Final Technical Report on Annex IX
Task I

Development of an Alternative Kraft Black Liquor Recovery Process
Based on Low-Temperature Processing in Fluidized Beds

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OBJECTIVES

Overall objective :

The overall objective of this research program was to provide the fundamental knowledge and experimental data from pilot scale operation for an alternative black liquor recovery technology which would have a higher overall energy efficiency, would not suffer from the smelt-water explosion hazard and would be lower in capital cost. In addition, the alternative process would be more flexible and well suited for incremental recovery capacity or for new pulping processes, such as the new sulphide-sulphide-AQ process.

Specific research objectives :

The research program consists of number of specific research objectives with the aim to achieve the ultimate objective of developing an alternative recovery process which is shown in Figure 1. The specific objectives are linked to individual unit operations and they represent the following research topics :

Figure 1 - General Flowsheet of Fluidized Bed Processing At a Low Temperature

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1. Superheated steam drying of kraft black liquors

It was our objective to perform studies necessary to determine process parameters governing the drying of black liquor from 75% solids concentration to 92% solids using bench scale laboratory equipment. Data from this part of the study were to be used to design, build and operate a rotating drum dryer where a thin film of black liquor covering the outer surface of the drum would be dried with superheated steam.

2. Fast pyrolysis of black liquor

The purpose of this study was to measure the distribution and composition of the char and gases produced during fast pyrolysis in a preheated tube furnace into which black liquor was suddenly introduced.

3. Hydrogen sulphide absorption from flue gas

Flue gas from gasification of black liquor at low temperature in fluidized bed contains most of the sulphur from black liquor solids in the form of hydrogen sulphide. The solution of sodium carbonate was used for the selective absorption of H_2S from the flue gas.

4. Reduction of sodium sulphate in solid phase with gaseous hydrogen

The specific objective of this study was to determine the kinetics and mechanism of sodium sulphate reduction in kraft black liquor ash by hydrogen with or without a ferric oxide catalyst and to investigate the technical feasibility of a sodium sulphate reduction step in an alternative low temperature recovery process.

5. Verification of the fundamental results in fluidized bed pilot plant

In order to verify findings obtained from bench scale fundamental studies, the pilot scale fluidized bed was operated as a reducer, gasifier and combustor. The main objective of this research was to study the combined effect of kinetics, transport processes and mixing as a function of operating variables in an existing fluidized bed pilot plant capable of processing 1 k of black liquor solids per hour.

ACHIEVEMENTS OF THE OBJECTIVES

1. Superheated Steam Drying of Kraft Black Liquors:

A) In the first part of this study the drying characteristics of concentrated black liquor films under an array of hot air and superheated steam jets were determined using the laboratory bench equipment shown on Figure 1. The conclusions of this study are as follows:

Figure 1 - Schematic of Experimental Apparatus

a) When Al_2O_3 slurry was used for calibration of the drying instrument, the inversion temperature was determined to be 215 and 230°C at given operating conditions and flow rates of drying media at 1.4 and 0.8 k/s.m², respectively (Figure 2). Below the inversion temperature the constant drying rates of air were higher than those of superheated steam and above this temperature the order was reversed.

Figure 2 - Inversion Temperature: Steam vs. Air

b) Both steam as well as air drying did not indicate a constant drying rate period. The rate of evaporation for black liquor was less by about 50% than that expected for a constant rate drying, thus indicating that the resistance was primarily in the black liquor film.

c) Drying rate of black liquor was higher in steam than in air when the temperature was about 200°C. When compared air to superheated steam, water evaporation in air drying began as soon as the black liquor was introduced in drying chamber, after removing the surface water, a crust built up and decreased the mass transfer from the surface of the film. The film surface temperature corresponded to the wet bulb temperature as far as free moisture was available in the film. In steam drying on the contrary, the black liquor surface temperature reached the boiling point almost immediately and as a result of the relatively high boiling temperature the viscosity and surface tension of the black liquor were low, so that the solidification led to a weak crust which could be easily disrupted by the boiling phenomenon. A comparison between air and steam is shown on Figure 3. It can be seen that the falling rate period decreases more gradually in steam than in air and hence, the drying rate in steam is higher than in air at higher solids content.

Figure 3 - Drying Rate: Air vs. Steam

B) Simple techniques were developed to measure the viscosity and thermal conductivity of black liquor at high solids levels. A modified Brookfield method was developed to measure viscosity by applying a thin film silicone oil on the surface of the black liquor to prevent evaporation and crust formation. The results of the modified method compared well with vibrating blade and coaxial cylinders viscometer (Figure 4). A line source method was used to measure the thermal conductivity for the first time up to 83% solids. It was found that the Harvin and Brown data reported in 1956 could be extrapolated to high solids (Figure 5).

