ABSTRACT

The chemicals and water balances for a special modified kraft cooking process were calculated. In addition, the effect on cooking selectivity of recycling the drained liquor after the impregnation in our laboratory cooking system was studied, and the application of the process on an industrial scale was elucidated. The process under discussion consists of impregnating wood chips with white liquor followed by cooking the impregnated chips in the vapor-phase in the first stage, and then in a liquid-phase stage by adding new white liquor.

Improved modified kraft cooking

Part 6: On the chemicals and water balances for the modified vapor-phase cook

BOFENG MAO

THE PREVIOUSLY REPORTED NEW process (1) has an initial vapor-phase stage followed by a liquid-phase stage with a high liquor-to-wood ratio (6:1). This new process in our laboratory cooking system using softwood chips as raw material shows a significantly improved cooking selectivity, i.e., a higher pulp viscosity at a given kappa number.

In order to supply the required chemicals to the initial vapor-phase stage, the wood chips must be impregnated with the cooking liquor at a high liquor-to-wood ratio prior to the vapor-phase stage, and all the free liquor must then be drained off. Due to the low liquor volume in the vapor-phase stage, the chemicals must be supplied at a concentration higher than that of a conventional white liquor. The drained liquor containing a large amount of active chemicals must be recirculated in an internal loop. In the transfer from the vapor-phase to the liquid-phase stage, a predetermined amount of white liquor must be added. In one of the cases studied, the white liquor charged in the initial vapor-phase stage contains considerably more sulfide and less hydroxide than in a standard kraft cook, and the white liquor charged in the liquid-phase stage contains no sulfide. The white liquor added to the process must consequently be separated into a "sulfide-rich" and a "sulfide-free" liquor.

All these modifications in relation to a standard kraft cook will influence the chemicals and water balances and probably also the delignification. This paper presents data concerning the chemicals and water balances for the process and the effect on cooking selectivity of recycling the drained liquor after the impregnation. The application of the process on an industrial continuous digester is also discussed.

The calculation of the chemicals and water balances is divided into four cases: (a) when the impregnation is carried out at room temperature and conventional white liquor is used, (b) when the impregnation is carried out at room temperature and divided white liquors (a "sulfide-rich" and a "sulfide-free" liquor) are used, (c) when the impregnation is carried out at 90°C and conventional white liquor is used, and (d) when the impregnation is carried out at 90°C and divided white liquors are used.

The study of the effect on cooking selectivity of recycling the drained liquor after the impregnation is divided into three cases: (a) a modified vapor-phase cook when drained liquor from the impregnation at room temperature is used, (b) a conventional kraft cook when drained liquor from the impregnation at room temperature is used, and (c) a modified vapor-phase cook when drained liquor from the impregnation at 90°C after recirculation five times is used.

EXPERIMENTAL

The outline of the procedure for the two-stage modified vapor-phase cook is shown in Fig. 1.

Wood chips

In this study, a mixture of industrial pine and spruce chips, air-dried, laboratory screened and hand sorted, was used.

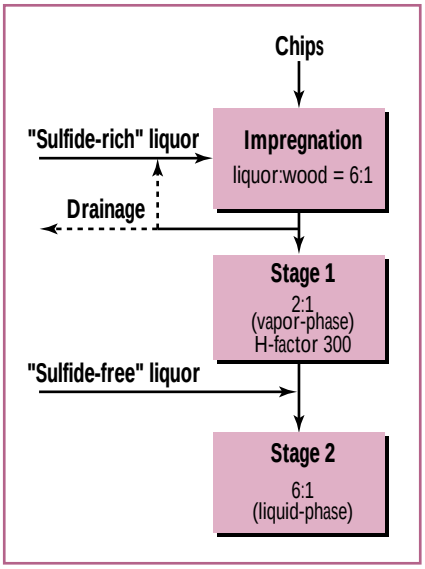
Impregnation

When the impregnation was carried out at room temperature, it was performed in exactly the same way as described previously *(1)*. Chips were first charged in 1 L conventional autoclaves, which were evacuated for 30 min. The cooking liquor was then sucked in to fill the autoclaves to a liquor-to-wood ratio of 6:1. An external pressure of 0.5 MPa was applied to the autoclaves in order to aid penetration. After 30 min, the pressure was released and the excess free liquor was drained off. The liquor-to-wood ratio in the autoclaves was then about 2:1.

