A new development in the treatment of spent liquor for small pulp and paper mills in china

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General situation of the papermaking industry and the importance of the treatment of spent liquor in China

The papermaking technique was invented in China 2000 years ago and has played a great role in human civilization. Currently the annual output of paper and paperboard in China is over 10 million tons. Due to the shortage of wood, non-wood fibrous materials are the main component of the paper. Rice straw and wheat straw account for about 40% of the raw materials used, with other straws composing 30%, wood 18%, cotton, kenaf and waste paper 12%. Wide distribution of non-wood fibrous materials and difficulties of transportation have resulted in the existence of many small pulp and paper mills, which represent 90% of the paper mills in the country. The majority of these mills use soda pulping or soda-AQ pulping though some mills use No_2SO_3, NaOH pulping or Na_2SO_3, Na_2CO_3 pulping. The spent liquors are usually drained off without any treatment of utilization, and heavily pollute the environment. In addition, much organic matter and alkali are lost, which has become a drawback to the development of the papermaking industry in China. In fact, pulp and paper mills are the third largest national cause of pollution, 90% of pollution load comes from spent liquor. In short, the treatment of spent liquor from small pulp and paper mills is a critical problem in our country and needs serious study.

Research development of the wet cracking process

The wet cracking process is a new method which continuously treat the spent liquor resulting from the straw pulping process. It was invented by professor Tan long of Tianj in Institute of Light Industry. The research work was begun in 1977. Batch trials were completed in 1980, continuous trials were performed, and an invention patent was applied in China in 1985. This technique was awarded a gold medal at The Second National Exhibition of inventions of China in Oct. 1986, a gold medat at The 15th International Exhibition of Inventions and New Techniques of Geneva in Apr. 1987, and was put on display several times at both national & international trade and technique fairs. In short, the technique has been recognized world-wide.

Research results about the wet cracking process, was published in *PPI* in June 1986; presented at an experts' working meeting organised by UNEP and published in *Proceedings of the Workshop on Environmental Aspects of Non-wood Fiber Pulp and Paper Manufacture* in 1986; published in *Infoterra, Exchange of Environmental Experience Series-Book One* in 1988 (edited and published by UNEP in English, French, Russian and Spanish); presented at the 1988 international Non-wood Fiber Pulping and Papermaking Conference called by CTAPI (China Technical Association of Paper Industry) & UNIDO and gathered in the proceedings; presented in 1989 to the CTAPI Technical Committee of Chemical Recovery.

After trials in 1986, the basic technological work had been completed, plans were made to begin the design and construction of a wet cracking treatment workshop for spent liquor, for a 5000 ton per-year straw pulp mill. Due to take of sufficient funds, the project was postponed. However, in 1989 the project was sponsored by our government, and construction was estimated to be begun in 1990 and completed in 1992.

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Technology of the wet crecking process of spent liquor

Spent liquor and straw chemical pulp from a rotary digester are separated by a horizontal belt vacuum washer, solid content of the spent liquor is about 12%. The spent liquor is evaporated to remove washing water and reach the solid content 16~18%, then wet cracking reaction is carried out, the reaction conditions are tem. 360~370°C, time 20~30 min., pressure 190~210 atm.

Because of a great deal of CO_2 produced in the wet cracking reaction, Na_2SiO_3 in the spent liquor is converted and becomes precipitated SiO_2 as follow, then it is removed.

$$Na_2SiO_3 + 2H_2CO_3 \rightarrow 2NaHCO_3 + H_2O + SiO_2 \downarrow$$

After the wet cracking treatment process, the spent liquor is turned into a yellow transparent liquor which we call "yellow liquor". It is comprised mainly of $NaHCO_3$. Na accounts for about 25% of the total and there is still small amount of organic matter in the yellow liquor.

