

Chemical Recovery Conference emphasizes high solids firing and mill system closure

ADRIAAN R. P. VAN HEININGEN

Repap-NSERC Professor, Department of Chemical Engineering, University of New Brunswick

BRIAN BLACKWELL

Senior Process and Energy Specialist, Sandwell Inc., Engineering and Construction Services Group

Many excellent, practical, and fundamental papers, especially in fume formation and gaseous emissions from recovery boilers, were presented at the 1995 International Chemical Recovery Conference held on April 24–27 in Toronto, Canada. Program chairman Honghi Tran and his Technical Program Committee put together a very interesting and well balanced program of 76 papers grouped in 14 sessions.

Prediction of the future

The conference started with a keynote address by Gullichsen of Helsinki University of Technology. In his talk on the impact of new pulping and bleaching technologies on chemical recovery, he questioned the wisdom to go to totally chlorine-free (TCF) bleaching and of a totally effluent-free (TEF) mill. His main concerns were that, with present day technologies, the TCF and TEF options are costly, lead to complications in the chemical recovery, and, most importantly, consume more wood. He predicted that ClO_2 bleaching will remain a part of the industry until well into the future and that the evolution toward a minimum impact mill will likely be slow.

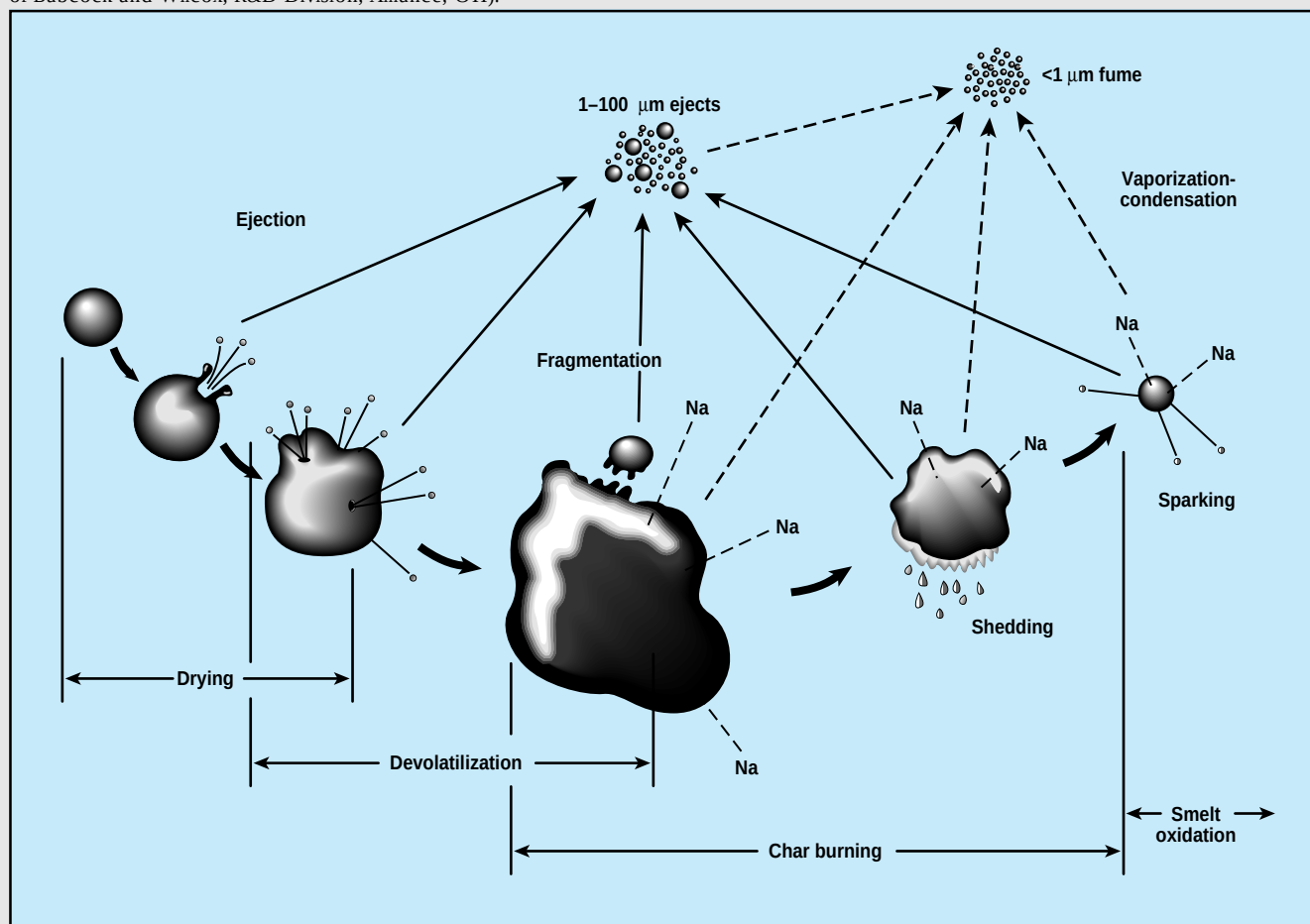
Mill closure

Terry Adams of the Institute of Paper Science and Technology (IPST), Atlanta, GA, modeled the effect of oxygen delignification, anthraquinone pulping, and bleach plant filtrate recycle on the recovery department. His conclusion was that the impact of any single change on black liquor solids and heating value is less than 5%. However, bleach plant filtrate recycle will lead to a large increase of the chloride input to recovery. Heiki Mannisto of Ekono Inc. evaluated the impact on recovery of five different mill concepts. He concluded that only mills that have no effluent discharges would be able to meet all the limits of the U.S. Environmental Protection Agency's (EPA) Cluster Rule. He also considered it unlikely that a retrofit of a mill from the 1960s to low-effluent concepts could be economically justified. The increases in recovery area loadings as well as the costs when a modern mill is converted to