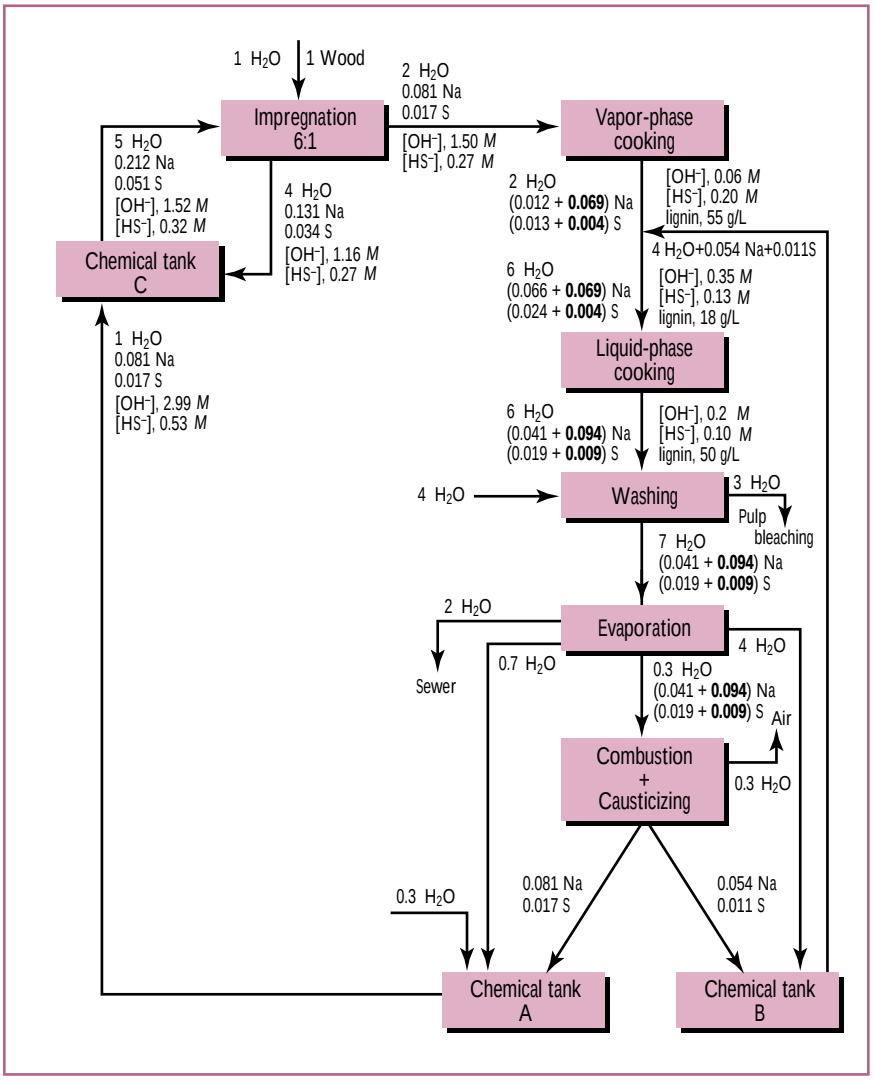
In the case of the impregnation at 90°C, all the procedures were the same as those at room temperature except that, after the application of the external pressure, the autoclaves were put in an electrically heated polyglycol bath at 90°C.

Cooking

The cooking procedure for the modified vapor-phase cook was the same as that described previously *(1)*. The total chemical charge of the



1. Outline of the laboratory procedure for the two-stage modified vapor-phase cook



2. Chemicals and water balances using a conventional white liquor when the impregnation takes place at room temperature. Na and S are the amounts of sodium and sulfur in weight-units per weight-unit wood. Na and S, in boldface, are the Na and S relating to the NaOH and Na_2S which have been consumed in the process. [OH^-] and [HS^-] are the concentrations of total effective alkali and sulfide, respectively.

cook was 22% effective alkali (e.a.) with 30% sulfidity. The "sulfide-rich" liquor with all the sulfide and 60% of the total NaOH was charged in the initial vapor-phase stage and the "sulfide-free" liquor with the remaining 40% NaOH in the liquid-phase stage. The liquor-to-wood ratio in the liquid-phase stage was 6:1. When the drained liquor was recirculated, the amounts of NaOH and Na_2S in the fresh liquor added to the vapor-phase stage were corrected with respect to the amount of residual NaOH and Na_2S in the recirculated liquor.