Figure 4 - Viscosity of Black Liquor

Figure 5 - Thermal Conductivity of Black Liquor

C) A simple mathematical model for superheated steam drying of black liquor films was developed and solved numerically using the Petrov-Galerkin finite element method. The initial increase of the liquor film thickness due to steam condensation followed by its decrease due to water evaporation resulted in a moving boundary problem that was accounted for in this study. Thermodynamic equilibrium dictated that the temperature at the evaporating surface be equal to the boiling point corresponding to the surface solute concentration. Figure 6 shows a comparison of drying rates experimentally determined with those predicted by the model. The discrepancies between model predictions and measured

Figure 6 - Experimental and Numerical Drying Rates

kinetic data could be explained by the fact that the black liquor drying rate is a strong function of the water diffusivity. Since the diffusivity of water used in this analysis was only a rough estimate, it should emphasize the need for further experimental studies to determine temperature and concentration dependence of water diffusivity in black liquor for reliable prediction of drying rate in the film of black liquor by superheated steam.

In order to learn more about a boiling phenomenon during black liquor evaporation with superheated steam, a mathematical model has been developed to find the temperature profile in the drum shell and liquor film and to determine the effect of condensating steam inside the drying drum on the rates of superheated steam drying of black liquor. Figure 7 shows the diagram explaining the problem. It represents a small portion of the drum shell covered with the liquor film. If it is assumed that the surface temperature is always at the boiling point, a pure conduction in steady state will take place. Preliminary results showed that when the temperature of condensating steam inside the drum dryer was between 160 to 180°C, the liquor reached the boiling point almost instantaneously and remained in this state up to 92% solids concentration. It means that under these conditions the whole layer

Figure 7 - Control Element For Numerical Analysis

of the liquor film is in the boiling state. It can be concluded that saturated steam at the temperature between 160 and 180°C inside the drying drum will contribute considerably to the drying process.

D) Using the physical properties and drying characteristics obtained from laboratory apparatus a pilot scale superheated steam dryer was designed and built (Figure 8). The equipment consists of the following parts:

1. Steam flow in
2. Steam flow out
3. Reservoir

4. Drum
5. Film thickness controller
6. Low velocity-High temperature zone of the hood
7. High velocity-Low temperature zone of the hood
8. Slot nozzle
9. Exhaust port
10. Doctors (Scrapers)

Figure 9 - Schematic view of the apparatus

Important design considerations :

1. Reservoir :

- a. Black liquor is heated up to 110°C before feeding the dryer and the temperature of the liquor is controlled by a thermocouple.
- b. To avoid the black liquor leakage, the head of liquor is kept at a certain level by using a flowmeter coupled with motor.

c. To avoid forming a crust on liquor surface in contact with air, the main reservoir is kept closed except for a small area in feeding.

2. Drum :

- a. The drum is driven by a 1/4 HP D.C. motor whose speed is adjustable (1.0-10.0 rpm).
- b. The drum is heated from inside by an electrical heater submerged in oil.
- c. The oil temperature is controlled by computer using a thermocouple submerged in oil.
- d. A thermocouple has been attached to the drying surface and can record the surface temperature at any time.

3. Hoods :

- a. The hood has been divided into two parts.
- b. The top section of the hood is wider, in order to achieve a stagnant flow.
- c. In the first section, there are ten slot nozzles and eleven exhaust ports.
- d. In the second section, there are 15 slot nozzles and 16 exhaust ports.
- e. The nozzle walls are adjustable in order to make a uniform flow rate along all the nozzles.
- f. The flow rate in the second section of the hood is much higher than that of first one.
- g. The exhaust ports have been located at intermediate between the nozzles.
- h. There are three thermocouples at the exit of three arbitrary exhaust ports.
- i. There are four small windows in order to take black liquor samples during the process.

