

MODELING OF THE ACID SULFITE PULPING PROCESS. – PROBLEM DEFINITION AND THEORETICAL APPROACH FOR A SOLUTION WITH THE MAIN FOCUS ON THE RECOVERY OF COOKING CHEMICALS

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This study investigates the requirements for modeling of acid sulfite pulping with regard to the recovery of cooking chemicals, especially SO₂. Such a model has to predict the temporal change of SO₂ distribution on solid, liquid and gaseous phase in the digester throughout the whole pulping process, dependent on the pulping parameters: total SO₂, free SO₂, liquor-to-wood ratio, temporal temperature course, maximum pressure and time. The approach is based on the mass balance of SO₂ to achieve data for determination of kinetics of relevant chemical reactions, such as

sulfonation of lignin, dissolution of lignosulfonate, or formation of sulfate, strong acids and carbon dioxide. Results from capillary electrophoresis measurements in laboratory experiments were used to determine the temporal change of inorganic sulfur components in cooking acid. Some experimental problems remain (pH- and gas measurements) for a comprehensive description acid sulfite pulping, considering the mass balance of sulfur dioxide.

Keywords: *modeling, pulping process, recovery, cooking chemicals*

Introduction

Contrary to kraft pulping, modeling of acid sulfite pulping process hasn't been a big issue in pertinent research efforts. Although the importance of acid sulfite pulping has decreased in recent years, it is still of interest because of the capabilities to gain chemical byproducts, such as xylose, acetic acid, furfural, etc. Lenzing AG (Austria) gains pulp from beech wood for production of viscose fibers by an acid magnesium sulfite pulping process. Results of laboratory pulping experiments suggest that the ratio of free SO₂ should be increased in order to achieve a higher yield of byproducts without an adverse effect on pulp quality. The simple solution of increasing the SO₂ charge is not desirable, because the loss of cooking chemicals would increase when no changes were done in the recovery process. This would certainly lead to an exceedance of the emission limit which is not permitted.

Developed Model

Therefore, a steady state model was developed to estimate the potential of emission reduction which covers the pulping and recovery process. The whole process can be subdivided into the pulping process itself and into three subprocesses of the recovery process which are:

- 1) Absorption of gaseous SO₂ of digester relief gases in raw acid at different pressure levels (primary recovery)
- 2) Countercurrent absorption of SO₂ with magnesium hydroxide regaining raw acid after combustion of thick liquor in the recovery boiler (secondary recovery)
- 3) Thermally splitting of excess magnesium monosulfite (ternary recovery)

The model is mainly based on process data and is evidently strongly simplified due to the complexity of the whole process. The use of the

process simulation software package Aspen Plus® has simplified the development.

Despite the simplifications, it has been successfully used for the pre-estimation of changes and improvements in the recovery process. In order to improve the reliability of the model predictions, it is necessary to replace the reproduction of a certain operation mode by a predictive model, which takes into account operation characteristics of the different process units. Thus, extrapolation should be possible, more precise and more reliable.

Required improvements

From the point of the recovery process, the pulping process is the „supplier“ and the „customer“ of cooking chemicals magnesium and sulfur dioxide. But they are treated in different ways: Magnesium is a component of the raw acid and remains after the pulping process in the liquid phase (spent liquor). In contrast, sulfur dioxide, or HSO_3^- respectively, reacts with wood components, mainly lignin. Gaseous SO_2 is integrated in the solid and liquid phase which changes the distribution of SO_2 in the solid, liquid and gaseous phases throughout the pulping process. Therefore, a model of the pulping process, with the main focus on the recovery of cooking chemicals, has to be capable to predict the SO_2 distribution on the solid, liquid and gaseous phase as well as the charge and discharge of SO_2 by the different process streams (spent liquor, pressure control relief gas, high-, medium- and low-pressure relief gas) dependent on the cooking parameters: time t , total SO_2 , free SO_2 , liquor-to-wood ratio, maximum pressure p_{max} , temporal course of temperature $T(t)$.

Literature

A literature study on modeling of acid sulfite pulping showed that no proper model exists which considers the behavior of the cooking chemicals, especially SO_2 . The main focus of the published models is put on the properties and quality of the pulp. Most of the models are empirical and are able to predict the kappa-number or the lignin content of the pulp [[1], [2], [3], [8], [13]]. Furumoto [4] developed a knowledge-based model due to mathematical and statistical analysis of process data. Such a model is just specific for the plant and its operation mode. Such deduced relations don't need to

follow the mechanism of the process. Hagberg & Schön [[5]-[7]] and Kilian & De Vaal [9], respectively, has chosen a mechanistic approach which enables to follow temporal changes during the pulping process. Hagberg & Schön determine kinetic data for the delignification, the dissolution of hemicellulose and the formation of strong acids from experimental results in laboratory. Their model considers the electroneutrality, the protolysis equilibrium of sulfurous acid, the phase equilibrium of gaseous and dissolved SO_2 , and the assumption that the total pressure is the sum of SO_2 - and H_2O -partial pressure. Kilian & De Vaal used the same relations, but adjust the model parameters to experimental data measured at a plant digester. Additionally, they implement degradation kinetics of cellulose to predict and control the viscosity of pulp.