In the conventional cooks, the chemical charge was also 22% e.a. with a sulfidity of 30%. The liquor-to-wood ratio was 4:1. When the drained liquor was recirculated, extra NaOH was added to the drained liquor in order to have the same charge of alkali and sulfide as the reference.

RESULTS AND DISCUSSIONS

Study of the chemicals and water balances

Results are presented for four separate cases. In the first two cases, the impregnation was carried out at room temperature. In the last two cases, the impregnation was carried out at 90°C in order to simulate a possible industrial impregnation stage. In each case, the results of using a conventional white liquor as well as of using divided white liquors (a "sulfide-rich" and a "sulfide-free" liquor) are reported.

Assumptions made in the calculation of the balances

The calculation of sodium and sulfur as well as of the water balance was based on the following common assumptions in all cases:

1. The dryness of the wood chips is 50%.
2. The total chemical charge is 20% e.a. with 30% sulfidity. In the case of a conventional white liquor,

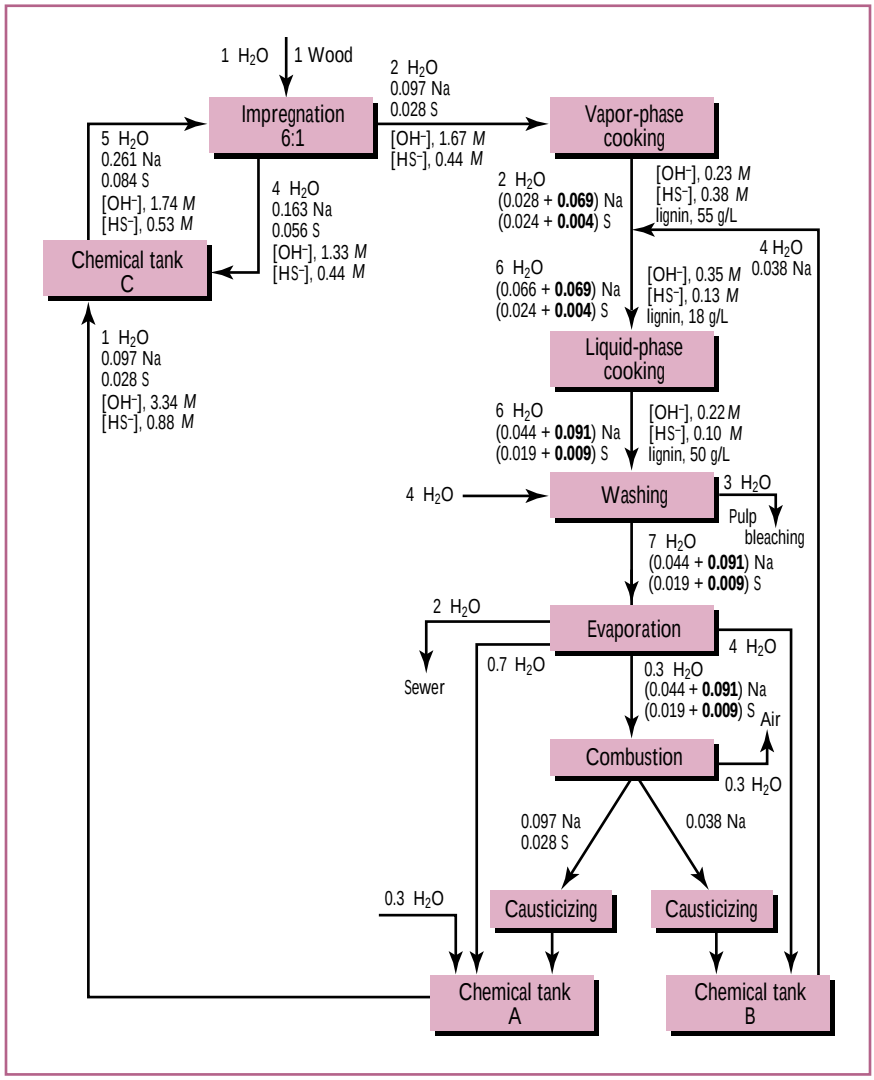
12% e.a. is charged in the initial vapor-phase stage and 8% e.a. in the liquid-phase stage. In the case of divided white liquors, all the sulfide together with 60% of the total NaOH is charged in the initial vapor-phase stage, the remaining 40% NaOH being charged in the liquid-phase stage.

