

# Chemical Recovery from the Pulping Waste Liquor in China

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## ABSTRACT

There are two main kinds of chemical pulping processes in China which are alkaline pulping process and sulfite pulping process. The waste liquor from alkaline pulping process is treated by soda recovery system to obtain soda. There are some differences between wood and non-wood pulp soda recovery plant. While the sulfite pulping waste liquor is mainly used to produce by-product such as alcohol, yeast and lignosulfonate

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Pulp and paper industry is one of the biggest industrial pollution sources in China. The quantity of its effluent is one tenth of the total industrial effluents and its BOD<sub>5</sub> issued is as much as quarter of the total industrial BOD<sub>5</sub> discharged. In China, in common with other developing countries, due to the insufficient forest resources most of the pulp and paper are produced from non-wood raw material, such as straw, bagasse, bamboo, reed, etc. reaching 60% of the total pulp output. Because of the low chemical recovery the black liquor plays an important part as a pollution sources.

In 1990 the usage of alkali for pulp making amounted to 1.2 million tons (referred to sodium hydroxide), but the recovered alkali reached only 350 thousand tons from 57 soda recovery plant in operation by that year, and the total alkali recovery in alkaline pulping was only around 30%. The small mills with the capacity less than 30 tons of pulp per day, most of which have not equipped with any recovery facilities, produced 60% of the total alkaline pulp. It is very difficult to run a chemical recovery system in those small mills economically and efficiently. So how to deal with the pollution sources from pulp and paper mills is still a challenge in China.

The total output of the pulp in China amounted to 12 million tons in 1990, and about 70% of those were chemical pulp. There are mainly two kinds of chemical processes to manufacture pulp in China, that refer to alkaline and sulfite pulping processes. The alkaline processes, including soda, kraft, and also lime

process, are the main technology for pulp production in China. The lime process is to manufacture the pulp for paper board making which is widely used as a packing material. From this process a waste liquor, what we call it yellow liquor since that the colour of it appeared to be yellow, is obtained.

In sulfite pulping process, three bases are generally utilized that are calcium, magnesium, and ammonium. There are actually three calcium sulfite pulp mills now operating in China to deal with wood pulp. Four magnesium sulfite pulp mills are operating for the production of reed and bagasse pulp; a significant number of ammonium sulfite pulp mills mainly to manufacture straw pulp.

Most of the soda pulp mills for wood pulping are big mills, for kraft pulp as well as bleaching pulp production. The capacity ranges from 100-500 tons per day. Some of the soda pulp mills for reed pulping have a capacity ranges from 60-100 tons per day. And the soda pulp mills for straw pulping are now very popular in China. The capacity usually ranges from 15-60 tons per day.

The soda wood pulp mills usually equipped with soda recovery plant. The main steps in the recovery of wood alkaline pulping chemicals are as follows:

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- a. Concentration of the black liquor to high solid content with evaporator.
- b. Burning the concentrated black liquor in recovery boiler to recover the heat and chemicals.
- c. Causticizing the sodium carbonate that comes from the recovery boiler to sodium hydroxide with lime.
- d. Regeneration of the lime from the filtrated calcium carbonate by burning.

Some losses of sodium and solid always take place during washing. In China, the extraction rate of the black liquor during washing the wood pulp reaches 90-95% of solid. The make up chemicals can be added as salt cake (sodium sulfate) and this material be added in black liquor before recovery boiler.

The black liquor leaving the pulp washer normally contains 10-12% solid. It is concentrated to 50% of solid with evaporator, then evaporated in the direct contact evaporator such as venturi scrubber and cascade evaporator to reach the concentration of 60% with the hot flue gas.

The multiple effect evaporator consists of series of evaporation stages, normally five effects are equipped for steam saving. Long tube rising film evaporators are the common type serving this purpose. The falling film plate type serving this purpose recently to meet the concentration required, such as to reach 60% even more, and it will omit the direct contact evaporation to reduce the pollutant released to the atmosphere.

When processing black liquor from high resin-content woods a soap deposit will appear on the tubes of the evaporator unless these materials are previously removed from the liquor by soap-skimming system when the solid concentration reaches 25-30% level. The removed soap is used as a raw material to produce tall oil. In China there are 4 tall oil production systems in operation.