Table I - The main design parameters

Parameter	Range
Drum diameter	40 cm
Drum width	7 cm
Jets width	10 mm
Exhaust ports width	16 mm
Space between two jet centrelines	52 mm
Nozzle to drum separation	50 mm

Steam mass flow rate in the 1st section	0.8-1.0 k/m ² s
Steam mass flow rate in the 2nd section	1.5-3.0 k/m ² s
Film thickness	0.7-0.8-1.0 mm
Bottom temperature	160 - 180 °C
Steam temp. in the 1st section	250 - 350 °C
Steam temp. in the 2nd section	170 - 200 °C
Steam pressure in both sections	1 atm.
Black liquor initial temperature	110°C
Black liquor initial concentration	65 - 70 %

E) In the first step described earlier in this report a numerical modelling of the superheated steam drying of black liquor film on the surface of rotating drum was completed. In the second step, impingement flows were studied extensively for various geometries and configurations, but because of a complexity of the turbulent flow and its severe dependency on the geometry of the flow, it was necessary to find the proper model for our case. A $k \sim \epsilon$ models were chosen from various models of turbulence available. They are divided in two major categories:

- High-Reynolds number $k \sim \epsilon$ models
- Low-Reynolds number $k \sim \epsilon$ models

The main difference between these two groups of models is their treatment near the wall. In H-R models the governing equations are written for whole domain except for the area which is adjacent to the wall where the turbulent Reynolds number ($R_T = k^2/\nu\epsilon$) is low. At these grids, some algebraic relations, which have been obtained empirically, can be used. On the other hand, in L-R models the governing equations are written by considering the non-isotropy flow near the wall. Using L-R models, fine grids near the wall could be obtained but it would have increased the computation time considerably.

In the computations, a hybrid finite volume method was employed to solve the full Navier-Stokes equations and both H-R and L-R models were investigated. Figure 10 shows the flow pattern as predicted by a selected model.

When the experimental data from pilot-scale drying experiments are available they will be compared with the numerical results.

Figure 10 - Flow Pattern from a High-Reynolds Model (Amano - Suqiyama)

Potential Benefits:

By achieving the black liquor evaporation to a very high solids content ($< 90\%$) the energy efficiency of the existing kraft recovery process will be considerably increased. It will be an essential step in a development of an alternative black liquor recovery process based on low temperature processing in fluidized beds which will result in higher energy efficiency, improved safety operation, and reduced air pollution.

List of Publications:

1. "Concentration of black liquor to high solids", Ramamurthy, P., Mujumdar, A. S., van Heiningen, A. R. P., Kubes, G. J., Tappi Journal, 75(4), 195 (April 1992).
2. "A simple model for superheated steam drying of black liquor", Ramamurthy, P., Mujumdar, A. S., van Heiningen, A. R. P., Kubes, G. J., Proc. of 8th Intern. Drying Symp., by Elsevier, pp. 1573-1583, 1992.
3. "Viscosity and thermal conductivity of black liquor", Ramamurthy, P., van Heiningen, A. R. P., Kubes, G. J., Tappi Journal, 76(11), 175 (November 1993).

4. "Numerical study of heat transfer and fluid flow in multiple turbulent impinging jets", Shiravi, A. H., Mujumdar, A. S., Kubes, G. J., paper accepted for presentation at 9th International Drying Symposium, August 1-4, 1994, Gold Coast, Australia.

All publications were written as technical reports and they were distributed to all member pulp and paper companies of the Pulp and Paper Research Institute of Canada. The Finnish, Swedish and U.S. pulp and paper industry received them through the International Energy Agency. Both papers published in Tappi Journal were also presented at International Tappi Pulping Conferences.

2. Fast Pyrolysis of Black Liquor

In this research topic, an influence of gas atmosphere on fast pyrolysis of kraft black liquor was studied under inert atmosphere with the aim to obtain the following information:

- A total mass balance with emphasis on carbon and sulphide.
- Kinetic description of the release of CO_2 , H_2 , and CH_4 .
- Kinetic description of the release of the prominent sulphur gases.

Figure 11 shows a flowsheet of a very sophisticated set-up which allowed for the first time the continuous measurements of the composition of gases produced by fast pyrolysis of black liquor. Details and functions of the tube furnace are explained in Figures 12 and 13.

Figure 11 - Black Liquor Fast Pyrolysis Flowsheet

Figure 12 - Tube Furnace

Figure 13 - Sample Thermocouple Probe

Pyrolysis of 20 mg black liquor droplets at 70% solids concentration was performed under inert conditions with a helium carrier gas over the temperature range 500-900°C at 100°C intervals. Experiments were also performed under partial CO and CO₂ atmospheres with the balance being helium. In most cases, dry-ice and acetone were used to cool the condenser. The final five experiments were completed with ice-water cooling of the condenser to obtain gas production rate data closer to the true processes occurring in the furnace. Sulphur mass balances were computed on those experiments for which gas, tar and char analyses were performed. The sulphur balance closures were on average 70% and were reasonable considering the small sample sizes used in the experiments. Several explanations are possible for the incomplete balance including: a) compounds which were neither detected by the mass spectrometer nor trapped in the condenser as tars; b) formation of COS at low temperatures; c) elemental sulphur formation; d) adsorption of sulphur compounds on tubing; and e) analytical error.