a TCF mill with combined bleach plant effluent and black liquor recovery were estimated. In spite of the high cost, Mannisto expected that the trend toward TEF processes will continue, driven by the proposed effluent limits. The session was concluded by presentations of B. M. Richardson of PAPRICAN and Brian Blackwell of Sandwell on the effects of bleach plant effluent recycle in kraft mill green liquors and process design options for concentrating kraft bleach plant effluent, respectively. Based on the keynote address and this session, it became clear that improvements in the following three areas are needed for system closure: (a) increased pulp yield for extended pulping and TCF bleaching, (b) decreased bleach plant water use, and (c) novel recovery approaches.

Nonprocess elements

An excellent study on the buildup of phosphorus in a kraft mill was presented by Per Ulmgren of STFI, Stockholm. The accumulation of phosphate occurs in the lime cycle due to a higher solubility of calcium phosphate in green than in white liquor. Since a concentration of 1% P by weight in the lime leads to a decrease in the available CaO by about 5%, a purge of about 5% of the lime mud must be considered for a closed cycle mill. Hans Lindberg of Ahlstrom discussed metal management strategies for bleach plant closure by removal of alkali insoluble metals in the recausticizing department with the dregs and lime mud purge. Reyhaneh Shenassa of the University of Toronto measured the flowrates of chloride and potassium around the electrostatic precipitator mixing tank in two mill studies. She also evaluated the removal of chloride and potassium from precipitator dust in the Bleach Filtrate Recycle (BFR) process of Champion International. W.B.A. Sharp of Westvaco reviewed the literature to identify corrosion problems in chemical recovery equipment which might be anticipated as a result of system closure. Björn Warnqvist of ÅF-IPK came to similar conclusions on the impact of extended delignification and effluent recycle on kraft recovery as presented earlier on this topic.