3. Neither sodium nor sulfur is lost from the system. In reality, small amounts are lost in the washing stage, in the evaporation of black liquor and in the recovery furnace, etc.
4. The amount of water existing as steam after the combustion is assumed to go to the atmosphere without any recovery.
5. 70% of the condensate from the evaporation of the black liquor is recirculated, while the remaining 30% is discarded to sewer.
6. The pulp yield after cooking is 45% on charged wood.
7. The dryness of the washed pulp, which goes to the bleaching stage, is 13%.
8. The solids content of the black liquor after evaporation is 71%.

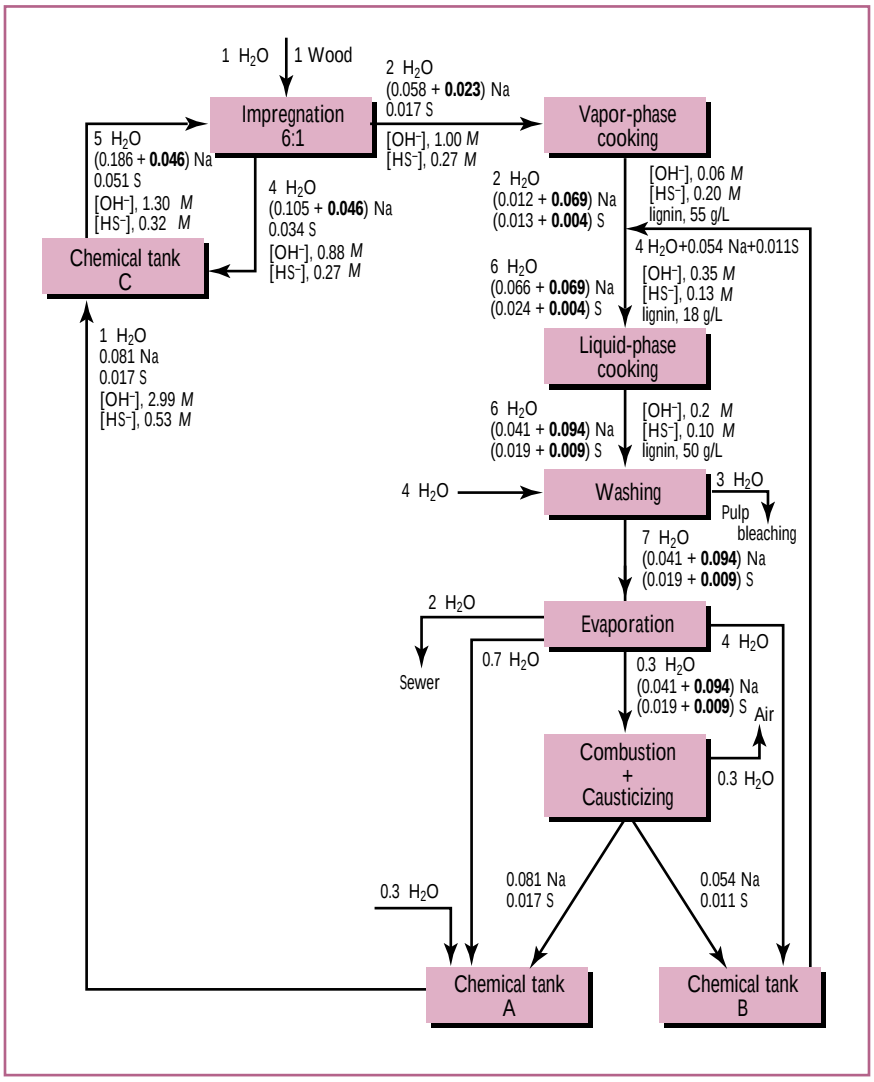
Chemicals and water balances at room temperature impregnation

In this case, it is assumed that neither sulfide nor alkali is consumed during the impregnation. The sulfide concentration inside the impregnated chips is the same as that in the drained free liquor. The concentration of NaOH inside the impregnated chips is, however, 38% higher than that in the drained free liquor due to the phenomenon of OH^- sorption *(1, 2)*. The calculated chemicals and water balances as well as the concentration profiles of alkali, sulfide, and lignin using a conventional white liquor are shown in Fig. 2.