Total char and gas yields as well as the yields of sulphur compounds in gas and char were presented. The decrease in char yield (Fig. 14) is expected with increasing temperature, since the volatiles are more rapidly produced and transported out of the pyrolysing material, thus reducing the condensation reactions which lead to the formation of char. In addition, thermodynamics predict low char yields at higher temperatures due to greater gasification of carbon. Total gas yield gradually rises with temperature up to 800°C, but increases sharply at 900°C as depicted in Figure 15.

Figure 14 - Char Yield
(experiments done with 20 mg droplets of 70% black liquor solids)

Figure 15 - Total gas yield

The yield of sulphur in char (Figure 16) increases with temperature as can be expected from thermodynamic considerations, and conversely the yield of sulphur in gas decreases (Figure 17) as predicted with increasing temperature.

Figure 16 - Yield of Sulphur in Char

Figure 17 - Yield of Sulphur in Gases

A rather important observation suggests that at 500°C the H_2S production is high, since the reaction of CO_2 and water vapour with Na_2S present in kraft black liquor is thermodynamically favoured throughout the experiment. Additional H_2S is produced from organically bound sulphur and possibly thiosulphate decomposition. As shown on Figure 18, by 600°C thermodynamics favour the retention of sulphur in the char as Na_2S , and the substantial drop in H_2S supports this prediction. The yield of methyl mercaptan in Figure 19 decreases linearly from about 9% of the sulphur in the black liquor solids at 500°C to less than 1% at 900°C.

Figure 18 - Yield of Hydrogen Sulphide

Figure 19 - Yield of Methyl Mercaptan

The following can be concluded for fast pyrolysis of kraft black liquor droplets, based on the results obtained in this study:

- a) A mass spectrometer coupled to a tube furnace can be successfully used to collect data from the pyrolysis of single droplets of kraft black liquor and provides a powerful tool for kinetic analysis when rate data are corrected using Fast Fourier Transform deconvolution methods.
- b) The sulphur yield of kraft black liquor char increases as expected thermodynamically with increasing pyrolysis temperature, but gas sulphur yield appears to be more influenced by kinetic and transport phenomena.
- c) The yield of sulphurous gases during pyrolysis of black liquor is not significantly affected by the presence of CO at 800°C and of CO₂ at 900°C.
- d) Carbon disulphide is formed in appreciable quantities during droplet pyrolysis at 800°C and 900°C and its source appears to be reaction of H₂S with CH₄. The presence of CO and CO₂ greatly reduces the amount of CS₂ formed at 800 and 900°C.
- e) At 800 and 900°C the rate of the endothermic reduction of sulphate by carbon is very rapid and causes droplet temperatures to decrease. This effect is even greater under CO and CO₂ atmospheres.
- f) Three phases of devolatilization are present during black liquor droplet pyrolysis: an initial devolatilization phase, the main devolatilization, and finally CO production through sulphate reduction by carbon.

Potential Benefits:

Results obtained from this study are essential contribution to the knowledge of pyrolysis and gasification of black liquor solids in the conventional recovery furnace operation and it can be even more useful to the understanding of the fundamental processes taking place in the fluidized bed technology.

List of Publications:

1. "New insights into TRS gas formation during pyrolysis of black liquor", Gairns, S.A., Kubes, G.J., van Heiningen, A.R.P., prepared for presentation at the Spring 1994 AIChE Conference.

3. Hydrogen Sulphide Absorption from the Flue Gas

The effect of operating parameters such as temperature, concentration of sodium carbonate in liquid phase, concentration of hydrogen sulphide and carbon dioxide in the gas stream at the inlet of the column as well as the gas and liquid flow rates on the absorption of H_2S and CO_2 were studied. The removal efficiencies of both gases and their overall mass transfer coefficients as well as the selectivity of the process for hydrogen sulphide were determined. The experiments were carried out on a pilot scale using a packed column operated counter-currently. The experimental set up is shown on Figure 20, and it was described in great detail in the previous technical report.

Figure 20 - Schematic Diagram of the Absorption Apparatus

The experimental work in this research topic was carried out in two main parts. The preliminary experimental part, where the repeatability of experiments, interactions between parameters, the material balance and the effect of the bed height on the absorption of both gases have been studied. In the final experimental part, the influence of the

operating parameters on the removal efficiencies and the overall mass transfer coefficients of H_2S and CO_2 and on the selectivity of the process have been investigated.

