

Modern Trends in the Field of Black Liquor Regeneration.

(A Review)

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The black liquor (b.l.) regeneration is an integral Part of Kraft Pulping Process, the most common and widely used method, for the manufacture of pulp and paper. Economics of the alkaline pulping process is very much tied up with the regeneration of cooking liquor from the black liquor. The first commercial and recovery process was evolved and developed by Dahl in Danzing in the 1880's almost simultaneously with the introduction of the alkaline pulping process.

During the period 1890-1920, attempts were made to improve the heat economy of the recovery furnace. The recovery process included all operations in the closed cycle from digester through washing, evaporation, incineration, lixiviation, causticization to digester again. Around 1925, Wagner² furnace was introduced and was a substantial improvement over the rotary furnace-smelt combination. A few years later, Tomlinson³ unit was developed in which spraying and dehydration of black liquor occurs on the furnace walls.

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During the current years, there has been increasing amount of attention towards the recovery of lignin complex along with soda regeneration from black liquor. The installation of lignin recovery unit in the soda recovery plant, is becoming a common practice in USSR, where approximately 15 to 20 percent of the total quantity of black liquor going to the soda recovery plant, is by-passed to lignin recovery unit, where it is precipitated out by carbonation (using flue gas as CO₂ source under pressure) and removed by coagulation and filtration. It is claimed that such mixing does not affect the overall heat recovery or the overall soda recovery percent of the soda regeneration plant.

Research was carried out later to isolate lignin by neutralising the alkaline liquor by passing CO₂, SO₂. In this method the caustic soda can be obtained more easily than that obtained in the previous method (that is, neutralisation with HCl). A number of investigators reported^{4,5,6} data on this type of precipitation.

Riman⁷ reported that of the CO₂ precipitate organic substances from soda black liquor, 33 percent of organic substances are soluble in alcohol.

Others⁸ observed that the lignin was isolated in maximum yield from a soda black liquor of specific gravity 1.1 by passing CO₂ into the solution at 80°C until a pH of about 7.5 is reached.

Wallenberger⁹ developed a process for regeneration of kraft black liquor by precipitation technique followed by electrolysis. Simonson¹⁰ isolated an almost lignin free hemicellulose by precipitation from sulphate liquor with ethanol after removal of acid insoluble lignin. On commercial scale, a number of companies are manufacturing alkali lignin by precipitation method. One of them is Mead Corporation, Ohio¹¹. Biggs *et. al*¹² reported world's first chemical plant at Hartsville, U.S.A., for the commercial production of acetic acid and formic acid from pulp mill black liquor. A soda lignin is also produced by Howard Smith Paper Mills¹³ at Ontario. Beckman and co-workers¹⁴ extracted lignin from rice straw with 2 percent NaOH in an aqueous alcoholic solution (60 percent) for 48 hours at room temperature. A number of researchers obtained lignin by fractional precipitation, by chromatographic separation¹⁵

and by employing dialysis technique^{16,17}.

Radical Changes in Conventional Recovery Process

There has been criticism of the conventional soda recovery process because of the complete destruction of the potentially available organic chemicals, present in black liquor as lignin and carbohydrate degraded soda complexes. Consistent attempts were made from time to time to furnish radical changes in the process to obtain valuable chemicals during the regeneration alkali.

Rinman¹⁸, Heuser¹⁹, Johansson²⁰ and White and Rue²¹ recovered organic chemicals from the black liquor recovery cycle by evaporating the black liquor to dryness and distilling the residue after a further addition of time. Bradley and McKeefe²² treated spent liquors with a sulphate such as sodium acid sulphate to precipitate the organic material, which was removed by sedimentation followed by filtration and drying. Richter²³ treated the spent liquors with sulphuric acid. McKeefe²⁴ developed a process for the recovery of caustic soda and organic acids (acetic and oxalic) from the alkaline black liquor. Schmidt and others²⁵ also suggested methods for the treatment of alkaline black liquor, aimed at the recovery of organic material and soda as much as possible and to minimise the necessary evaporation and incineration stages of the conventional soda recovery process.

A Spanish patent²⁶ claimed the

development of a process for the recovery of caustic soda and thermal recovery of the black liquor residue from the manufacture of cellulose. Schoeffel and Gitche²⁷, Rayonier²⁸ and Masao *et al*²⁹ also patented processes to recover sodium hydroxide and sodium carbonate from black liquors.

Yutaka Kimura³⁰ reported a process whereby alkaline spent liquor (soda or kraft) was converted into acid pulping liquor, after precipitating out lignin by SO₂ treatment. The purification of spent sulphite liquor and kraft bleach effluent by reverse osmosis was studied by Willey *et al*³¹.

Findley³² studied the economic feasibility of manufacturing lignin and organic acids from kraft pulping black liquor by putting some modification steps in the conventional soda recovery process.