The assumption, that total pressure is the sum of SO_2 and H_2O partial pressure, is not transferable to beech wood pulping due to the fact that CO_2 is evolved during the pulping process. Additionally, the phase equilibrium of gaseous and dissolved SO_2 is influenced by other dissolved substances in the cooking liquor, which has an effect on the activity coefficient of the dissolved SO_2 and further on the phase equilibrium.

Another issue, which is not considered in any published model so far; is the pressure control relief. The main function of pressure control relief, beside compliance of maximum pressure, is the heat removal from the digester in order to control the temperature in the digester. Otherwise the generated heat, which is released by exothermal reactions during pulping, would result in exceeding the temperature limit.

All these neglected factors have an impact on gas composition and mass flow of digester relief gases which are especially important for primary recovery.

In order to eliminate these deficiencies of the models, the requirements were analyzed which are needed for establishing a sufficient model.

Analysis

Process Characteristics

The pulping process is very complex and can be characterized as follows:

Pulping is an unsteady reactive process. In a digester, three phases exist in parallel: solid, liquid and gaseous phase. The single phases are inhomogeneous in temperature and concentration and change their composition and their volume ratio during the pulping process. Therefore the three phases are under permanently mass and heat exchange, where the difference of real and equilibrium state is the driving force. The different chemical reactions can be subdivided in

- Reactions with involvement of sulfur components; e.g. formation of

lignosulfonates, α -hydroxysulfonates, sugar sulfonates, sulfates and thiosulfates.

- Reactions of the organic matter; e.g. acid hydrolysis of cellulose and hemicellulose, lignin condensation, formation of organic acids like formic and acetic acid and release of carbon dioxide CO_2 from carbonyl-groups

A simplified scheme of the most important chemical reactions, chemical and phase equilibria is shown in Figure 1.

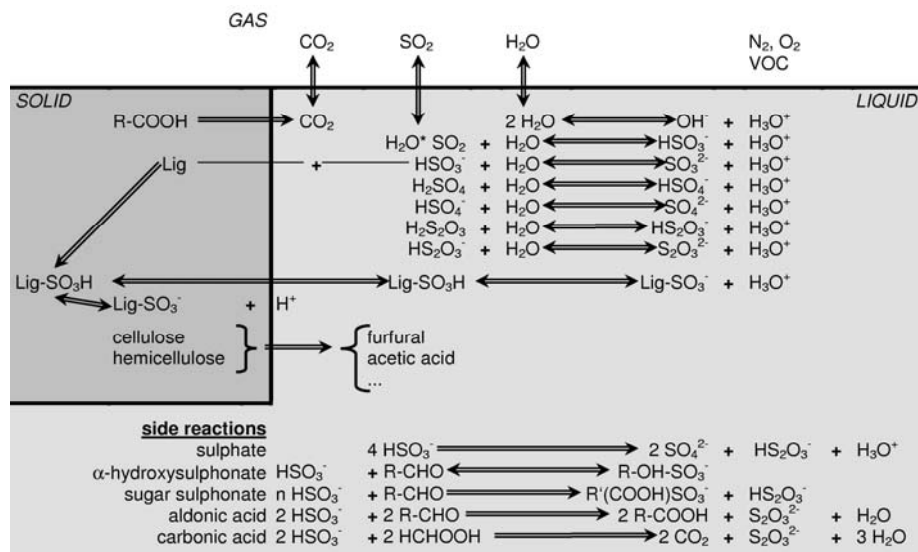


Figure 1. Scheme of phase equilibria and chemical reactions during acid sulfite pulping

Data basis

The basis of each model are relevant and reliable experimental data. The basis for an acid sulfite pulping model, considering recovery aspects, is the mass balance of the sulfur components during the pulping process. The different components and their distribution on the three phases:

- Solid phase (sol)
 - $[\text{Lig-SO}_3^-]_{\text{sol}}$ undissolved lignosulfonate
 - $[\text{R-SO}_3^-]_{\text{sol}}$ undissolved org. S-compound
 - Liquid phase (liq)
 - $[\text{Lig-SO}_3^-]_{\text{liq}}$ dissolved lignosulfonate
 - $[\text{R-SO}_3^-]_{\text{liq}}$ dissolved org.c S-compound
 - $[\text{H}_2\text{SO}_3]$, $[\text{HSO}_3^-]$, $[\text{SO}_3^{2-}]$ sulfite – S(IV)
 - $[\text{H}_2\text{SO}_4]$, $[\text{HSO}_4^-]$, $[\text{SO}_4^{2-}]$ sulfate – S(VI)
 - $[\text{H}_2\text{S}_2\text{O}_3]$, $[\text{HS}_2\text{O}_3^-]$, $[\text{S}_2\text{O}_3^{2-}]$ thiosulfate - S(II)
 - Gaseous phase (gas)
 - $[\text{SO}_2]_{\text{gas}}$ sulfur dioxide
- where:

$[i]_{\{j\}}$..concentration of substance i in phase j, mol/mol

LigLignin

Rcarbohydrate

Other essential parameters are:

- $[\text{H}_3\text{O}^+]$ -concentration in liquid phase: required for kinetics of chemical reactions and for dissociation equilibria
- $[\text{CO}_2]_{\text{gas}}$: increases total pressure and is required for determining the formation rate of CO_2
- $[\text{H}_2\text{O}]_{\text{gas}}$: is a monitoring parameter for gas concentration measurements
- \dot{V}_{gas} is required for mass balancing the pulping process and for estimating heat formation due to exothermal reactions

A conclusion of this analysis results in 21 unknown parameters:

3 phases, 17 concentrations and 1 gas flow.

An equivalent number of measurements, constraints, relations, assumptions and simplifications are needed for the determination of these 21 parameters; these are:

- Measurements
 - 1) capillary electrophoresis (CE)-measurement Σ sulfite S(IV)
 - 2) CE-measurement Σ sulfate S(VI)
 - 3) pH-measurement
 - 4) $[\text{SO}_2]_{\{\text{gas}\}}$ measurement
 - 5) $[\text{CO}_2]_{\{\text{gas}\}}$ measurement
 - 6) $[\text{H}_2\text{O}]_{\{\text{gas}\}}$ measurement
 - 7) flow measurement of total relief gas
 - 8) determination of total sulfur in liquid phase
- Constraints, relations
 - 9) $\text{pK}_a(\text{T})$ sulfurous acid 1. protolysis equil.
 - 10) $\text{pK}_a(\text{T})$ sulfurous acid 2. protolysis equil.
 - 11) $\text{pK}_a(\text{T})$ sulfuric acid 1. protolysis equil.
 - 12) $\text{pK}_a(\text{T})$ sulfuric acid 2. protolysis equil.
 - 13) $\text{pK}_a(\text{T})$ thiosulfuric acid 1. protolysis equil.
 - 14) $\text{pK}_a(\text{T})$ thiosulfuric acid 2. protolysis equil.
 - 15) volume balance
 - 16) mass balance sulfur
- Assumptions
 - 17) Σ thiosulfate = 0
 - 18) organic sulfur in solid phase is bound to lignin
 - 19) organic sulfur in liquid phase is bound to lignin
 - 20) gas volume = constant
 - 21) change of liquid volume proportional to dissolved organic sulfur

The assumption; that thiosulfate is not a component of the cooking liquor; is based on results of former CE-measurements.

For a model focusing on recovery of SO_2 it is not important to distinguish whether the sulfur is bound to lignin or to another organic compound. Therefore all sulfur bound to an organic compound is counted as a lignosulfonate. This assumption overestimates lignin sulfonation, but minimizes the experimental and analytical effort.

Unfortunately, volume measurements during cooking are not feasible because of undefined surfaces and interfaces of the different phases.

These experimental data can be used to determine the parameter for the chemical kinetics of

- Sulfonation of lignin in the solid phase

- Formation of strong organic acid anions
- Dissolution of solid lignosulfonate
- Formation of sulfate
- Formation of carbon dioxide

Especially the temporal courses of $[\text{HSO}_3^-]$ and $[\text{H}^+]$ can be determined, which are the basis for each sulfite pulping model considering chemical kinetics. ([5]-[7], [9]).

Also a relation can be deduced for the phase equilibrium of $\text{SO}_{2\{\text{gas}\}}$ and dissolved SO_2 from these data. A comparison with data from literature should allow an evaluation whether during gas relief thermodynamic equilibrium is reached or not.

Kinetic parameters valid for a broader range of pulping parameters can be obtained from a series of experiments, in which following parameters are varied:

- time
- total SO_2
- free SO_2
- temporal course of temperature
- temporal course of pressure
- liquor-to-wood ratio

These data establish a basis for the development of a comprehensive model of acid sulfite pulping focusing on recovery of sulfur dioxide.

Experimental and Evaluation Problems

Several questions arise for the determination of the essential data, summarized above:

CE-measurement

CE-measurement is a well established method to determine sulfite and sulfate concentration in the cooking liquor during the pulping process [[12]]. It was used several times at our lab digester and at our plant digester as well. The uncertainty in CE-measurement is about 5%.

pH measurement

Fundamental problems arise for the measurement of pH under conditions typically for acid sulfite pulping (up to 160°C, 10 bar, low pH), which are the long term resistance of the glass electrode, the precision and drift of pH measurement. The determination of pH is necessary for calculating $[\text{H}^+]$ and $[\text{HSO}_3^-]$ concentrations which are essential for chemical kinetics. An indirect determination of pH, by measuring concentration of strong acids in

liquid phase, does not consider solid lignosulfonate that also influences pH.