Concentrated black liquor comes from the evaporators, burns in the recovery boiler and discharges as molten smelt into a tank where it is dissolved to form green liquor. In China we have a series of the recovery boilers to deal with the pulp capacity ranging from 25 tons of the pulp per day to 300 tons of the pulp per

day. Solid carried in the flue gas leaving the recovery boiler should be removed from the gas prior to its discharge to atmosphere. Two methods are used for this purpose: with scrubbing and electrostatic precipitation.

In causticizing system, which consists of green liquor clarifier, causticizing tank, white liquor clarifier, lime mud washer, vacuum filter, etc., the green liquor is converted into white liquor ready to cook the wood for pulp making.

Lime burning system, to incinerate the calcium carbonate to generate lime, usually equipped with rotary lime kiln, which is a long cylindrical refractory-lined vessel, 2-3m in diameter, 70m in length, sloping from feed to discharge end. The fuel used is oil or gas.

In non-wood pulp soda recovery plant, the flowsheet is similar to that mentioned above. But due to the properties of the non-wood pulp black liquor the equipment and the flowsheet is a little bit different. For instance, there are only three steps in the recovery plant. Because of the high silica content in the black liquor the lime regeneration seems to be inadequate to the purpose. The lime mud cake discharged from the causticizing system has been used as a part of raw material for cement production, and also purified as an additive for printing paper. At the moment, only a pilot plant has been set up in China for silica removing, but it has not been operated yet. It seems that foaming formation during acidification of the black liquor is still a problem to be solved.

Owing to the high silica content and high viscosity, the evaporation of straw pulp black liquor is much difficult than that of wood pulp black liquor. We use long tube rising film type evaporators and also short tube submerged type for straw pulp black liquor evaporation. The tube length is 7 and 3 metres respectively. The concentration of the black liquor after evaporation is limited to 40% solid. The evaporation strength is around 6 - 8 kg water/m<sup>2</sup> hr.

A series of falling film evaporators were set up recently to deal with non-wood pulp black liquor. It is emerging a satisfying result with a concentrated liquor to 50% solid. Consequently the application of the falling film evaporators seems to be a trend in straw pulp soda recovery plant in China.

Because of the low calorie value of the straw pulp black liquor, the recovery boiler has been made some change from that of wood pulp mill. Two types of the recovery boilers that are equipped with a square smelter and a round smelter now are available in China. The boiler with a square smelter is similar to that used for the wood pulp mill but with some modification to meet the low calorie value of the black liquor. The recovery boiler with the round smelter appears to be much different. The round smelter is a refractory lined vessel which can be moved away during its maintenance. Another newly repaired one take the place of the original unit in operation. Inside the smelter there are two layers of the refractory bricks. The function of the bricks is to protect it from the corrosion by the heated alkali. The bricks last only 3-6 months, so it should be repaired at least two times per year.

There is always an argument for which one of the two types of the recovery boilers is more suitable for non-wood pulp black liquor burning. The different points come up from the fact that someone believes that since there is no tube wall inside the unit to extract heat, the round type one would be easier for the burning of the black liquor with low calorie value. Others think that the maintenance of the round type smelter costs too much. Whatever it would be, these two different types of the recovery boiler are running smoothly in many pulp mills in China nowadays.

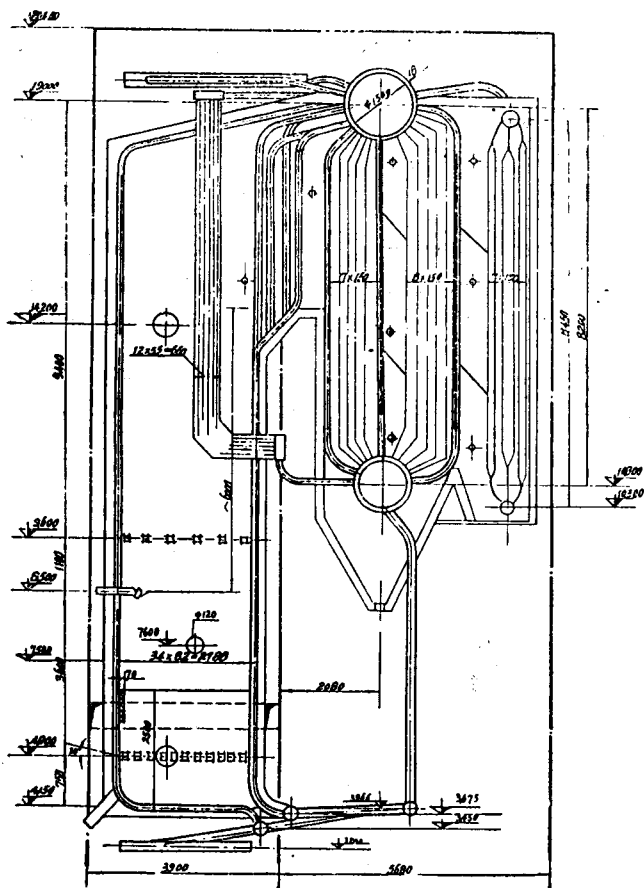
Figures 1 and 2 show the two kinds of the recovery boilers and their specifications listed in table 1.