High-solids firing

Spread among various sessions were four papers on good mill results with high-solids firing in recovery boilers: Canadian Forest Products Ltd. in Prince George; Pope and Talbot in Halsey, OR; Willamette Industries/Pennotech; and Metsa-Botnia in Kemi. The paper about the Kemi mill contained other interesting innovation measures. Bio-sludge is mixed with weak black liquor and thus burned in the recovery boiler. Also, there is a special system for burning concentrated noncondensable gases (NCG) and stripper off-gas in a dedicated nozzle at the secondary air level. Furthermore, high-volume low-concentration NCGs are fired through a separate nozzle at the tertiary air level in the recovery boiler. These are all smart process measures, even though burning NCGs in a recovery boiler goes against historical safety concerns.

Pressurized storage of heavy black liquor between the concentrator and the recovery boiler is becoming standard. The liquor experiences some viscosity drop and liquor heating at the boiler is avoided.

Black liquor evaporation

Besides the discussion of the concentrators in the four papers on high-solids firing, there were five other papers concerning black liquor evaporation. The topics included sulfur removal from strong black liquor during pressurized concentration, the effect of mill effluent closure on the corrosion of evaporators, and the use of liquor chemistry studies in concentrator design. Kvaerner described the use of vapor recycling to significantly increase the heat transfer coefficient in concentrators. Hyer of Goslin-Birmingham described how blow heat from batch digesters can be used as an energy source for foul condensate stripping and pre-evaporation of weak black liquor. This technique can be used to improve mill energy efficiency and to add black liquor evaporation capacity.

Recovery boiler operation and control

Verloop of Jansen discussed the challenges of operation at low load. Wag of Oregon State University discussed the use of a mathematical model of char burning, developed from experimental studies of black liquor burning, to gain insight into reduction and sulfide reoxidation. The model results indicate that reduction efficiency is increased by higher temperatures

Conference Report

and the use of larger liquor spray droplets. Reoxidation is minimized by burning the char on the bed, as much as possible. There were two papers on control strategies for recovery boilers, one of which involved fuzzy logic.

Recovery boiler design, construction, upgrade

Herczeg of ABB described innovative construction techniques to cut costs and achieve short shutdown schedules. Paldy of Simons proposed the use of shop fabricated equipment to reduce the cost of small pulp mills. Toews of ABB described precipitator improvements, including controls and new internals that cut particulate emissions in half at Fletcher challenge, MacKenzie. Rounsley of Mead outlined the mathematical modeling of a fluidized bed in a neutral sulfite semichemical (NSSC) mill.

Recovery boiler safety

A session on recovery boiler safety included smelt water explosion experience, a laboratory investigation of the critical heat flux on boiler floor tubes, field testing of air-cooled smelt spouts and a process simulator for recovery boilers. Also, laboratory and field results were presented for methanol emissions from direct contact evaporators.

Recovery boiler fireside deposits

The session on recovery boiler fireside deposits had three papers that provide more information on the influence of potassium and chlorides on deposit formation. Travares of the University of Toronto kicked off the great fume debate by describing the results of fume sampling in the E. B. Eddy boiler. Hiner of Babcock and Wilcox presented some operational results on liquor spraying, using "perimeter firing." Wedges were added to splash plate nozzles to direct the spray toward regions in front of the primary air ports, and less in the center of the furnace. Uloth of PAPRICAN described the use of on-line temperature sensors to examine the dynamics and effectiveness of soot blowing. The information should encourage mill operators to modify soot-blowing strategy to reduce steam use.

Fume formation

This session showed dramatic progress in the understanding of the mechanisms underlying fume formation. The enrichment of potassium and chloride during black liquor combustion in a laminar entrained flow reactor and in mill furnaces were described by E. K. Vakkilainen of Ahlstrom in a joint paper with Oregon State University. Explanations were given for the potassium enrichment in electrostatic precipitator (ESP) dust and why boilers operating at high SO_2 concentrations and high temperatures tend to have lower chloride enrichment factors for ESP dust. Jorma Jokiniemi of VTT, Aerosol Technology Group (Espoo, Finland), described the most sophisticated model to date to predict fume formation, fume particle growth, and deposition throughout the whole recovery boiler. It is based on fundamentals of gas phase equilibrium, homoge-