Measurement of gas concentration

The problems of gas concentration measurement are sampling during the cooking period without gas relief and the difficulties in measuring the composition of wet gas.

Determination of the exothermal effects during cooking

An exact determination of exothermal heat of reaction would need to solve the complete heat balance of the pulping process considering the heat loss to ambience, the heat capacity of digester and its content. Most of the generated heat is released by evaporation of water. Therefore the exothermal heat of reaction can be estimated by the amount of steam evolved during gas relief.

Evaluation of inorganic sulfur concentrations

Another issue is the combined evaluation of pH- and CE-measurements to calculate the temporal course of $[\text{H}_2\text{SO}_3]$, $[\text{HSO}_3^-]$ and $[\text{SO}_3^{2-}]$ concentrations or $[\text{H}_2\text{SO}_4]$, $[\text{HSO}_4^-]$ and $[\text{SO}_4^{2-}]$ concentrations, respectively. Therefore, the temperature dependency of the dissociation constants is needed that can be calculated according to equation (1) using the thermodynamic data of Table 1 [10].

Figure 2 shows the calculated pK values for H_2SO_3 and H_2SO_4 dependent on temperature. These curves are calculated with a constant value of $\Delta_r C_p$ and therefore they show only a slight dependency on temperature.

Figure 3 illustrates the good compliance of the calculated data with data from literature of pK_a for the first stage of protolysis of H_2SO_3 . The compliance can be improved when a quadratic temperature dependency of Cp is assumed, and the parameter fit to the data from literature (see Figure 3).

material data	$\Delta_f H_0$	$\Delta_f G_0$	C_{p0}
	[kJ/mol]	[kJ/mol]	[J/K mol]
$\text{H}_2\text{SO}_4(\text{aqu})$	-909,3	-744,5	-393
HSO_4^-	-887,3	-755,91	-84
SO_4^{2-}	-909,3	-744,53	-293
$\text{SO}_2(\text{aqu})$	-323,2	-300,5	195
H_2O	-285,8	-237,13	75,3
HSO_3^-	-626,8	-527,03	-1,9
SO_3^{2-}	-630,4	-486,09	-263,9
H^+	0	0	0

Reactions	$\Delta_r H_0$	$\Delta_r G_0$	$\Delta_r C_{p0}$
	[J/mol]	[J/mol]	[J/K mol]
$\text{H}_2\text{SO}_4(\text{aqu}) \rightleftharpoons \text{HSO}_4^- + \text{H}^+$	21960	-11410	309
$\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$	21930	11380	-209
$\text{SO}_2(\text{aqu}) + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{H}^+$	-17800	10600	-272
$\text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}^+$	-3650	40940	-262

Table 1. Thermodynamic data for the calculation of the temperature dependency of the thermodynamic equilibrium constant [[10]] where

$\Delta_f G_0$ free enthalpy of formation at T_0 , kJ/mol

$\Delta_f H_0$ enthalpy of formation at T_0 , kJ/mol

C_{p0} heat capacity at T_0 , kJ/K mol

$\Delta_r G_0$ free enthalpy of reaction at T_0 , kJ/mol (see equation (2))

$\Delta_r H_0$ enthalpy of reaction at T_0 , kJ/mol (see equation (3))

$\Delta_r C_{p0}$ heat capacity of reaction at T_0 , kJ/K mol (see equations (4))

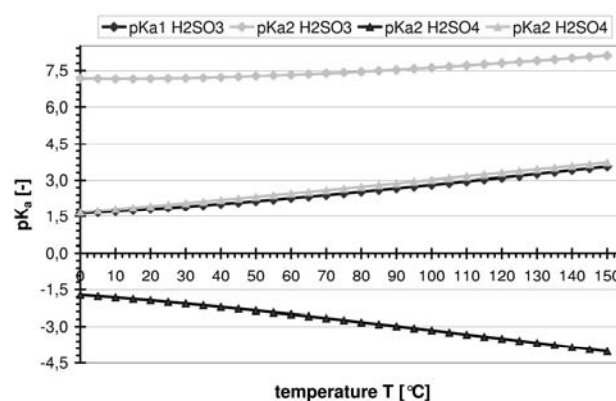
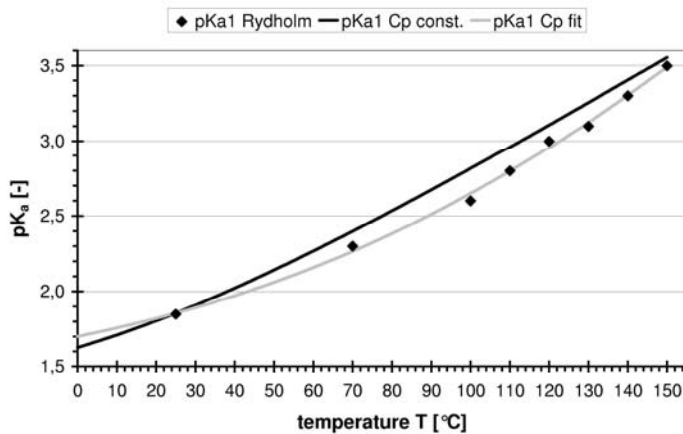