One weight-unit (WU) of wood chips (50% dryness) is first impregnated with 0.212 WU sodium and 0.051 WU sulfur. After the impregnation, 0.081 WU sodium and 0.017 WU sulfur (corresponding to 12% e.a. and 30% sulfidity) and 2 WU water accompany the wood chips into the vapor-phase stage. Because 0.131 WU sodium and 0.034 WU sulfur remain in the drained liquor, it is then mixed with the regenerated fresh cooking liquor and recirculated to the impregnation. After the vapor-phase stage, new white liquor with 0.054 WU sodium and 0.011 WU sulfur as well as 4 WU water is charged to the liquid-phase stage. During the washing stage, 4 WU external fresh water are added. The washed pulp with 3 WU water goes to bleaching proper. The black liquor with 0.135 WU sodium, 0.028 WU sulfur, and 7 WU water goes to the evaporation. In this stage, 6.7 WU water are evaporated from the black liquor. Of the total condensate (6.7 WU water), the most contaminated



3. Chemicals and water balances using divided white liquors when the impregnation takes place at room temperature. Na and S are the amounts of sodium and sulfur in weight-units per unit weight of wood. Na and S, in boldface, are the Na and S relating to the NaOH and Na_2S which have been consumed in the process. $[OH^-]$ and $[HS^-]$ are the concentrations of total effective alkali and sulfide, respectively.



4. Chemicals and water balances using a conventional white liquor when the impregnation takes place at 90°C. Na and S are the amounts of sodium and sulfur in weight-units per unit weight of wood. Na and S, in boldface, are the Na and S relating to the NaOH and Na_2S which have been consumed in the process. [OH^-] and [HS^-] are the concentrations of total effective alkali and sulfide, respectively.

(2 WU water) is discarded. The remaining 4.7 WU purified condensate water goes to dilute the regenerated chemicals, with 0.7 WU in chemical tank A and 4 WU water in chemical tank B. In the combustion stage, 0.3 WU water is evaporated to air. After causticizing, the sodium and sulfur are divided in proportions of 60:40 between the chemical tanks A and B. In the chemical tank A, 0.3 WU external fresh water is added in order to reach the desired chemicals concentration. The chemicals in tank A, after being mixed with the drained liquor from the impregnation in chemical tank C, are charged to the impregnation stage. The chemicals in tank B are charged to the liquid-phase stage. In Fig. 2, Na and S, in boldface, are the Na and S relating to the NaOH and Na_2S which have been consumed in the process. [OH^-] and [HS^-] are the concentrations of total effective alkali and sulfide, respectively.

It can be seen in Fig. 2 that the concentrations of total effective alkali and sulfide in the regenerated liquor to be charged to the impregnation are 2.99 mole/L and 0.53 mole/L, respectively. According to the literature *(3)*, the concentrations of total effective alkali and sulfide in an industrial white liquor can be as high as 4.52 mole/L and 0.65 mole/L respectively. It can thus be concluded that no evaporation of the regenerated white liquor is required in the case studied. A certain amount of black liquor can even be recirculated without going to the chemical recovery loop.

The calculated chemicals and water balances as well as the concentration profiles of alkali, sulfide, and lignin using divided white liquors are shown in Fig. 3. The principle of the calculations is the same as in the case when the conventional white liquor is used. The difference is that the chemicals recovery system must be able to produce a "sulfide-rich" and a "sulfide-free" liquor. In addition, the "sulfide-rich" and the "sulfide-free" liquors are separated after the combustion and then causticized separately. It is known that several processes, such as the cooling crystallization of green liquor *(4)*, the Tampella recovery process *(5)* and the black liquor gasification processes *(6–9)* can produce "sulfide- rich" and "sulfide-free" (or "sulfide-poor") white liquors, although their commercial applications are limited or in the course of development.

As shown in Fig. 3, the concentrations of total effective alkali and sulfide in the regenerated "sulfide-rich" liquor are 3.34 mole/L and 0.88 mole/L, respectively. The higher concentration of total effective alkali in the case of divided liquors obviously results from the

higher sulfide in the liquor. As discussed before, a commercially available chemical recovery process is able to produce a white liquor with concentrations of total effective alkali and sulfide as high as 4.52 mole/L and 0.65 mole/L, respectively.