neous and heterogenous condensation, and particle agglomeration and deposition. This paper was perhaps the best theoretical contribution at the conference. Chris Verrill of Babcock and Wilcox presented data and modeling results of sodium loss during black liquor drying and devolatilization. A detailed conceptual picture (see figure) of the inorganic aerosol formation was described, which included small particles ejection during initial pyrolysis, and sodium vaporization at high-temperature combustion. An advanced engineering model of black liquor droplet combustion developed by coauthor Richard Wessel was also outlined. Based on the results obtained with three different laboratory setups by E. J. Kauppinen of VTT Aerosol Technology Group, it was concluded that the evaporation of sodium during in-flight pyrolysis of the droplets in the recovery furnace does not significantly contribute to the sodium fume observed downstream in the boiler. A new finding presented by Gairns *et al.* was the suppression of sodium release during kraft black liquor pyrolysis in an environment containing 15% CO_2 . The presence of elemental sodium in the char was demonstrated. It was also proposed that reduced sodium could form an explosive gas mixture when water accidentally contacts the char bed, thus creating a possible trigger for a smelt-water explosion.

Recovery boiler emissions

This session dealt almost solely with the release of nitrogen as NO or NH_3 . Honghi Tran studied the NH_3 emission from the vent stack of the smelt dissolving tank at Peace River Pulp. In a later paper by Mikko Hupa on nitrogen oxide release during black liquor char combustion and gasification, the source of NH_3 formation in the dissolving tank was identified as a nitrogen containing inorganic salt. Responding to a question from the audience, Hupa considered that the salt could be NaCN, since many nitrogen containing salts decompose under release of NH_3 in alkaline aqueous solutions. Hupa also presented a modified scheme of the major NO formation pathways in the recovery furnace. This scheme was confirmed by mill measurements of L. M. Thompson in a joint study of IPST and Georgia-Pacific. Kristiina Iisa of Oregon State University provided interesting experimental data on the kinetics of formation and destruction of NO during black liquor pyrolysis. It was found that black liquor char is very effective in reducing NO to N_2 . Iisa suggested that it may be possible to abate NO emissions during black liquor combustion by improving the contact between black liquor char and NO. Kauko Janka of Tampella Power showed experimental and modeling results for sulfate reduction during pyrolysis and gasification of black liquor solid particles in the laminar entrained-flow reactor at Oregon State University.

Fundamentals

New laboratory data was presented with relevance to high-solids combustion as well as black liquor gasification. A common theme in audience questioning was how the experimental results could be applied to actual boiler or gasifier operation.

Raimo Alén of the University of Jyväskylä, Finland, presented data, which indicated that the gas chromatographic analysis of primary combustion products of kraft black liquor might possibly be used for characterization of liquor combustion properties. Jim Frederick (OSU), the conference chairman, presented new results of black liquor pyrolysis that suggest that tar formation may be a problem for low-temperature gasification. He also described the complex process of sulfate reduction. Pat McKeough of VTT Energy described pressurized grid heater experiments, which allow investigation of both the primary and secondary phases of pyrolysis. From these results, a system of 12 pyrolysis reactions was proposed to describe sodium and sulfur chemistry. This mechanism appears to fit observed industrial trends in fume formation and sulfur emissions when black liquor dry solids content is increased. Kari Saviharju also of VTT presented new data on pressurized gasification of kraft black liquor, which suggested that the reduction in the gasification rate with increasing pressure is not as large in practice as previous laboratory data indicated.

