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Kraft Recovery Process Technology

1.0 OVERVIEW

The annual world production of paper and board places the paper industry in the category of being a commodity industry and has shown remarkably steady and sustained growth for more than half a century. **Figure 1.1** shows for the most recent period that growth rates are higher in the developing countries than in Europe and North America, making the paper industry a truly global one.

The production of paper and board in the United States is shown in **Figure 1.2**. During most of the past three decades, production levels of the major paper and paperboard segments have been roughly comparable. Also shown is the total installed capacity from 1980 to 2000. Comparison with total production figures indicates over 90% of the capacity has been utilized over this period.

The kraft process is currently the dominant pulping process, now accounting for over 80% of the total wood pulp production (**Figure 1.3**). It occupies this favored position largely because kraft pulp is characterized by having high quality, most notably its high strength, and having a chemical recovery process that is efficient and environmentally compliant. The kraft recovery process is a mature technology that is quite standardized. Other alkaline pulping processes, such as soda or soda-AQ, may use the same chemical recovery technology as kraft. Alkaline sulfite pulping processes can use part of the kraft recovery system, but regeneration of pulping chemicals is more complicated. This book will be concerned with kraft chemical recovery because of its dominant position.

The kraft recovery process doesn't make pulp or paper, but it is essential to the production of both. The kraft recovery system has four basic functions:

1. Recovery and reuse of the inorganic pulping chemicals.
2. Removal and sale of valuable organic by-product chemicals.
3. Destruction of the remaining organic material and recovery of its energy value as process steam and electrical power.
4. Performance of these functions in an environmentally responsible and compliant manner.

In most kraft recovery operations, the organic by-products are a small fraction of the total dissolved wood substances and do not play a critical role in the economic viability of the kraft process. The essential requirements are recovery of the active pulping chemicals, namely sodium hydroxide (NaOH) and sodium sulfide (Na_2S), and effective use of the fuel value of the dissolved wood substances.

To underscore the tremendous importance of the kraft recovery process, a quick look at the immensity of production scale will be instructive. Typical kraft pulp mill capacities range from 300–2400 metric tonnes per day. As a rule of thumb, for every tonne of pulp produced, 1.5 tonnes of black liquor solids are generated, which, at a typical weak liquor solids concentration of 15%, means that 10 tonnes of weak black liquor are fed to the recovery process. Hence, typical kraft recovery process capacities range from 3,000–24,000 metric tonnes of weak black liquor per day. This has important economic implications for a kraft paper mill. The chemical recovery

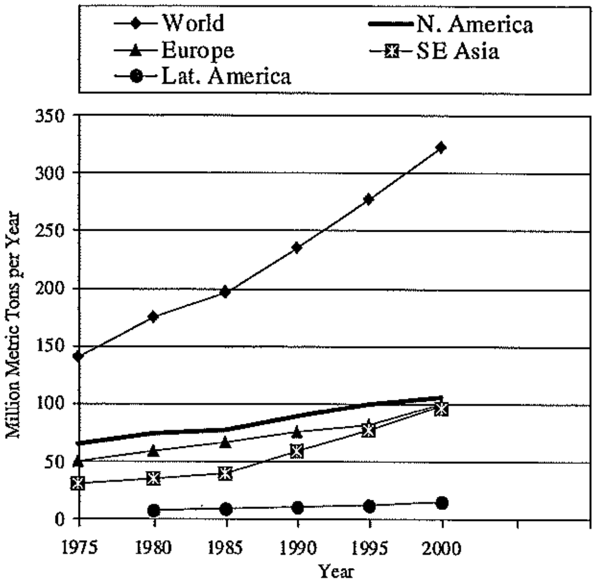

Figure 1.1. World production of paper and board (source: *Pulp & Paper International Ann. Reviews*).

process accounts for about 35% of the capital cost of a modern pulp and paper mill. The heart of the kraft recovery process is the recovery boiler, which processes concentrated liquor and recovers over 98% of the inorganic pulping chemicals while producing nearly 50% of the mill's total energy needs. An approximate capital cost for a 2000 tonne/day state-of-the-art recovery boiler at the turn of the century was $100 million. This represents over 20% of the total capital cost of a greenfield kraft paper mill, an astounding figure given the recovery boiler is only one piece of equipment in the capital-intensive mill. Nonetheless, there were 190 kraft recovery boilers in 117 U.S. paper mills in 2004 [1]. Because many of these are past their useful life and because of mill shutdowns, this number dropped to 180 units in 114 mills in 2006 [2]. Their capacities range from 200–3000 tonnes of black liquor solids per day.

With the cost of energy continually on the rise, the energy recovery component of the kraft recovery boiler needs to be emphasized. **Figure 1.4** shows historically the U.S. paper industry energy consumption and the various energy sources for that need. It is evident that nearly half of the mill's total energy needs come from black liquor recovery boilers.