Wet cracking process is suitable for the treatment of spent liquor from rice straw, wheat straw other straws, cotton linter and kenaf pulping. The process is also suitable for treatment of spent liquor resulting from pulping process of two kinds of cooking reagents soda or soda AQ pulping and Na_2SO_3 pulping. For the two kinds of spent liquor, the further treatment process is not quite identical after the wet cracking reaction.

The treatment of spent liquor from soda or soda AQ pulping.

Research has been done on the treatment of spent liquor produced in rice straw chemical pulping with soda as a cooking reagent. With regard to the treatment of spent liquor, the first step is to determine the degree of wet cracking reaction. Many experiments showed that the "wet cracking level" can do this; then we must select a target to measure the degree of the reaction. Experiments demonstrated also that the recovery ratio of titratable inorganic salt ($NaHCO_3$) of yellow liquor (titratable inorganic salt of yellow liquor to total salt of yellow liquor) can be considered as the target, this target is accurate and simple.

Effects of some variables on wet cracking level aer as follows,

A. Effect of temperature on wet cracking level

Table—1

the reaction temp.°C	325	341	355	365	370
the recovery ratio%	32.52	46.24	54.04	55.62	58.86

note: spent liquor solid content is 7.95%; reaction time is 25 minutes.

It can be seen that temperature has a significant effect on the wet cracking level in the range of temp, discussed. Also, it was discovered that a gradual raising of the temp. causes a gradual increase of the output of wet cracked gas, but decreases the amount of tar oil. Another result is that the removal ratios of BOD, COD, SS and SiO_2 in the spent liquor were enhanced by raising the temp. Roughty speaking, temp. is the most important factor affecting wet cracking level and that temp. has a limit. If the temp. exceeds the critical point of water (374°C), liquid water in the equipment will not exist and difficulties in the opcration will occur. As a wet cracking temp. 360~370°C may be considered the most reasonable.

B. Effect of pressure on the wet cracking level

Pressure has no obvious effect on the wet cracking level in the range discussed. However during reaction, in order to prevent spent liquor from being boiled to evaporation, the working pressure must be slightly higher than that of the saturated steam of water at the working temp. The pressure during trials was 200 atm.

C. Effect of time on the wet cracking level

Wet cracking time means the time kept at the reaction temp.

Table 2

the reaction time min.	12	25	28	37	42	60
the recovery ratio%	51.48	53.12	54.58	54.54	55.80	55.72

note : spent liquor's solid contet is 7.78%, wel cracking temp. is 365°C

It can be seen that the recovery ratio of inorganic salt increases with the length of time, that is compared with the effect of temp., the effect of time on the wet

crocking level is weaker. It was discovered that the reaction could yield less tar oil and more wet cracked gas if it lasted a long period, in this case, the colour of the yellow liquor became light and had a higher stability in a long time. On one hand, the reaction should approach fundamental completion, on the other hand, if the reaction time is too long, the reactor will need to be so huge that the reaction system would become unreasonable both technology and economy. As a wet cracking time;25～35 minutes may be considered most reasonable.

D. Effect of spent liquor's solid content on the wet cracking level

According to the results above, when the effect of the spent liquor's solid content was examined, the reaction temp. and time were 365°C, 25 minutes respectively.

Table 3

the solid content	%	6.24	10.68	15.12	21.50
the recovery ratio	%	54.40	58.66	58.88	59.72

It can be seen that there is an increase in recovery ratio when the solid content is enhanced. When the solid content is below about 10%, the increase trend is more evident, when above 10%, the increasing appears to reduce relatively. As the requirement of spent liquor's solid content, 10～18% may be considered most reasonable.