Because of the high silica content in the green liquor of the straw pulp it is rather difficult to settle the lime mud from white liquor. There is a trend to use a belt vacuum filter instead of the traditional sedimentation system. The typical simplified flowsheet is shown in figure 3.

Three causticizers being laid horizontally in series in traditional systems, but in this flowsheet only one unit, which is divided into three compartments, is set up to serve the same purpose.

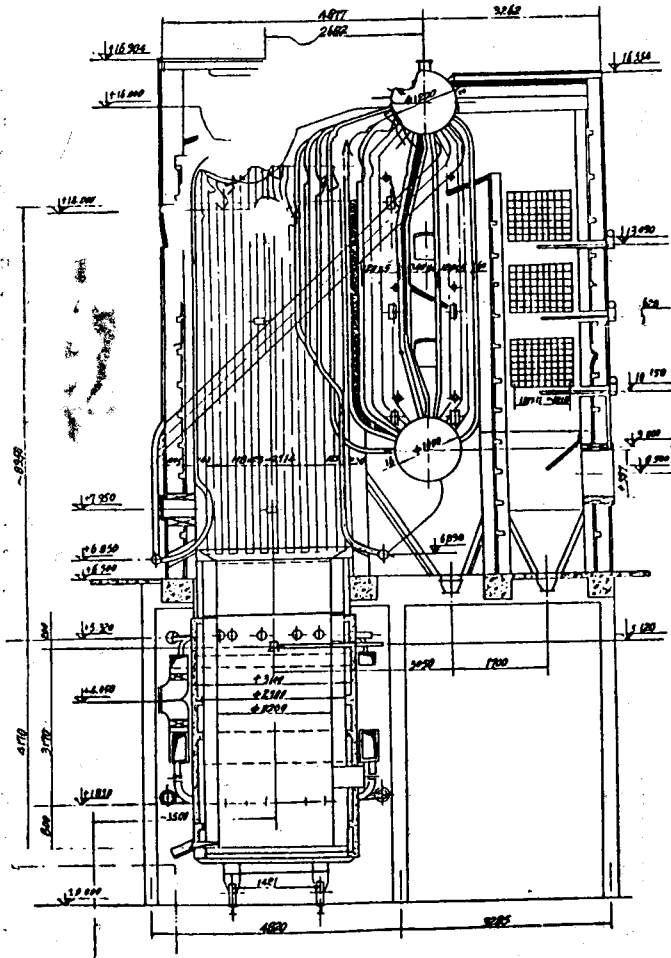
The belt vacuum filter is a vacuum sucking continuous solid liquor separation equipment. A stainless steel drum is covered with a sheet of polypropylene woven cloth. The cloth moves along with drum when it rotated, and the cloth is disengaged from the drum and goes into a discharge roll. After discharge roll it goes to a cloth washing device and then return to the drum again.

