Acetate\ balance:\ m_{Acetate\,total} - m_{Acetate-(aq)} - m_{HAcetate\,(aq)} - m_{NaAcetate\,(s)} = 0 \quad (23)$$

$$Formate\ balance:\ m_{Formate\,total} - m_{Formate-(aq)} - m_{HFormate\,(aq)} - m_{NaFormate\,(s)} = 0 \quad (24)$$

To propose a recovery process concept, the speciation results were analysed with respect to the measurable and adjustable conditions: water evaporation, pH and temperature. The water evaporation was considered since the feed concentrations are too low to recover salts. However, 50% water evaporation is still insufficient for salt recovery; therefore, Figure 4 shows only acid recovery. Even after 80% water evaporation, sodium formate cannot be recovered and sodium acetate recovery is only 20-25%, as

shown in Figure 5. The pH value influences the distribution of the dissolved formate and acetate to the ionic form and acidic form. At low pH values, the dissolved acetate and formate content are in acidic form; therefore, ion concentrations are so low that the system does not reach supersaturation with respect to the salts. Acid concentrations decrease at pH higher than 2 and approach zero at pH around 7.
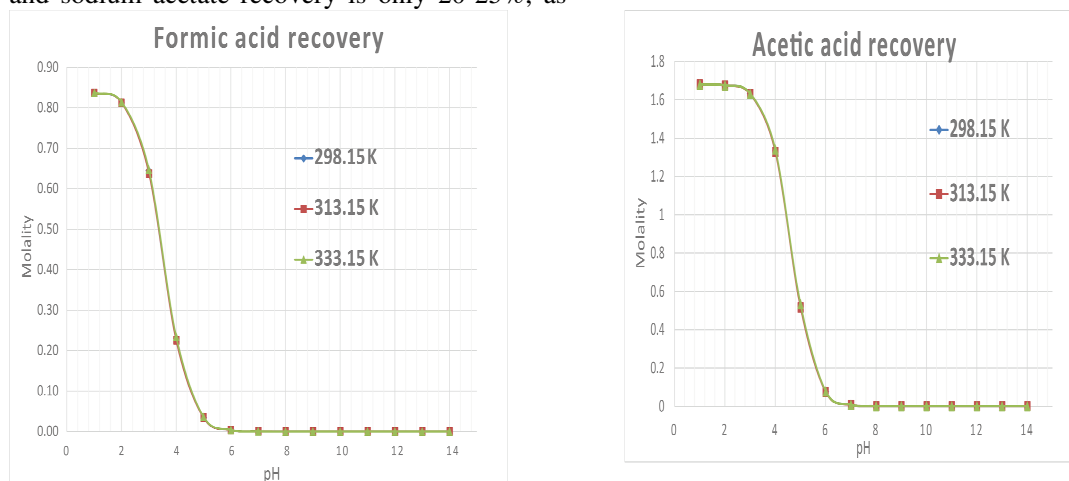

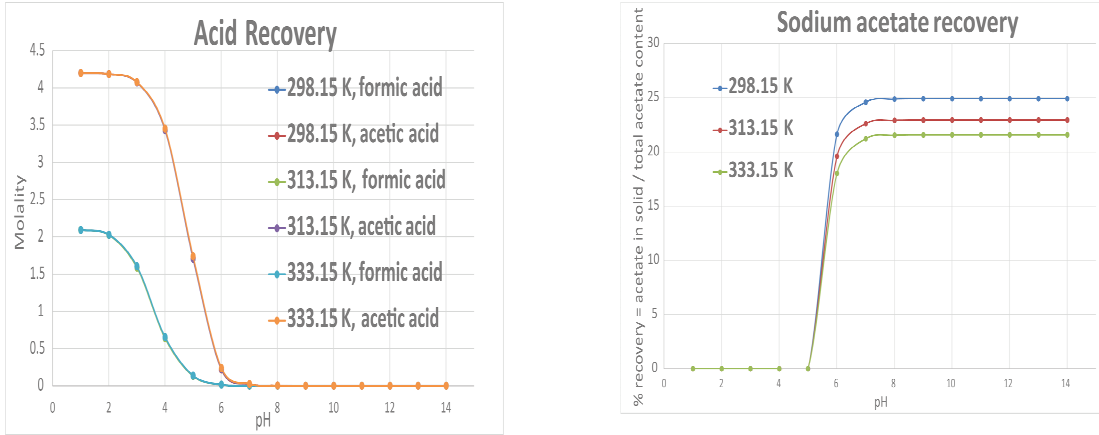Figure 4: Acid recovery after concentrating the stream by water evaporation of 50%

Figure 5: Acid and solid recovery after concentrating the stream by water evaporation of 80%

The sodium acetate recovery can be observed at pH higher than 5. The sodium acetate recovery increases with pH and reaches the maximum values at pH 8 while the acid concentrations reaches almost zero. To sum up, salt recovery requires high pH (above 5). In contrast, recovering acids requires low pH. Temperature has only a minor impact on the speciation: no noticeable impact on acid recovery and a slight impact on sodium acetate recovery.