In order to minimize the total number of experiments, the interactions between parameters were studied on the set of 16 experiments, they are summarized in Table II. The values 1 and 2 corresponds to the lowest and highest level of each parameter as shown on Table III. Both gas and liquid flow rate were combined in a single parameter by calculating their ratio, G/L . The value 1 of G/L corresponds to the lowest level of G divided by the highest level of L while the value 2 is the highest level of G divided by the lowest level of L . In this experimental design, each parameter was repeated at the same level eight times, and any level combination for any two parameters appeared only four times in the whole set of experiments.

Table II - Preliminary Experimental Design

Run No.	T	$[CO_3^{=}]$	$y_o(H_2S)$	$y_o(CO_2)$	G/L	$\eta(H_2S),\%$	$\eta(CO_2),\%$
A-1	1	1	1	1	1	74.50	10.01
A-2	1	1	1	2	2	78.90	9.50
A-3	1	1	2	1	2	86.13	7.25
A-4	1	1	2	2	1	80.23	11.13
A-5	1	2	1	1	2	86.80	5.10
A-6	1	2	1	2	1	81.09	9.30
A-7	1	2	2	1	1	88.10	7.17
A-8	1	2	2	2	2	90.91	6.29
A-9	2	1	1	1	2	77.13	12.36
A-10	2	1	1	2	1	72.20	16.81
A-11	2	1	2	1	1	78.41	14.50
A-12	2	1	2	2	2	81.90	13.34
A-13	2	2	1	1	1	79.29	12.45
A-14	2	2	1	2	2	82.80	11.39
A-15	2	2	2	1	2	89.88	9.39
A-16	2	2	2	2	1	83.86	13.27

Table III - Operating Conditions

Operating Parameter	Minimum	Maximum
Temperature ($^{\circ}\text{C}$)	25.0	60.0
Carbonate concentration (<i>mole/l</i>)	0.5	5.0
Hydrogen sulfide concentration (<i>mole %</i>)	0.1	1.0
Carbon dioxide concentration (<i>mole %</i>)	1.0	10.0
Gas flow rate (<i>l/min.</i>)	20.0	50.0
Liquid flow rate (<i>l/min.</i>)	0.5	1.5

From the preliminary experiments, the concentration of hydrogen sulphide and carbon dioxide in the outlet gas stream was determined analytically. Then the removal efficiencies (E_i) for both gases were calculated. They are defined as the amount of gas (i) being absorbed by the carbonate solution divided by the total amount of that gas entering the column. By evaluating data from preliminary experiments, it was found that repeatability of experiments was very good and interactions between parameters were negligible. Figure 21 shows the removal efficiencies of H_2S and CO_2 with respect to operating parameters. It is apparent from the graph that the carbonate concentration has major relative effect on H_2S removal and that the operating temperature has the major relative effect on that of CO_2 . However, it was found that the concentration of H_2S did not affect the absorption of CO_2 and the same can be said about the absorption of H_2S being very little affected by the concentration of CO_2 gas. The repeatability of experiments was investigated by repeating some of the experiments twice under the same operating conditions. Results showed that the deviation between the first experiments and the repeated ones was less than 5%. For all sixteen experiments, the concentrations of ionic species (HS^- , HCO_3^- , CO_3^{2-}) in the outlet liquid stream were determined analytically and compared with those calculated from the total and component material balances based on the composition and flow rates of the gas streams at the inlet and the outlet. The deviation in all cases was found to be within the acceptable range (less than 5%).

a) H_2S absorption

b) CO_2 absorption

Figure 21 - Relative Effect of Parameters on the Removal Efficiency of H_2S and CO_2

Furthermore, the effect of the bed height on the absorption of both gases has been investigated by analysing gas samples across the height of the column. Results of this investigation are summarized in Figure 22 and Figure 23. It is apparent that hydrogen sulphide in the gas phase is not in equilibrium with that in the liquid phase as the curve appears to be linear. On the other hand, carbon dioxide absorption goes towards equilibrium conditions, which means that if the column height is increased, for example by 50 cm, the absorption of hydrogen sulphide will be improved, while the absorption of carbon dioxide will not be affected significantly.