Saburo *et al*³³ developed a new process for high sulphidity spent liquor, which can be obtained by absorbing SO₂ in the flue gas in a solution of Na₂CO₃ separated from the melt, and buring the resulting Na₂S solution together with spent liquor. Shick *et al*³⁴ described a new green liquor carbonation process, applicable to recovery of chemicals. According to a Japanese patent³⁵ the smelt obtained by concentrating and burning soda pulp waste liquors was mixed with 20 per cent TiO₂, heated at 1150°F in an oxidizing gas atmosphere and mixed with water to give a white liquor

having a causticizing efficiency 99 percent.

Use of Lignin

Purified lignin from alkaline cooking liquors has been suggested for many uses³⁶. Alkaline lignin has been suggested as a stabilizer for slow-break asphalt emulsions, modifier and extruder for latex emulsions, compounding agent in vinyl plastics, soil conditioner, binder in printing inks, wood stain, protective colloid in soap emulsions, dispersing agent for clays, fire foam stabilizer, oil-well drilling mud additive, insecticide dispersant, and foundry sand binder. Alkali lignin combines and forms precipitates with proteins and other nitrogenous substances, and this property is utilized in the removal of proteins from process waters and in the clarifying of sugar juices. Over a limited pH range, alkali lignin acts as an effective sequestering agent. It is used as a filler in plastics and resin-impregnated papers. Coprecipitated with latex, alkali lignin has been used as a reinforcing agent in the synthetic rubber^{37,38} for which purpose it is best given an oxidative treatment³⁹. It has been used in lead-acid storage batteries as an absorber. Derivatives of alkali lignin offer promise as flavourings, medicinal, and preservatives. Vanillin can be obtained from sulfate black liquor lignin if the lignin has not been excessively degraded.

Black Liquor Stabilization for the Improvement of Soda Recovery Process

Stabilization or fixation of sulphide

sulphur in kraft black liquor by oxidation is an interesting recent development. Originally introduced by Bergstroem and Trobeck⁴⁰ in 1939, for the abatement of odour nuisance problems in kraft paper mills, caused by the volatilizations of malodorous gases (CH_3SH , H_2S , CH_3SCH_3 , etc.) from the digesters, multieffect evaporation plant and the recovery furnace stack, the black liquor oxidation (BLD) method offers considerable economic advantages in the form of reduced corrosion and improved heat transfer in the evaporators recovery of sulphur values through the fixation malodorous sulphide sulphurs, lime saving in the causticization plant (due to increased sulphidity of the green liquor), improvement of pulp quality and yield.

During the last few decades, considerable amount of developmental research had been carried out by various researchers^{41,42,43,44} on the improvement of BLO process which resulted in the evolution of different BLO technique, viz. Bergstroem—Trobeck (B-T) system⁴⁰, Tomlinson system⁴¹, British Columbia Research Council (BCRC) system, A BBT Metoder system, Weyerhaeuser system, etc. Landry⁴⁵ critically reviewed the black liquor oxidation practice and its development. A series of papers on the subject of black liquor oxidation have been published by Collins, Jr.⁴⁶, of the Thilmann Pulp and Paper Co., Wisconsin. In fact, he was

the first to recognize and propose the basic idea of reducing the loss of sulphur from kraft recovery process through aeration of black liquor to oxidise the sulphide sulphur.

Experimental investigations carried out recently^{47,48} on the oxidation of bamboo based kraft black liquor, indicated stabilization feasibility to the extent of 89 percent sulphide sulphur by BLO at 80°C, with the possibility of lime saving to the equivalent of 25 kg per ton of pulp product.

Electrodialysis for the Regeneration of Black Liquor

In 1933, the possibility of recovering caustic soda by dialysis with parchment paper as diaphragm from alkaline black liquor was studied⁴⁹. Further study on alkaline black liquor was confined to separating the organic matter electrolytically. Several investigators⁵⁰ studied the removal of alkali and lignin from sulphate liquor by electrolytic process in diaphragm cell. Realizing the inherent defects in dialytic or electrolysis process for the treatment of electrolyte mixtures containing organic constituents, attempts^{51,52} were made afterwards to study the applicability of electrodialysis for the recovery of cooking liquor along with organic products from black liquor.

Mintz *et al*⁵³ reported the technical feasibility of applying electrodialysis process to spent pulping liquor and emphasised its economic advantage through the recovery of cooking chemicals, lignin

products, organic acids, hemiacetals.

A number of patents were taken in developing the electrodialysis process and equipment. An interesting patent to be mentioned in this connection is the Canadian Patent which was subsequently adopted by Dubey *et al*⁵⁴, who successfully operated a pilot plant to separate sulphite spent liquor into three fractions—pulping chemicals, lignosulphonic acids and lower molecular weight organics. Electrodialytic regeneration of paper mill spent liquor (B.L.) is particularly suited in smaller capacity plant, where due to prohibitive capital investment requirement and uneconomical operation, conventional soda recovery process is not applicable. Moreover pollutional hazards associated with kraft recovery process is reduced considerably in electrodialysis process. Availability of purified Lignin as a by-product along with cooking chemical is expected to give the electrodialysis process good amount of economical benefit.