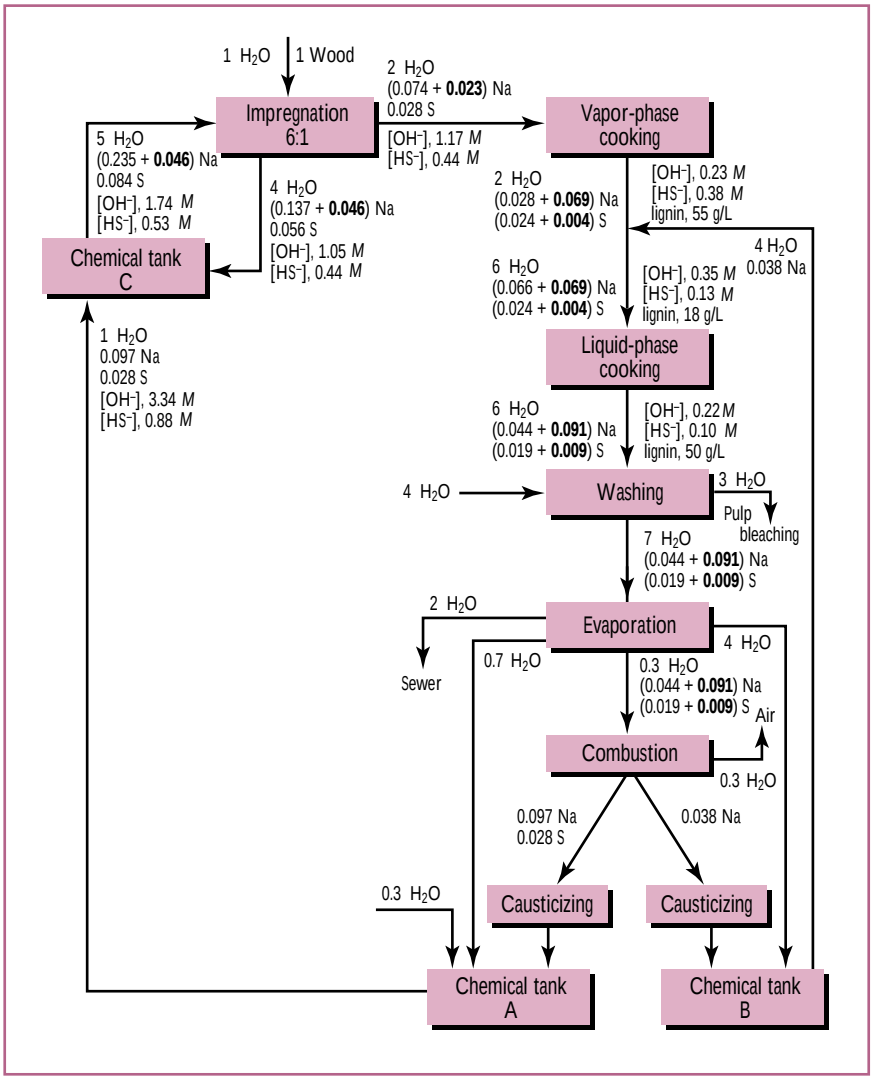
Therefore whether or not the "sulfide-rich" liquor needs evaporation prior to the impregnation is dependent on the chemicals recovery system commercially available in the future. If the future system is able to produce a "sulfide-rich" liquor at a concentration as high as 0.88 mole/L, no evaporation of the liquor will be required. Otherwise, evaporation of the liquor prior to the impregnation will be necessary.

Chemicals and water balances at 90°C impregnation

In order to simulate an industrial impregnation, the impregnation was performed at 90°C in the laboratory. In addition to the common assumptions mentioned before, two more assumptions are made in this case:

1. During the impregnation, no sulfide is consumed, but the consumption of NaOH is assumed to be 4% (based on wood).
2. No other sodium forms, e.g., carbonate, sulfate, etc., existing in an industrial recovery system are included in the calculation.