Figure 22 - Effect of Bed Height on the Absorption of H_2S

Figure 23 - Effect of Bed Height on the Absorption of CO_2

The final experimental design consisted of sixteen experiments with main parameters tested at four levels equally spaced. The liquid flow rates were tested separately with the other parameters at their medium level. The final results were evaluated in terms of the effect of parameters on the removal efficiencies of H_2S and CO_2 , overall mass transfer coefficients and the selectivity factor. Figure 24 shows that the increasing temperature reduces the absorption of hydrogen sulphide and increases that of carbon dioxide. While, as shown on Figure 25, the removal efficiency of H_2S increases appreciably with increasing concentration of carbonate in the liquid phase. The H_2S absorption also increases considerably with increasing concentration of H_2S at the inlet (Figure 26).

Figure 24 - Effect of Temperature on the Removal Efficiency of H_2S and CO_2

Figure 25 - Effect of Carbonate Concentration on the Removal Efficiency of H_2S and CO_2

Figure 26 - Effect of H_2S Concentration on the Removal Efficiency of H_2S and CO_2

From Figure 27, the removal efficiency of H_2S is considerably increased if the gas flow rate is increased, while the removal efficiency of CO_2 is not affected significantly. Opposite results were obtained for the liquid flow rate (Figure 28). This is because H_2S absorption is controlled by the gas side mass transfer resistance while CO_2 is controlled by the liquid side resistance.

Figure 27 - Effect of Gas Superficial Velocity on the Removal Efficiency of H_2S and CO_2

Figure 28 - Effect of Liquid Superficial Velocity on the Removal Efficiency of H_2S and CO_2

The selectivity of the process for H_2S is defined as the tendency of the ratio of $\text{H}_2\text{S}/\text{CO}_2$ content in the liquid phase to be larger than it is in the gas phase. As a measure of the process selectivity, the selectivity factor, S , was introduced, and it is given as the ratio of the overall mass transfer coefficients ($S = K_G\text{-H}_2\text{S}/K_G\text{-CO}_2$). Thus, with increasing selectivity factor the absorption process becomes more efficient. Figures 29 through 33 show the effect of temperature, carbonate concentration, concentration of H_2S in the inlet gas, and gas and liquid flow rates on the selectivity factor.

Figure 29 - Effect of Temperature on the Selectivity Factor

Figure 30 - Effect of Carbonate Concentration on the Selectivity Factor

Figure 31 - Effect of H_2S Concentration on the Selectivity Factor

Figure 32 - Effect of Gas Superficial Velocity on the Selectivity Factor

Figure 33 - Effect of Liquid Superficial Velocity on the Selectivity Factor

In conclusion, the maximum removal of hydrogen sulphide accompanied with the minimum removal of carbon dioxide can be achieved by the method of absorption into aqueous sodium carbonate solutions in a packed column counter-currently operated under the following conditions:

- a) Low operating temperature - it minimizes absorption of carbon dioxide by reducing its reaction rate;
- b) High concentration of sodium carbonate in liquid stream - it increases the driving force which results in increasing the absorption rate of hydrogen sulphide;
- c) High total pressure - it increases H_2S partial pressure, thus, higher driving force is generated between the liquid phase and the gas phase;
- d) High gas flow rate and low liquid rate - the absorption of H_2S is gas side controlled while that of CO_2 is liquid controlled.

Potential Benefits:

The results of this work suggest very strongly that green liquor can be produced by this process and it is a very important contribution to the development of an alternative black liquor recovery process based on low temperature processing in fluidized beds.

Experimental work on this research topic was completed and data evaluated. M. Eng. thesis has been submitted and a complete technical report is being prepared. Draft of a report is attached.

4. Reduction of Sodium Sulphate in Solid Phase with Gaseous Hydrogen:

The objective of this research topic was to study kinetics and mechanism of solid state reduction of sodium sulphate in kraft liquor ash by hydrogen with addition of iron oxide as catalyst. A thermogravimetric analysis set-up, shown on Figure 34, equipped with CO and CO₂ analyzer was used to carry out the reduction experiments.

The research work was divided into three parts:

- Reduction of pure sodium sulphate by hydrogen with addition of iron oxide;
- Reduction of a model mixture of sodium carbonate, sodium sulphate and iron oxide;
- Reduction of kraft black liquor ash mixed with ferric oxide.