Figure 2. Calculated pK_a-values of sulfurous acid and sulfuric acid dependent on temperature



With experimental data of laboratory pulping experiments and an assumed temporal pH-course it is possible to calculate time-dependent concentrations of sulfurous and sulfuric acid anions using the equations (5) to (10), see Figure 4 and Figure 5).

Figure 3. Comparison of calculation and literature data of pK_{a1} of H_2SO_3 with different mathematical relations for C_p (black line: $C_p = C_{p0}$; gray line: $C_p = C_{p0} + A \cdot T + B \cdot T^2$ - A, B...fit parameters) [11]

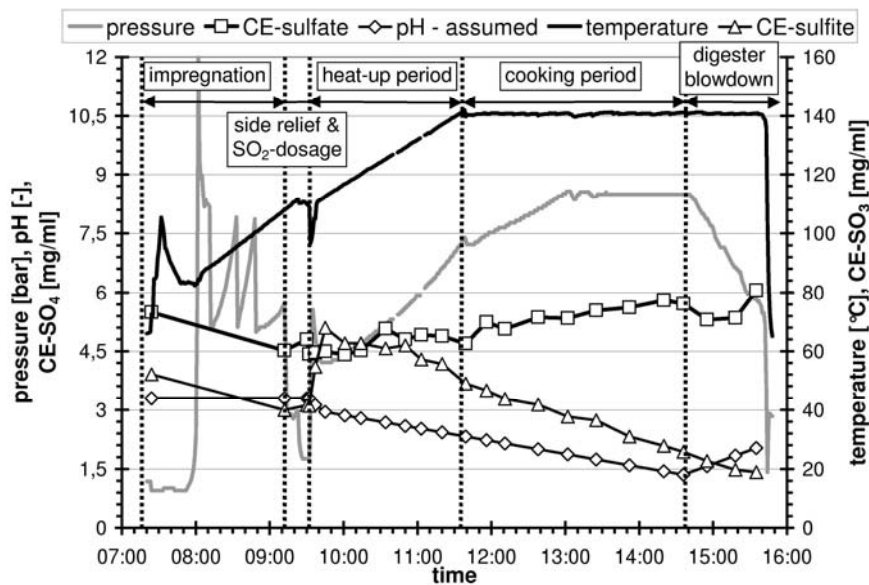


Figure 4. Experimental data and an assumed course of pH of a laboratory pulping experiment

The assumed pH in Figure 4 is based on:

- 1) In the period of impregnation and side relief the pH is assumed to be constant at the level of raw acid: On one hand the calculated pH based only on CE-measurement would estimate a slight increase of pH and on the other hand the dissolution of some acetic acid and other organic acids from the wood chips would decrease pH.
- 2) The decrease of pH in the cooking period was estimated with results of pH-measurements at a pilot digester. The experiments were carried out at different temperature, total SO_2 and free SO_2 than in the laboratory experiment. A linear

correlation with time was assumed and the measured data were extrapolated to the conditions of the laboratory experiment resulting in a pH decrease of about 0,3 per hour.

- 3) The linear increase of pH in the period of digester relief is based on pH-measurements carried out by Fischer [3].

The constraint of electroneutrality (equation (11)) determines the concentration of strong acid anions $[A^-]$ formed during pulping considering that the concentration of magnesium cation $[Mg^{2+}]$ is constant after side relief (see Figure 5).