The U.S. pulp and paper industry has been under significant political pressure to address environmental issues and work toward "mill closure." This of course does not mean closing down the mills, but rather closing up the process cycle whereby effluent wastes, atmospheric emissions, and fresh water use are minimized. The recovery cycle must meet compliance standards for atmospheric emissions, liquid effluents, and solid wastes. Atmospheric emissions include reduced sulfur gases (TRS), SO_2, CO, nitrogen oxides (NO_x), noncondensible gases (NCGs), and particulates. Liquid effluents are monitored for BOD, COD, toxicity, color, adsorbable organic halides (AOX), and pH. The principal solid wastes from the recovery cycle include non-process element (i.e., other than sodium or potassium) compounds coming from clarifiers and filters, most notably as green liquor dregs and slaker grit. Closing up the recovery cycle by minimizing effluent streams poses special operating problems associated with unwanted buildup of these non- process element compounds. This necessitates identification of places within the process to purge these compounds in an environmentally compliant way, unfortunately resulting in increased operating costs.

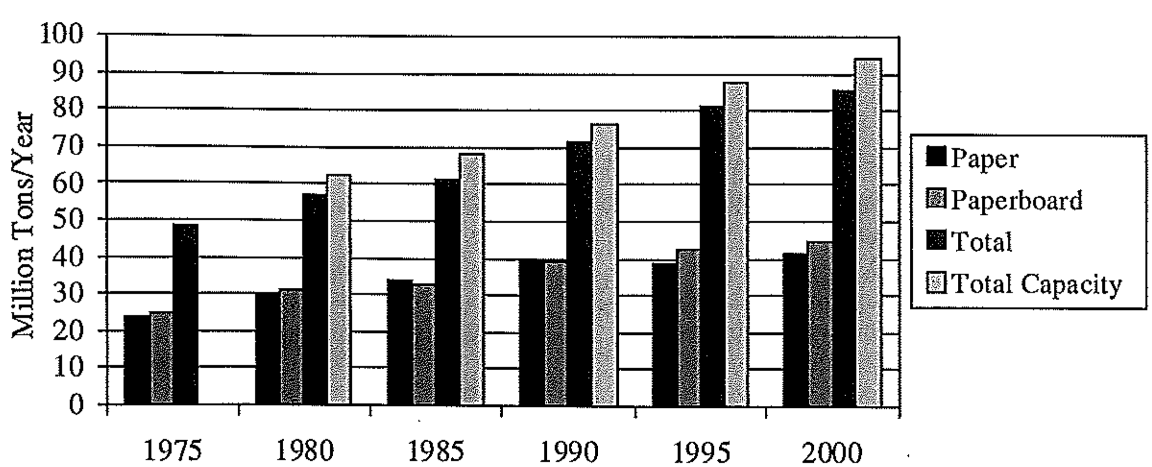

Figure 1.2. U.S. Production of paper and board (source: *Pulp & Paper International Ann. Reviews*).

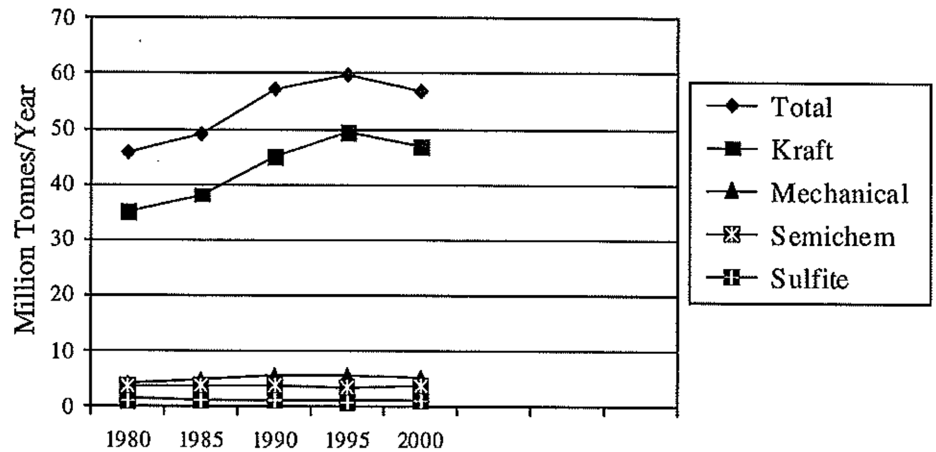

Figure 1.3. U.S. Wood pulp production (source: *Pulp & Paper International Ann. Reviews*).

1.1 KRAFT RECOVERY PROCESS FLOWSHEET

Figure 1.5 details the several unit operations in the kraft recovery process. What is first noticeable is that it is a chemical process embodying nearly all of the fundamentals of chemical engineering. Included are mass and energy balances, fluid dynamics, mass transfer, heat transfer, reaction kinetics, separations, thermodynamics, and mixing phenomena. The four major unit processes are evaporation, combustion, causticizing, and calcining.