Figure 34 - Thermogravimetric Analysis (TGA) System

a) Reduction of pure sodium sulphate by hydrogen:

This part of the research topic was described thoroughly in the previous technical report. To summarize briefly here, it was concluded that an addition of 1% by weight of ferric oxide is essential for the reduction process, and that the reaction rate increases with increased concentration of hydrogen in the gas phase and also with increased reaction temperature. Kinetics of sodium sulphate reduction by hydrogen was also investigated and it was found that the initial stage of reduction up to 90% conversion could be well described by nucleation and growth model. The value of the Arrhenius activation energy for nucleation and growth period was calculated ($E_a = 265$ kJ/mole).

b) Reduction of sodium sulphate by the gas containing H_2 and CO in Na_2SO_4 - Na_2CO_3 model salt mixed with Fe_2O_3 catalyst:

The reduction kinetics of Na_2SO_4 by H_2 - CO reducing gas mixture in a model salt mixture representing kraft black liquor ash and mixed with 1 wt. % Fe_2O_3 catalyst was studied in a thermogravimetric system. It was found that at least 10% CO had to be added in the feed gas to suppress the decomposition of sodium carbonate by hydrogen according to the following reaction:

As shown on Figure 35, it was also found that the conversion-time curves of the Na_2SO_4 reduction are sigmoidal in shape and could be well described by third order nucleation and growth model over a wide range of conversions. The complete reduction of Na_2SO_4 was achieved in spite of the fact that the model mixture after reduction appeared to be locally sintered. The reduction of Na_2SO_4 is well described, as seen on Figure 36, by third order nucleation and growth model over a wide range of conversions according to the following equation: $[-\ln (1-X)]^{1/3} = kt$.

Figure 35 - Typical Reduction Data

Figure 36 - Fitting the Data to the Third Order Nucleation and Growth Model

An activation energy of 336 kJ/mole was obtained for the nucleation and growth period and the nucleation and growth rate constant was found to be proportional to $[H_2]^{0.69}$. Last portion of the conversion-time plots fitted well a shrinking-core model as shown on Figure 37. The rate constant of this product layer diffusion controlled period is proportional to H_2 concentration. The Figure 38 shows the comparison of both models with the experimental data. The possible reduction and catalytic mechanism was proposed suggesting that, at first, Na_2SO_4 reduction was autocatalyzed by Na_2S , then the reduction of sodium sulphate follows the pass where it is firstly reduced to sodium sulphite, in a slow reaction, and then very fast to sodium sulphide. The small amount of Na_2S formed on the external of the particles reacts to form an intermediate, which is subsequently reduced by the reducing gas to Na_2S in a fast reaction.

Figure 37 - Fitting of the Data to the Selected Shrinking-Core Model

Figure 38 - Comparison of Models Predictions with Experimental Data

c) Reduction of sodium sulphate by H_2 -CO gaseous mixture in the kraft black liquor ash mixed with Fe_2O_3 :

The reduction kinetics of Na_2SO_4 in the kraft black liquor ash, mixed with 1 wt. % Fe_2O_3 catalyst, by H_2 -10% CO reducing mixture was also studied in a thermogravimetric system described earlier (Figure 34). Very similar results to those obtained for a model salt mixture were found in this part of the study. An activation energy of 222 kJ/mole was obtained for the nucleation and growth period and the nucleation and growth rate constant was found to be proportional to $[H_2]^{0.48}$. Contrary to the model salt kinetics, the long induction period was observed at temperatures between 680 and 700°C (Figure 39). In conclusion, the reduction of Na_2SO_4 in kraft black liquor ash is also well described by third order nucleation and growth model over a wide range of conversion ($0.2 < X < 0.95$). 10% CO must be added to the reducing feed gas to suppress decomposition of Na_2CO_3 by hydrogen. Although kraft black liquor ash after reduction is sintered/fused locally, the complete reduction can be achieved. As shown also on Figure 40, the reduction of sodium sulphate in the kraft black liquor ash is faster than that of the ash model mixture.

Figure 39- Typical Curves Showing a Long Induction Time at Low Temperatures

Figure 40 - Arrhenius Plot of Rate Constants for Kraft Black Liquor Ash and Model Mixture

Potential Benefits:

This research study brought enough scientific evidence which suggests that it is possible to consider a flowsheet of low temperature fluidized bed technology in which the pyrolysis and gasification would result in production of sodium sulphate in char which then would be reduced to sodium sulphide with the mixture of hydrogen and carbon monoxide in the presence of Fe_2O_3 catalyst

The experimental work on this research topic was completed and a PH. D. thesis has been defended. Three technical papers are in preparation.

List of Publications:

1. "Kinetic study of the reduction of sodium sulphate by $\text{H}_2\text{-CO}$ in a model mixture of kraft black liquor ash mixed with Fe_2O_3 ", Tiwari, A.K., Kubes, G.J., van Heiningen, A.R.P., presented at the 1993 Annual Meeting of AIChE, November 7-12, 1993, St. Louis, Missouri; accepted for publication in 1993 AIChE Forest Products Symposium Series.