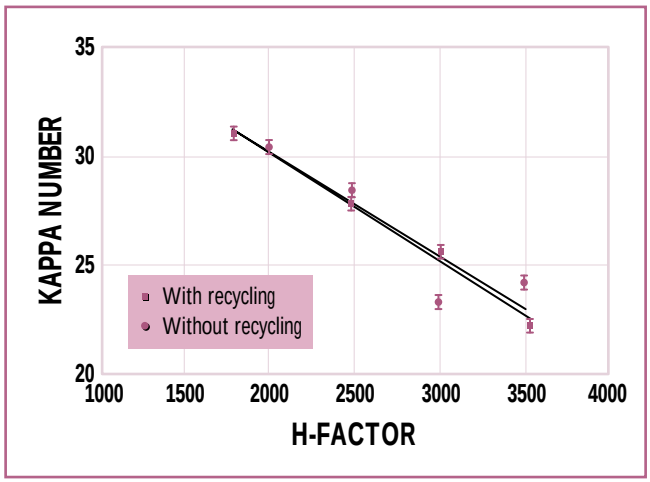
According to these assumptions and the laboratory results, the concentration of alkali (free alkali plus the alkali re-formed later from the reversion of the neutralization which took place by the reaction between dissociated hydrogen ions from the wood and OH^- ions in the impregnation liquor) inside the impregnated chips was calculated to be 20% higher than that in the drained free liquor. Note that the concentration of NaOH inside the impregnated chips is 38% higher than that in the drained free liquor when the impregnation takes place at room temperature. According to our assumptions, the OH^- sorption did not therefore disappear totally after impregnation at 90°C.



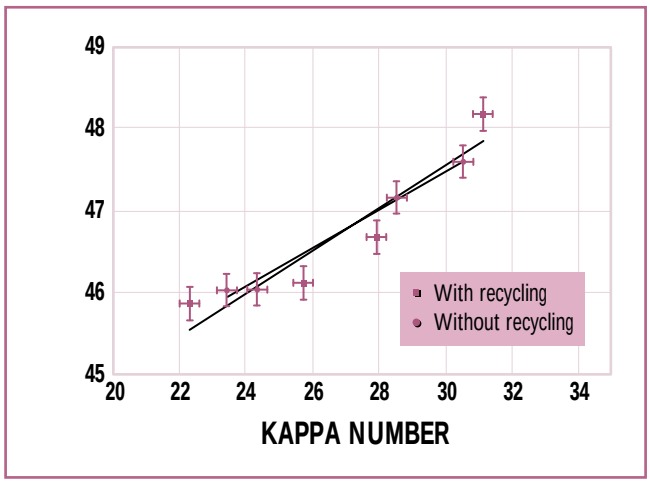
5. Chemicals and water balances using divided white liquors when the impregnation takes place at 90°C. Na and S are the amounts of sodium and sulfur in weight-units per weight-unit wood. Na and S, in boldface, are the Na and S relating to the NaOH and Na_2S which have been consumed in the process. [OH^-] and [HS^-] are the concentrations of total effective alkali and sulfide, respectively.

The consumption of NaOH at 4% (based on wood) was equal to 0.023 units by weight of sodium per unit of wood. When the whole system reaches a balance, the Na consumed during the impregnation must leave the impregnation loop and follow the impregnated chips to the cooking cycle.

The results of the chemicals and water balances as well as of the concentration profiles of alkali, sulfide and lignin using a conventional white liquor and using divided white liquors are shown in Figs. 4 and 5, respectively. As shown in the figures, 0.023 WU sodium was consumed during the impregnation,



6. Effect of recycling the drained liquor on delignification rate in the modified vapor-phase cook



7. Effect of recycling the drained liquor on pulp viscosity in the modified vapor-phase cook

accompanied the impregnated chips and went further to the cooking cycle, while 0.046 WU sodium recirculated in an internal impregnation loop. The change in the impregnation temperature did not influence the concentrations of total effective alkali and sulfide in the regenerated liquors.

EFFECT OF RECIRCULATION OF THE DRAINED LIQUOR FROM THE IMPREGNATION

The drained liquor from the impregnation must be reused in any industrial application of the modified vapor-phase process. It therefore is important to know whether the recycling of the drained liquor influences the subsequent cooking result.

In order to see the effect on cooking selectivity of recycling the drained liquor from the impregnation, the drained liquor (from impregnation at both room temperature and 90°C) was added to the fresh liquor in the modified vapor-phase cook. The cooks without any recirculation of the drained liquor were compared to the cooks with recirculation with respect to pulp viscosity, yield, and delignification rate.

In another series of studies, the drained liquor (from impregnation at room temperature) was also added to a conventional kraft cook, and its influence on cooking selectivity as well as on the delignification rate was studied.

Influence of drained liquor from the room temperature impregnation

In this trial, the drained liquor used is the liquor drained off after the first impregnation at room temperature. The drained liquor contains little organic substance. The most likely reactions taking place at room temperature are the deacetylation and dissolution of extraneous components in the wood chips. As shown in Figs. 6–8, there is no significant difference in delignification rate, pulp viscosity, and yield at a given kappa number between the two-stage modified vapor-phase cooks without any recycling of the drained liquor and those with recycling of the drained liquor.