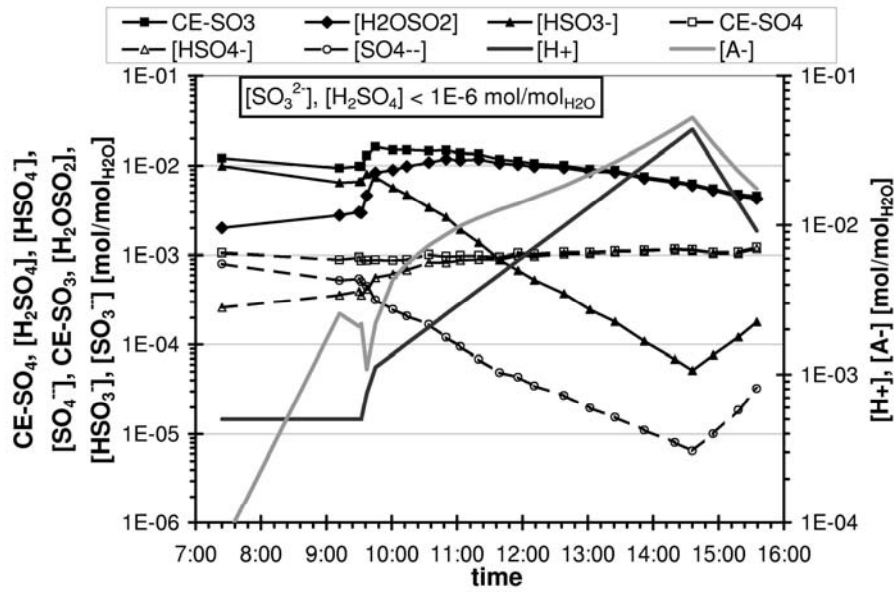


Figure 5: Calculated time-dependent concentrations of hydronium ion, strong acid, sulfurous acid and sulfuric acid anions in a laboratory pulping experiment

Not all experimental problems are solved up to now, especially some basics have to be clarified for the implementation of pH- and gas concentration measurement.

New Digester Model

For a better explanation of the model the digester is divided in two zones: a head space and a solid/liquid phase (see Figure 6). Both zones are described as ideal stirred tank and are corresponding by gas exchange.

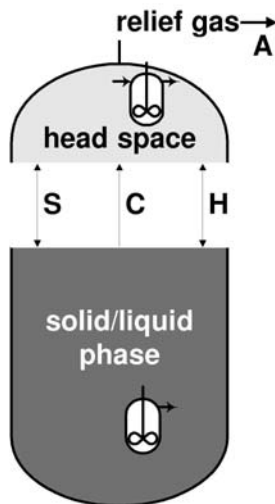


Figure 6: Scheme of digester model

Necessary inputs for both sections are

- Temporal temperature course
- Maximum pressure or the time-dependent pressure decrease during digester relief

- Initial values for load, liquor-to-wood-ratio, charge of SO₂ and ratio of free SO₂
-

Assumptions for modeling head space

Input streams:

- S ensuring gas exchange with
- C solid/liquid phase.
- H

Outlet stream A:

three periods have to be distinguished:

- Heat up and cooking period without gas relief
 $A=0$,
 $p_{total}=f(T, \dot{r}_{CO_2}, \text{phase equilibrium gas/liquid})$
- Cooking period with gas relief
 $A= f(T, \dot{r}_{CO_2}, \text{phase equilibrium gas/liquid, exothermal effect}),$
 $p_{total} = p_{max}$
- Digester relief –
 $A= f(T, \dot{r}_{CO_2}, \text{phase equilibrium gas/liquid, exothermal effect}),$
 $p_{total}=f(t)$

where:

S, C, H, A (see Figure 6)

Ttemperature, K

t.....time, s

p_{total} ..total pressure, bar

p_{max} ..maximum allowable pressure, bar

\dot{r}_{CO_2} ..formation rate of carbon dioxide

Chemical reactions:

- none

Constraints:

- Head space and solid/liquid phase are in phase equilibrium

Further assumptions:

- Head space is homogeneous
- Volume of head space is constant.

A mathematical analysis of the head space results in 11 variables:

- ✓ 3 streams of known composition:
S ($x_{SO_2,S} = 1$), C ($x_{CO_2,S} = 1$), H ($x_{H_2O,S} = 1$)
- ✓ 1 relief gas stream of unknown composition:
A, $c_{SO_2,A}$, $c_{CO_2,A}$, $c_{H_2O,A}$
- ✓ 1 head space of unknown composition:
G, $c_{SO_2,G}$, $c_{CO_2,G}$, $c_{H_2O,G}$

The corresponding mathematical relations to calculate these variables are summarized in the appendix (see equations. (12) to (22)).

Assumptions for modeling the solid/liquid zone

Input streams:

- none

Output streams:

- S ensuring gas exchange with solid/liquid phase.
- C
- H

Chemical reactions:

- Sulfonation of lignin in solid phase
- Dissolution of lignosulfonates
- Formation of strong acids
- Formation of sulfate
- Formation of carbon dioxide

Constraints:

- Protolysis equilibrium of sulfurous acid
- Protolysis equilibrium of sulfuric acid
- Electroneutrality
- Mg^{2+} -concentration is constant

Further assumptions:

- Solid/liquid phase is homogeneous, its volume is constant
- Only lignin reacts with sulfur
- No thiosulfate in the cooking acid

A mathematical analysis of the solid/liquid zone results in 17 variables:

- ✓ 3 streams of known concentration:
S ($x_{SO_2,S} = 1$), C ($x_{CO_2,S} = 1$), H ($x_{H_2O,S} = 1$)
- ✓ 1 solid/liquid phase with 13 unknown concentrations:
Lig.....lignin
LS_{sol}.....lignosulfonate in solid phase
LS_{liq}.....lignosulfonate in liquid phase
[H₂SO₃], [HSO₃⁻], [SO₃²⁻].....sulfurous acid
[H₂SO₄], [HSO₄⁻], [SO₄²⁻].....sulfuric acid
[H⁺], [Mg²⁺].....cations

[A⁻].....anions of strong acids

[CO₂].....carbon dioxide

The corresponding mathematical relations to calculate these variables are summarized in the appendix (see equations (23) to (31)).