Another alternative can include an evaporative crystallizer operating at high temperature (e.g. around 100 ºC) – instead of a separate evaporation unit – followed by a cooling crystallizer (e.g. around 30-40 ºC) and pH reduction as shown in Figure 7.
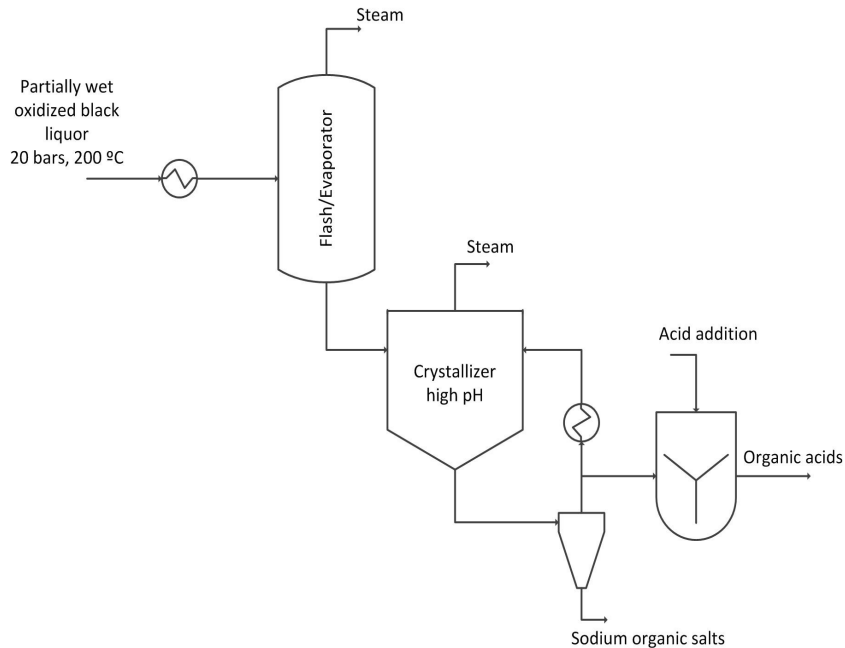

Figure 6: A process diagram for salt and acid recovery: flash/evaporator-crystallizer-pH
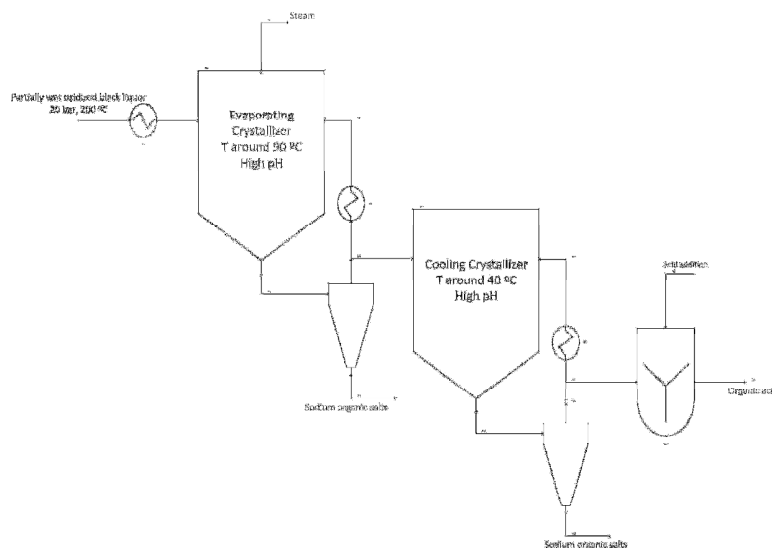
Figure 7: Selective salt recovery: evaporative crystallizer-cooling crystallizer-pH reduction