Ion Exchange Technique for B.L. Regeneration :

Large number of investigations were carried out to separate the components of spent liquor by ion-exchange technique. Manchester and Termini⁵⁵ first attempted to recover base from spent sulphite liquor by Abiperm ion exchange process in which the base is directly transformed to a cation exchange resin per Permutit Q and then released as a

reusable bisulphite solution as effluent by regenerating the resin with sulphur dioxide solution.

The possibility of employing this technique in the recovery of ammonia-base spent liquor was examined by Effer *et al*⁶⁶. An extensive work was done on this subject by McCarthy *et al*⁶⁷.

Uptill now, there is no data on the applicability of ion exchange technique to regeneration of alkaline black liquor on large scale. However, a number of investigators employed this technique on laboratory scale and also in the analysis of alkaline black liquor.

Regeneration of B.L. by Pyrolysis

Organic and inorganic chemicals were recovered from spent kraft or sulphite liquor by concentrating it to 23.7 percent solids, separating tall oil soap, concentrating to 50-65 percent solids, adding a water-immiscible oil, e.g. a hydrocarbon fuel, evaporating substantially all water in a multiple effect evaporation and pyrolyzing the oil suspensions at 550-650°F and 1-10 atm for 20-40 min., washing the solid suspension with water to remove soluble salts, carbonizing the solids at $\geq 1400^\circ\text{F}$, utilizing the activated carbon for water purification, and recovering the inorganic solids from the aqueous solution for reuse in pulping liquor. The above process⁶⁸ resulted in a completely closed system containing no recovery boiler, with essentially no water loss through evaporation, no obnoxious waste gases, and no effluent production.

Timpe⁶⁹ found a new approach to kraft chemical recovery by hydropyrolysis process. St. Regis Paper Co.⁶⁰ also developed the process and recovered activated carbon, phenol, cresols, ethylene, methane, hydrogen, hydrogen sulphide and sodium sulphide from black liquor.

Salt-Cake-makeup Substitutes for Kraft Recovery Process

The amount of salt cake available has been insufficient to satisfy the total requirements of the sulphate pulp industry in India. Modern mills with low soda losses frequently supplement in the use of salt-cake by adding elemental sulphur in order to maintain the required sulphidity. The reserves of elemental sulphur are limited and may, in the future, have to be supplemented with sulphur from other sources. A number of alternative sources of make-up chemicals have been suggested and investigated. These attempts have mostly been motivated by periodic salt cake shortages, changes in sodium to sulphur ratio of make-up requirements, regional economics, and availability of waste chemicals from other manufacturing process.

Developments that have reduced saltcake usage per ton of product in kraft pulp mills are described in 1949 by Collins and West⁶¹. McCarthy⁶² described developments and improvements in equipment to reduce stack losses, particularly the high efficiency electrostatic precipitators. The developments

in recent times were summed up by Whitney. Wenzl⁶³ and Pesch⁶⁴ discussed a number of possible make-up chemicals for kraft recovery in his reviews. Recently Collins and Date⁶⁵ have reviewed the past and future of kraft recovery salt-cake make-up substitutes. Savell⁶⁶ described a 'synthetic salt-cake' introduced by the Mathieson Alkali works. Synthetic salt cake is a mixture of soda ash and sulphur sintered together in proportions to give a chemical equivalency of sodium sulphate. Woodside *et al*⁶⁷ claimed that synthetic salt cake is more efficiently utilized if it is added to the green liquor. Bray and Singer⁶⁸ claimed that sodium sulphite and sodium thiosulphate have value as kraft pulping chemicals. Recent work⁶⁹ completed at the IIT-Bombay indicated the feasibility of salt cake substitution by gypsum, when kraft black liquor solid is incinerated under a strong reducing atmosphere with gypsum as the make-up chemical salt. It was found that reduction of calcium sulfate to sulfide stage can be achieved to a level of 90% within 1½ hours time at a temperature around 95°C during incineration stage of black liquor solids⁷⁰.

Conclusions

- (1) Regeneration of Lignin along with Soda is expected to give good amount of economical benefit to the conventional B.L., recovery process.
- (2) Electrodialysis process offers great possibilities as a simpli-

fied one step method for the regeneration of Soda chemical along with purified Lignin as by-product.

- (3) Purified Lignin offers potentially as a renewable feed stock for the generation of multitudes of useful organic chemicals.
- (4) Substitution of salt cake by gypsum as a make-up salt indicates the techno-economic feasibility of salt-cake substitution by gypsum, available in abundant quantity as a natural deposit and from the phosphatic Fertilizer industry as by-product

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