The total system is a differential-algebraic equation system which can be solved with commercial software packages or routines. It enables to calculate temporal course of [H⁺] and [HSO₃⁻] which are the main factors of chemical reactions of cellulose and hemicellulose. Therefore, the model can be extended for these reactions predicting pulp properties, too.

Conclusion and further developments

The essential parameters of acid sulfite pulping have been elaborated by a systematic analysis of the process considering published knowledge and relations. The temporal course and change of concentration of cooking chemicals on the solid, liquid and gaseous phase is required for a pulping model regarding recovery aspects. This leads to the problem to determine the sulfur components in each phase which is necessary for the sulfur mass balance. The temporal courses of [H₃O⁺] and [HSO₃⁻] are the basis for the determination of kinetic parameters of relevant chemical reactions, such as sulfonation, dissolution of lignosulfonate, formation of sulfate, strong acids and carbon dioxide.

The most important experimental problems, which have to be solved, are the measurement of pH under pulping conditions and the gas sampling during the cooking phase without gas relief. Afterwards an experimental program has to be conducted varying the pulping parameters: total SO₂, free SO₂, liquor-to-wood-ratio, temporal courses of temperature and pressure and time. In ideal case a universal set of kinetic parameters can be deduced for the essential chemical reactions, such as sulfonation of lignin in the solid phase, dissolution of solid lignosulfonate, formation of strong organic acid anions, sulfate and carbon dioxide. But these parameters are only valid for the lab digester and can't be used for modeling the pulping process at the plant. Therefore some additional measurements at the plant digester have to be done, but their number should be minimized due the experience from laboratory experiments.

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Appendix

$$-\ln(K(T)) = \frac{\Delta_r G_0}{R_{gas} \cdot T_0} + \frac{\Delta_r H_0}{R_{gas} \cdot T_0} \cdot \left(\frac{T_0}{T} - 1 \right) + \frac{\Delta_r Cp_0}{R_{gas}} \cdot \left(1 - \frac{T_0}{T} - \ln \left(\frac{T}{T_0} \right) \right) \quad T_0 = 298,15K \quad (1)$$

$$\Delta_r G_0 = \sum_i \nu_i \cdot \Delta_f G_{i,0} \quad (2) \quad \Delta_r H_0 = \sum_i \nu_i \cdot \Delta_f H_{i,0} \quad (3) \quad \Delta_r Cp_0 = \sum_i \nu_i \cdot Cp_{i,0} \quad (4)$$

where

- K..... equilibrium constant
- T temperature, K
- R_{gas}..... universal gas constant, kJ/mol K
- Δ_rG₀ ... free enthalpy of reaction at T₀, kJ/mol
- Δ_rH₀ ... = enthalpy of reaction at T₀, kJ/mol
- Δ_rCp₀ . heat capacity of reaction at T₀, kJ/mol K
- Δ_fG_{i,0}.. free enthalpy of formation of substance i at T₀, kJ/mol
- Δ_fH_{i,0}.. enthalpy of formation of substance i at T₀, kJ/mol
- Cp_{i,0} ... heat capacity of substance i at T₀, kJ/mol K
- ν_i..... stoichiometric coefficient

$$SULFITE = \frac{MG_{SO_3}}{MG_{H_2SO_3}} \cdot [H_2SO_3] + \frac{MG_{SO_3}}{MG_{HSO_3}} \cdot [HSO_3^-] + [SO_3^{2-}] \quad (5)$$

$$K_{H_2SO_3}(T) = \frac{[HSO_3^-] \cdot [H^+]}{[H_2SO_3]} \quad (6) \quad K_{HSO_3}(T) = \frac{[SO_3^{2-}] \cdot [H^+]}{[HSO_3^-]} \quad (7)$$

$$SULFATE = \frac{MG_{SO_4}}{MG_{H_2SO_4}} \cdot [H_2SO_4] + \frac{MG_{SO_4}}{MG_{HSO_4}} \cdot [HSO_4^-] + [SO_4^{2-}] \quad (8)$$

$$K_{H_2SO_4}(T) = \frac{[HSO_4^-] \cdot [H^+]}{[H_2SO_4]} \quad (9) \quad K_{HSO_4}(T) = \frac{[SO_4^{2-}] \cdot [H^+]}{[HSO_4^-]} \quad (10)$$

where:

SULFITE..... total sulfite concentration (CE-measurement), mol/mol_{H2O}

SULFATE total sulfate concentration (CE-measurement), mol/mol_{H2O}

MG_i..... molecular weight of substance i, kg/kmol

K_i protolysis equilibrium constant of substance i

[] concentration, mol/mol_{H2O}

$$[A^-] = 2 \cdot [Mg^{2+}] + [H^+] - [HSO_3^-] - 2 \cdot [SO_3^{2-}] - [HSO_4^-] - 2 \cdot [SO_4^{2-}] \quad (11)$$

where:

[] concentration, mol/mol_{H2O}

Total mass balance: $G \cdot \frac{dc}{dt} = S + C + H - A$ (12)

SO₂-mass balance: $G \cdot \frac{dc_{SO_2,G}}{dt} = S - A \cdot c_{SO_2,A}$ (13)

H₂O-mass balance: $G \cdot \frac{dc_{H_2O,G}}{dt} = H - A \cdot c_{H_2O,A}$ (14)

Constraints of ideal stirred reactor: $c_{SO_2,G} = c_{SO_2,A}$ (15) $c_{CO_2,G} = c_{CO_2,A}$ (16) $c_{H_2O,G} = c_{H_2O,A}$ (17)

Constant gas volume: $G = konst. = G_0 = f(\text{load, } V_{\text{digester}}, \text{liquor} - \text{wood} - \text{ratio})$ (18)

Phase equilibrium of H₂O: $c_{H_2O,G} = c_{H_2O}^* = f(T)$ (19)

Phase equilibrium of SO₂: $c_{SO_2,G} = c_{SO_2}^* = f(T, [HSO_3^-], [H^+])$ (?) (20)

Total pressure: $P_{\text{total}} = P_{SO_2} + P_{CO_2} + P_{H_2O}$ (21)

Temporal course of total pressure or relief gas flow resp.: $A = 0 \Rightarrow P_{\text{total}} = f(\quad)$ (22)

$P_{\text{total}} = P_{\text{max}}$ bzw. $P_{\text{total}} = p(t) \Rightarrow A = (\quad)$

where:

t..... time, s

G..... volume of head space, m³

S, C, H, A in- and outlet streams, kg/s

c_{i,X}..... concentration of substance i in stream X or zone X resp. , mol/m³

c_i^{*} concentration of substance i in equilibrium, mol/m³

p_i partial pressure of substance i, Pa

V_{digester} total volume of digester, m³

Volume balance $LiqSol = V_{\text{digester}} - G_0$ (23)

Lignin mass balance $Lig(t) = Lig_0 - \frac{Lig}{LS} \cdot \int dLS_{sol}$ (24)

$\frac{Lig}{LS}$ "ratio of sulphonation"

Sulfonation of lignin $\frac{dLS_{sol}}{dt} = f([L], [HSO_3^-], [H^+])$ (25)

Dissolution of lignosulfonate $\frac{dLS_{liqu}}{dt} = f([LS_{sol}], [H^+])$ (26)

Formation of carbon dioxide $\frac{dCO_2}{dt} = f(?)$ (27)

Formation of sulfate / sulfate mass balance $\frac{dSULFATE}{dt} = f(?)$ and equ. (8) (28)

1. protolysis equilibrium $K_{H_2SO_4}(T) = \frac{[HSO_4^-] \cdot [H^+]}{[H_2SO_4]}$ (9)

2. protolysis equilibrium $K_{HSO_4}(T) = \frac{[SO_4^{2-}] \cdot [H^+]}{[HSO_4^-]}$ (10)

1. protolysis equilibrium $K_{H_2SO_3}(T) = \frac{[HSO_3^-] \cdot [H^+]}{[H_2SO_3]}$ (6)

2. protolysis equilibrium $K_{HSO_3}(T) = \frac{[SO_3^{2-}] \cdot [H^+]}{[HSO_3^-]}$ (7)

Formation of strong acids $\frac{d[A^-]}{dt} = f([HSO_3^-], [H^+], ?)$ (29)

Constance of Mg-ions $[Mg^{2+}] = [Mg^{2+}]_{t=0} = f(SO_{2,total,t=0}, \%SO_{2,free,t=0})$ (30)

electroneutrality $2 \cdot [Mg^{2+}] + [H^+] = [HSO_3^-] + 2 \cdot [SO_3^{2-}] + [HSO_4^-] + 2 \cdot [SO_4^{2-}] + [A^-]$ (31)

Sulfur mass balance

Constraint of head space S, C, H

where:

LiqSol volume of solid and liquid phase, m³

Lig concentration of lignin in solid/liquid-phase, g/m³

LS concentration of lignosulfonate, g/m³