This can provide selective separation of salts in a multicomponent system. The salts having low solubility at high temperature can be separated first in the evaporative crystallizer and then the salts with low solubility at low temperature can be separated at the cooling crystallizer. On the other hand, these process concepts have two issues to be investigated during process design study: solid recovery performance and purification of the recovered acid mixture. Regarding solid recovery, the speciation results show a possible issue of low solid recovery: 20-25% sodium acetate and no sodium formate even after 80% water evaporation. Consequently, high salt recovery can require unfeasibly high water evaporation rates due to very high heat duty. Furthermore, the separation of individual acids in the liquid product is also an important challenge, especially considering a multi-component system including lactate, oxalate, galactate and succinate besides formate and acetate. These two issues might result in the need of some modifications in the concept and even in the product aim. As an alternative approach, the crystallizer can be removed to aim only at acids in case of very low salt recovery. In addition, syngas can be aimed instead of acids, considering the potential challenges of separation. Then, rather than typical gasification, hot compressed water gasification (sub- or super-critical water conditions) can be the potential option for further processing and producing

syngas. Hot compressed water gasification has more promising potential for feedstock with high water content since water is also involved in the reaction mechanism as reaction medium and/or a reactant.

FUTURE ASPECTS

The future aspects of this study can be investigated from two viewpoints: regarding the aqueous thermodynamics modelling and regarding the conversion route of black liquor through a biorefinery process.

From the thermodynamics viewpoint, the minimization of the total Gibbs free energy is fundamental to the equilibrium constant concept and multicomponent modelling. This kind of model involves the formation energy at the standard state, specific heat and the activity coefficient model. On the other hand, the data are limited to carboxylic acid salts: the missing data include the temperature dependence of the specific heat of each ion, specific heat and its temperature dependence for hydrate solid forms and activity coefficient data versus concentration under various temperatures. Thus, collecting these data can be an essential future research, to enable fundamental modelling without the simplifications applied in this study. In addition, another future aspect is to add the other components as well, such as oxalate, succinate, lactate and carbonates.

From the process viewpoint, each step of the route is to be investigated and to be developed more effectively. To begin with, non-wood black liquor contains a high amount of silica of which separation requires enabling fluid transport. In addition, the separation of lignin can also be investigated with respect to lignin influence on partial wet oxidation. Furthermore, complete first-principle knowledge is unavailable in the literature about the mechanism and kinetics of thermal decomposition of lignocellulosic compounds.

This might be too challenging, considering the number of involved compounds; however, a more precise modelling approach is needed. Then, another future aspect is to process the downstream of the recovery section: the investigation of alternatives, such as the separation of acids or hot compressed water gasification aiming at syngas production. After selecting the unit operations of the biorefinery route, the integration of these unit processes is the final task of the development of the whole biorefinery process.

CONCLUSION

Integrated biorefinery processes have recently become more important in producing biofuels, energy and chemicals. Investigating an alternative utilization of black liquor is crucial in this field due to its lignocellulosic content. Therefore, this study investigates the recovery of carboxylic acids and their sodium salts by illustrating the speciation of two major salts of partial wet oxidation downstream.

The thermodynamic model in this study involves the equilibrium constants and the mean activity coefficient. The equilibrium constants are based on either experimental data in the literature or calculation based on thermodynamic functions provided in NBS Tables. The mean activity coefficient of ions is calculated with Bromley's method. Then, the speciation is determined with respect to temperature and pH by solving the model to maximize the ionic strength with the constraints of equilibrium constants and mass balances. On the other hand, the model in this study includes some simplifications due to lack of relevant data, such as assuming anhydrous solid forms and constant specific heat values. Therefore, the future aspect can be to collect the relevant data in order to enable the fundamental model without simplifications. The speciation results indicate the need for water evaporation for salt recovery. Furthermore, the results also demonstrate that salt recovery requires high pH whereas low pH is required for acid recovery. As a result, water evaporation should be implemented in high pH to avoid steam-acid mixture in the vapour phase. This enables the direct utilization of steam without any additional separation need. Temperature slightly influences salt recovery but has no major influence on acid recovery. Therefore, the recovery concept is based on initial salt recovery mainly with water evaporation and/or with temperature control under high pH followed by acid recovery by reducing pH. One alternative process can include the following units in order: single or multistage flash/evaporator-crystallizer-pH reduction. Alternatively, the selective separation of salts can be achieved by an evaporative crystallizer at relatively high temperature followed by a cooling crystallizer. The future aspects from the process viewpoint include deeper investigations of the previous parts of the route: silica removal in case needed, lignin separation and influence on partial wet oxidation, partial wet oxidation of lignocellulosic compound.

On the other hand, salt and acid recovery might have issues of solid recovery performance and purification of individual acids. These aspects are to be investigated with more precise thermodynamic models and mass and energy balances. In a case of insufficient acid separation, salts and syngas can be produced by evaporation and crystallization followed by hot compressed water gasification. Alternatively, only syngas can be aimed through hot water compressed gasification if both solid recovery and acid purification are unfeasible.

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