Under the treatment conditions mentioned above, the experimental results were as follows:

Table 4

pH of yellow liquor		about 8
removal ratio of BOD_5	%	60～70
removal ratio of COD_{ct}	%	70～80
removal ratio of SS	%	93～95
removal ratio of SiO_2	%	96～98
recovery ratio of inorganic salt of yellow liquor	%	above 50
yield of wet cracked gas	M^3	120～13
yield of tar oil	Kg	100～120
yield of char powder	Kg	90～110

note ; yield bases on one ton of organic matle in the spent liquor

The treatment of spent liquor from Na_2SO_3 pulping

When Na_2SO_3 is used as a main cooking reagent the usual processes are Na_2SO_3—NaOH, Na_2SO_3—Na_2CO_3, Na_2SO_3—NaOH—AQ, Na_2SO_3—Na_2CO_3—AQ, Na_2SO_3—Na_2CO_3—NaOH—AQ and so on. The Sulfidation degree ($Na_2SO_3/(Na_2SO_3+Na_2CO_3$ + NaOH)) is about 60～80%; by these processes, the yield and quality of the pulp are superior to that of soda or soda —AQ pulping.

In the wet cracking process, technology, technique conditions and equipment are roughly the same for treatment of spent liquor from Na_2SO_3 and soda pulping to produce chemical pulp. For these two types of spent liquor, the wet cracking reaction of spent liquor from Na_2SO_3 pulping can be carried out more easily; that is, under the identical technological conditions, the spent liquor from Na_2SO_3 pulping has a higher wet cracking level.

The yellow liquor originating from the Na_2SO_3 pulping is comprised mainly of $NaHCO_3$ Substances containing sulfur exist principally in a gas phase. After combustion, the sulfur compound in the gas phase is converted into SO_2 which is absorbed by yellow liquor and changed into Na_2SO_3 After the absorption, the yellow liquor is reptenished with some cooking reagents, then reused in the pulping process.

Other practical techniques in treatment of spent liquor for small pulp and paper mills in China

A. Conventional chemical recovery system

The Conventional chemical recovery system is used in treatment of spent liquor from the bamboo, reed, bagasse and wheat straw pulping process, when there is a capacity of 10000 tons of pulp per year. The ratio on alkali recovery can reach 80% for reed pulp and 70% for wheat straw pulp in some mills.

Some new equipment has been created and applied widely to production of the chemical recovery system of straw pulp. The horizontal belt vacuum washer is an example; for the spent liquor from wheat straw soda pulping producing chemical pulp collection efficiency of the liquor can be attained by 90～95%. In evaporation of spent liquor, short tube evaporators are usually utilized; the length of tube is 2～2.5 m. Scale in these tubes can be restrained or the tubes can

be washed conveniently, high pressure water (320 atm) is used by some mills to eliminate the sale, the results are salisfactory. Plate falling film evaporators designed and manufactured in our country have been put into triat production. Water-walled recovery furnaces are replaced by air-watted ones, the risk of smell-water explosion is avoided. Additionally, the temp, of the recovery furnace can be improved by raising that of the entrance air, in the combustion of spent liquor from wheat straw soda pulping, oil as fuel is not needed. A great improvement has been achieved in silica removal of spent liquor mentioned above, CO_2 in stack gas is absorbed by the yellow liquor to produce SiO_2 which is separated by centrifuge, the removal ratio of silca can reach over 80%.

B. Comprehensive utilization of spent liquor

When CO_2 is introduced into the spent liquor or $(NH_4)_2SO_4$ or H_2SO_4 is added to liquor, lignin precipitated by acid or lignosulfonate is produced. Then, it can be used either as a diluent of drilling mud, a dye diffusion agent, a concrete agent reducing water, or a forage additive, which has been manufactured in small quantities.

C. Biochemical treatment of spent liquor

Several mills such as $Ca(OH)_2$ semichemical pulping mills with rice straw as fibrous material, and soda pulping mills with cotton linter or wheat straw as fibrous material, have applied anaerobic fermentation in treatment of spent liquor to generate marsh gas. Research work on biochemical treatment of spent liquor is in progress continuously in many research instiiutes and mills.

For the sake of effective harnessing of spent liquor pollution from small pulp and paper mills, research, development and popularization of many new technologies & methods are being carried out in China. Some methods which are suitable for our situation will certainly be figured out in the days to come.