1.1.1 Evaporation

Weak black liquor from the pulp washers typically has a dissolved solids content of 13–17%. This concentration must be increased to 65–80% before the liquor can be fired in the recovery boiler. Steam-heated, energy efficient multiple-effect evaporators are used for this purpose. Prior to the 1970s it was standard practice (in North America) to concentrate the black liquor to about 50% solids in the multiple-effect evaporator and then complete the concentration in a direct contact evaporator using the hot flue gases from the recovery boiler as the energy source. Many systems of this type are still in existence; however most have been replaced at a steady rate because of odor control problems and process energy inefficiencies due to their inability to generate high solids black liquor for firing to the recovery boiler. The current state-of-the-art system uses multiple-effect systems for the entire concentration process to the final solids concentration desired because these limitations are avoided.

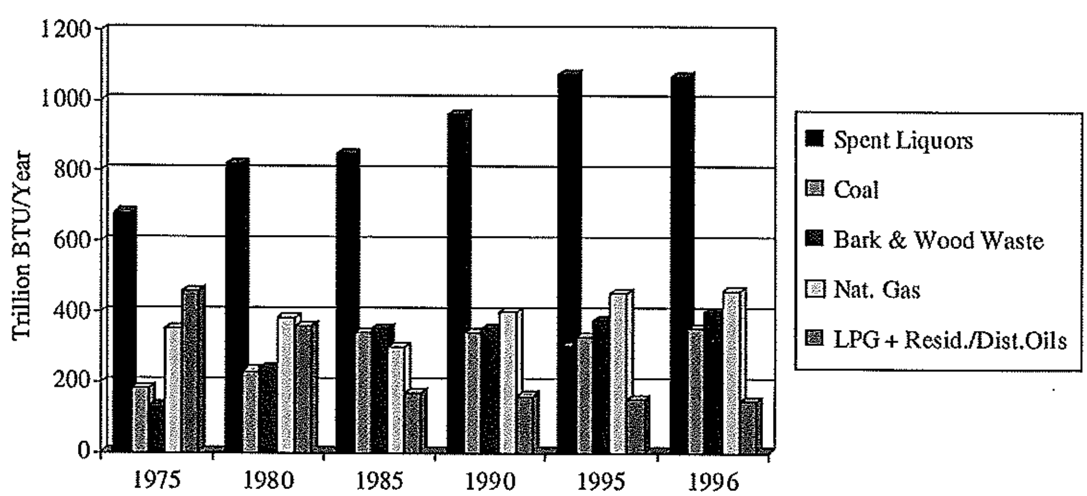

Figure 1.4. Energy consumed by U.S. pulp and paper industry (source: AF&PA).

2

Black Liquor Properties

2.0 OVERVIEW

Black liquor is a complex aqueous fluid mixture containing organic compounds removed from the wood, along with the spent inorganic pulping chemicals. The sodium compounds no longer exist only as inorganic salts, but are also combined with many of the organic species to form organic salts. Together, these organic and inorganic compounds form the black liquor solids, which typically are 13–17% of the total liquor flow from the pulp washers. At this concentration and process temperature, the liquor is a solution, but as the liquor is concentrated, its viscosity increases, and the salt solubility limit is reached at 50–55% solids. These two properties are important because both can adversely affect heat transfer rates in evaporators and combustion performance in recovery boilers.

2.1 BLACK LIQUOR CHEMICAL PROPERTIES

Black liquor has a complex and unique chemical composition that impacts most of the unit operations in the kraft recovery process. Its inorganic content is responsible for scaling phenomena in multiple-effect evaporation and green liquor processing, as well as providing sodium hydroxide (NaOH) and sodium sulfide (Na_2S) for recycle to the digesters. Its organic content has to be recovered in part as tall oil, turpentine, and various resins, after which it must be partially combusted in the recovery boiler to generate recoverable energy for use elsewhere in the mill while providing carbonaceous reductant to convert sulfate into sulfide. Its volatiles content can be the source of unwanted atmospheric emissions that must be controlled within state and federal compliance limits.

2.1.1 Composition

The composition of black liquor is derived from two sources: wood and white liquor. The dissolved wood substances consist of the following classes:

- Ligneous materials (polyaromatic in character)
- Saccharinic (hydroxy) acids (degraded carbohydrates)
- Low molecular weight organic acids
- Extractives (fatty acids and resins)

These organic constituents are combined chemically with NaOH and Na_2S in the form of sodium salts. The main inorganic constituents in black liquor solids are:

- Sodium hydroxide (NaOH)
- Sodium sulfide (Na_2S)
- Sodium carbonate (Na_2CO_3)
- Sodium sulfate (Na_2SO_4)
- Sodium thiosulfate ($Na_2S_2O_3$)
- Sodium chloride (NaCl)

Most of these chemicals originate from the white liquor used for pulping, but small amounts can enter with the wood. They also exist in minor amounts as the analogous potassium salts.

The composition of black liquor depends on the alkali charge (white liquor composition), pulp yield, and the wood species used. Considerable