5. Verification of the Fundamental Results in Fluidized Bed Pilot Plant:

Pyrolysis and steam gasification of dry kraft black liquor solids were investigated in fluidized bed pilot plant (Figures 41 and 42) between 500°C and 700°C. Total mass balances were obtained for carbon, sodium, and sulphur in the solid char and gaseous products. Above 600°C, the addition of steam resulted in significant increases in CO₂ and H₂, and a decrease in CO; however, the production of CH₄ was unaffected. The overall gasification rate of carbon increased fourfold from 0.003 min⁻¹ at 600°C to 0.013 min⁻¹ at 650°C. It was proposed that the carbon gasification rate for black liquor char is controlled by the kinetics of the C-H₂O reaction. Catastrophic defluidization was observed at 700°C for steam gasification but not for pyrolysis. SEM micrographs of the char particles revealed that surface melting had occurred. Low-melting-point eutectic mixtures containing chloride and potassium were suggested as the primary cause. It was proposed that the stickiness of the char surface is controlled by the quantity of amorphous carbon under these conditions.

For pyrolysis in N₂, a total mass balance over the temperature range 500-700°C showed that the reaction of sulphur in the solid char product increased from 60 ± 11 wt% to 91 ± 8 wt%. Between 500-550°C, the major sulphur compounds in the char were Na₂SO₄, Na₂SO₃, and Na₂S in decreasing order. The production of Na₂SO₃ was attributed to the decomposition of sodium thiosulphate, which was present in the kraft black liquor solids. Between 600 and 700°C, the reduction of Na₂SO₄ and Na₂SO₃ by carbon and CO/H₂ led to an increase in the production of sodium sulphide. The reduction of steam led to a decrease in the concentration of solid Na₂S in the kraft black liquor char throughout the temperature range studied. Between 650-700°C, the emission of H₂S in the particulate phase of the fluidized bed was in equilibrium with the gasification product gases.

The yield of organic carbon in the fluidized bed char during pyrolysis and steam gasification is shown on Figures 43 and 44, respectively, and the distribution of sulphur compounds between solid phase and gas phase is exhibited on Figures 45, 46, and 47.

Potential Benefits:

This study was done in parallel with other topics of this program. It has proved, for the first time, that a fluidized bed can be operated at low temperature in reducing mode and it can process kraft black liquor by following the flowsheet of alternative recovery process where hydrogen sulphide is produced rather than Na₂S. H₂S can then be converted to Na₂S in subsequent step.

List of Publications:

1. "A novel method of recovering chemicals and energy from kraft liquor in a fluidized bed: A review", Fallavollita, J.A., Avedesian, M.M., Mujumdar, A.S., Can. Journal Chem. Eng., 65(10), 812-817,(1987).
2. "Operating characteristics of a fluidized bed for the treatment of black liquor powder", Fallavollita, J.A., Avedesian, M.M., Mujumdar, A.S., Peirce, D., van Heiningen, A.R.P., Proc. 37th Can. Chem. Eng. Conf., Montreal, 137-9, (1987).

Figure 41 - Schematic Diagram of Fluidized Bed Pilot Plan

Legend: 1) Fluidizing gas inlet; 2) Multi-orifice plate; 3) Steel enclosure; 4) Resistance heater; 5) Insulation; 6) Reactor shell; 7) Reactor flange gasket; 8) Off-gas to cyclones; 9) Solids injector lance; 10) Fluid bed; 11) Bed sampling line; 12) N₂ purge; 13) Vacuum line; 14) Quench vessel; 15) Liquid N₂; 16) Holding vessel; 17) Insulation; 18) Wire-mesh screen; 19) Distributor plate gasket.

Figure 42 - Fluidized Bed Reactor

Fig. 1 : Schematic of drum dryer

Concentration Profiles — C
 Temperature Profiles T

Fig.3: Schematic temperature and concentration profiles during condensation and evaporation.

Fig.2: Schematic of heat and mass balance for liquor film.

Fig.4: Comparison of moisture content vs time curves.

Fig.5: Comparison of drying rates vs moisture content.

Fig. 6a: Moisture profiles in liquor film

Fig. 6b: Temperature profiles in liquor film

Fig. 7: Influence of film thickness

Fig. 8: Influence of initial moisture

Fig. 9a: Moisture profiles at 0.36 kg water/kg BLS from Fig. 8

Fig. 9b: Moisture profiles at 0.3 kg water/kg BLS from Fig. 8.

Fig. 10: Effect of diffusivity

Fig.11: Effect of inlet steam temperature

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