The slurry, containing suspended solid, is fed to the drum vat. Then it goes on the cloth forming a layer of cake due to the vacuum suction of the drum. The filtrate, passing through the inside parts of the drum, continuously discharged from suction valve on the drum end. The solid cake sticking on the cloth is running out of the slurry level as drum rotated, and continuously drying owing to the vacuum suction of the drum. The formed cake can be washed by fresh water to remove the soda containing in it. Together with the cloth the cake is disengaged from the drum goes into the discharge roll and falls down as it is bending suddenly. The cloth, free from cake, is then washed with water shower. After washing, the filter



WGC50-12/13 Recovery Boiler with Square Smelter

Figure 1



WGZ40-6.5/13 Recovery Boiler with Round Smelter

Figure 2

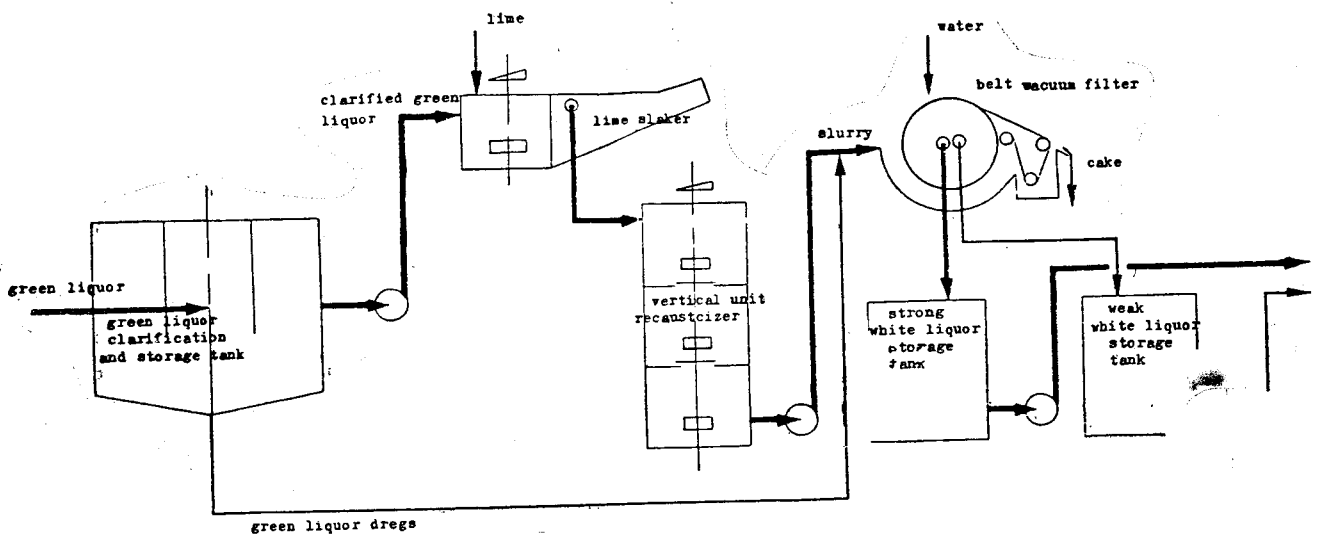


Figure 3

cloth recovers its filtration ability, returns to the drum surface and starts the new cycle again.

Specifications of the recovery boilers

Table—1

Type	WGZ 40-6.5/13	WGC 50-12/13
Scale t pulp/day	40	50
Solid for burning t/day	60	75
Steam produced		
Capacity t/hr	6.5	12
Pressure Kg f/Cm <sup>2</sup>	13	13
Temp. °C	194.13	194.13
Feed water temp. °C	105	105
Air temp. °C	150	150
Flue gas temp. °C		
After economizer	260	260
Flue gas heat content		
Kcal/kg	339.4	339.4
Boiler heat efficiency %	62.5	69.6
Black liquor temp. °C	100	100
Black liquor cone.		
Soild %	60	60
Black liquor amount		
Kg/hr	4166	5280

This arrangement is suitable to filtrate the liquor containing fine solid particles, which is usually easy to clog the filter cloth and leads to difficult filtration.

This equipment used in the causticizing system can replace white liquor clarifer, lime mud washer, and

vacuum filter in the traditional system to get a satisfactory result.

A unit with 7.5 m<sup>2</sup> filtration area has been operated in a soda recovery plant of the straw pulp mill for several years reaching the following specifications :

- Capacity for strong white liquor 12m<sup>3</sup>/hr which is equivalent to 80-100 tons/day of the straw pulp
- Turbidity of the filtrated strong white liquor (suspended solid content, below 100 ppm
- Soda content in the discharge cake below 1%
- Solid content in the cake above 40%

This simplified system is suitable for the recovery plant of the non-wood pulp mills to causticize the green liquor into white liquor where the lime mud is in poor settling. The following benefits can be achieved :

- Provides reliable operation with reduced maintenance and downtime
- Requires a minimum amount of space
- Reduced operating cost
- Reduced capital cost
- Less operator attention

As regard to the yellow liquor from the lime process for straw pulp, there is no chemical recovery system for this kind of waste liquor. At the moment only a pilot plant has been set up to treat yellow liquor that is to digest it by anaerobic method to produce methane and at the same time reducing its pollution load.