Recovery boiler modeling

Recovery boiler modeling continues to become more important as a design tool and as a means to evaluate the impact of process changes on boiler operation. Babcock and Wilcox proposed an 11 metric tons/day facility for testing and validation of numerical modelling of kraft black liquor recovery boilers. Andy Jones of ABB illustrated how computational fluid dynamics (CFD) modeling can be used to supplement the existing engineering tools for evaluation of recovery boilers. He also reported that boiler capacity appears to be limited at a furnace hearth heat release of 1.15×10^6 Btu/h ft² for the air system examined thus far. Predictions of gas velocities, carryover, and temperatures in a recovery boiler were presented in the next two papers given by university-based groups, IPST (Atlanta) and UBC (Vancouver), respectively. Finally, Erik Uppstu of Oy Polyrec Ab proposed a new vertical air distribution system for increasing the firing load of recovery boilers.

Recausticizing

The recausticizing session had papers on mixing in the smelt dissolving tank, computer simulation of the recausticizing system and a control system for lime addition to the slaker, based on temperature and conductivity in the slaker. There was a focus on green liquor dregs. Liden of MoDo discussed the origin of dregs and their impact on the various recaust operations. Some rare data was given on the concentration of hydrogen in the smelt dissolving tank vent gases. The most intense rumblings in the dissolving tank correlated with high hydrogen concentrations. Interest in possible recycle of bleach plant effluents to the liquor cycle gives some credibility to the application of green liquor filters. There were two papers on new cassette-type green liquor pressure filters that are working well. Winby of Kvaerner described the unit at Stora Billerud and Skrifvars of Åbo Akademi presented results at Wisafors in Finland.

Lime kilns

There were five papers on lime kilns. Lewko of Weyerhaeuser Canada described a kiln upgrade involving the addition of a product cooler and the installation of a large lime mud precoat filter. Strand of Pacific Simulation found that mill results for kiln stack particulates correlated well with kiln stack flow rate. Watkinson of UBC described successful results from burning lignin in a pilot-scale kiln. Most of the fossil fuel used in the kiln could be replaced without derating kiln capacity. The lignin would be obtained via precipitation from weak black liquor, thereby off-loading the recovery boiler. Other papers included the sintering of lime by carbon dioxide and operational experience with a lime mud dryer kiln.

New recovery technologies

The conference was concluded with a joint session on new recovery technologies. The first paper by Robert Scott-Young of Australian Paper described the world's only commercially sized Direct Alkali Recovery System (DARS). After an extended startup and redesign period, the DARS plant at the soda-AQ Burnie pulp mill in Tasmania is considered to be a successful prototype for commercialization. Four different black liquor gasification technologies, which are presently under development by Chemrec, MTCI, ABB, and Tampella, were compared by Thomas Grace. He concluded that the atmospheric Chemrec process is now commercially proven for incremental recovery capacity and that the ABB process has the highest conversion efficiency of black liquor to net product gas. Lars Stigsson of Kvaerner Pulping described the operating experience with a 1.5–2-MPa, 250-kg dry black liquor solids/h pressurized Chemrec gasifier. Carbon conversions of typically 99.5% (at 970°C) and sulfur reduction efficiencies over 98% were reported. Alkali contents down to 0.01 ppm Na + K, and more than 99% H₂S removal were obtained for the treated gasification gas. The next step is now a pressurized gasification demonstration plant. The next paper gave a status report of the 2 metric tons/h MTCI pilot black liquor gasifier at the Weyerhaeuser, New Bern, NC, mill. Carbon conversion of 92% and sulfur reduction efficiencies of 80% were reported. After correction of a number of technical problems, further trials will be done later in 1995 in cooperation with the engineering firm Stone and Webster. Pat McKeough of VTT Energy presented experimental data on the recovery of H₂S from a CO₂ containing high pressure gas by co-current absorption into a spray of green liquor droplets. The experiments indicated that the increase in causticizing requirement due to co-absorption of CO₂ from a kraft black liquor gasification gas could be kept below 10%. He also presented performance and cost studies of the overall black liquor integrated-gasification-combined-cycle (IGCC) process. The last paper of the conference by Niklas Berglin of Chalmers University of Technology, Göteborg, Sweden, investigated energy options with IGCC for two black liquor gasification processes under development by Kvaerner (Chemrec) and ABB, respectively. 