In China, there is only one chemical recovery plant with evaporation, burning and absorption steps in magnesium sulfite pulp mill. It has been set up for several years, but it still not operate for the time being. The main problem seems to be that due to the low calorie value of the red liquor from reed pulping, an assistant fuel must be added for burning the liquor. Since the fuel costs too much, it can not operate economically.

The calcium base sulfite pulping waste liquor has been treated by the traditional method that is to produce alcohol, yeast, and lignosulfonate. The flowsheet

is shown in figure 4. For the alcohol production, a stripping column is set up for the red liquor stripping by steam to remove the volatile compounds which can be harmful to the yeast for fermentation hexose to alcohol. Then the red liquor is neutralized with lime, cooled and added some nutrition agent such as (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> to meet the fermentation condition. After fermentation there is a distillation system to purify and concentrate the alcohol to the concentration of 95%.

Flow Sheet for Production of Alcohol Protein & Lignosulfonate in Calcium Base Sulfite Pulp Mill

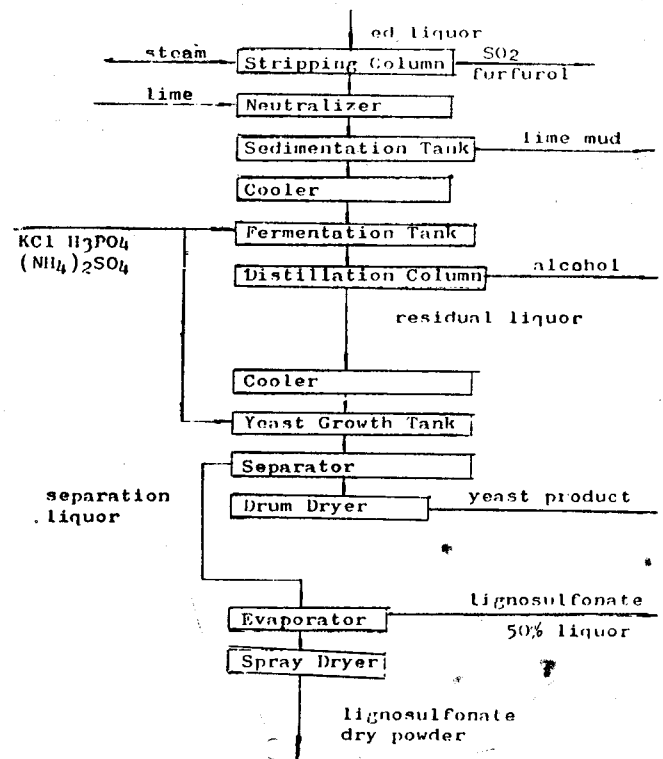


Figure 4

The residual liquor comes out from the bottom of the distillation column discharges to the yeast growth system. The residual liquor contains pentose and organic acid which are easily digested by bacteria..... candida utilis to form a high protein contained material.... yeast. The yeast grows rapidly and all the growth requirements are synthesized from simple organic compounds.

A separated waste liquor, which are already removed sugar and organic acid, will be obtained after separated from the yeast. This separated liquor can be concentrated to produce lignosulfonate. Two kinds of the lignosulfonate commercial products now are available in China. One is in liquid form with 50% of solid; another is a dry powder with 92% of solid.

These lignosulfonate products are used for a wide range of applications, that are based on their adhesive, dispersant, and surface-active properties. They have been used as a binder for cement, adhesive for refractory, and also as a mineral deposit flotation agent in China. The lignosulfonates also have a large market as dispersants for oil-drilling pesticide and agricultural sprays, and also as a binder for animal-feed pellets.

The ammonia based sulfite waste liquor are mainly used for irrigation and discharged directly to the farmland as a fertilizer. But some of the mills do con-

centrate it to 50% of solid and sell it during the non-irrigation period as adhesives or fertilizer, that can reduce the pollution problem of the waste liquor.

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