Table I shows the influence of the drained liquor on cooking selectivity in a conventional kraft cook. The addition of the drained liquor from impregnation at room temperature has almost no effect on pulp viscosity or yield.

Influence of drained liquor from the 90°C impregnation

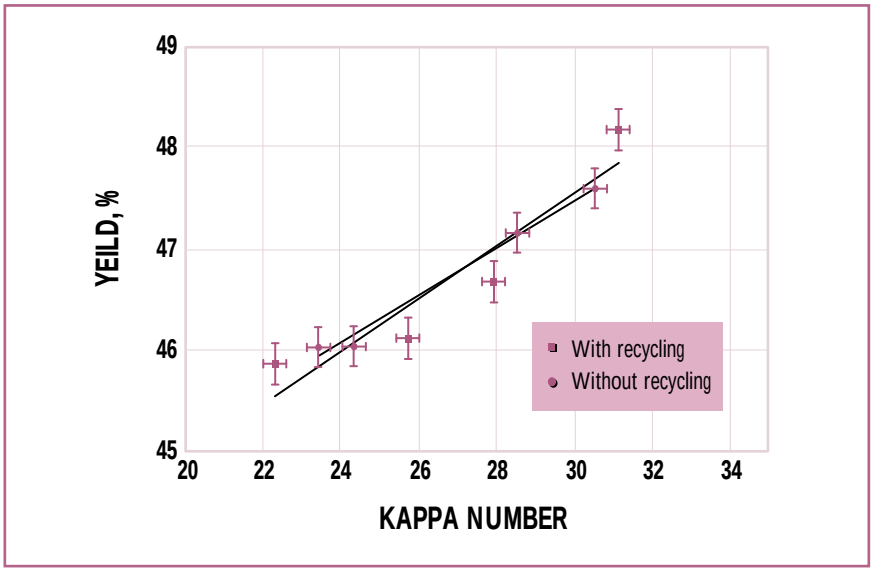
In all the above-mentioned cooking studies, the impregnation was carried out at room temperature. Consequently, the drained impregnation liquor did not contain much organic substance. However, it is unrealistic to carry out the impregnation at room temperature on a large scale. On a mill scale, impregnation will be carried out at higher temperatures and a certain part of the hemicelluloses would be dissolved out of the chips, resulting in some hemicelluloses in the drained impregnation liquor. Some of the dissolved hemicellulose will be readsorbed onto the fibers if the liquor were recycled to the cooking liquor, which might lead to an increase in pulp yield. Dillen and Noréus *(10)* studied kraft pulping with the recirculation of cooking liquor containing hemicellulose. They drained off the cooking liquor at 140–158°C or 165°C for birch and 170°C for pine. The drained liquor was then recirculated back to mix with the initial white liquor.With this technique, an improvement in pulp yield in the range of 1–1.5% (lignin-free yield based on wood) was obtained for birch cooks, and 0.5–1% for pine cooks. Sjöblom *(11)* studied

KEYWORDS
Chemicals, cooking liquors, liquid phases, materials balance, modified kraft process, recycling, sodium, sulfur compounds, two stage process, vapor phase pulping, water, white liquors.

the influence of cooking conditions on the xylan adsorption and pulp yield, and found that the adsorption of xylan onto fibers led to an increase in pulp yield.

Therefore, a new series of impregnation trials were carried out at 90°C in our laboratory in order to see whether the drained liquor from the impregnation at this temperature had any effect on pulp viscosity and yield. Note that another chip sample of the same kind was used in these trials. The effect of the recycled drained liquor on cooking selectivity is shown in Table II. The drained liquor from the impregnation at 90°C after recirculation five times has no significant effect on pulp viscosity or yield. The reason may be that only a small amount of hemicellulose is dissolved during the impregnation at this relatively low temperature.

The content of hemicelluloses increases with increasing recirculation time until an equilibrium is reached in the impregnation loop. It is known that xylan is the main component which readsorbs onto wood fibers and leads to an increase in pulp yield. According to a study by Aurell and Hartler *(12)*, about 1% xylan (based on wood) was lost when pine chips were cooked from 70°C to 100°C within 30 min. If we assume that the loss of xylan during the impregnation at 90°C within 30 min is also 1% and that the dissolved xylan remains stable, the content of xylan in the drained liquor after recirculation five times will be 1.7% (based on wood). When equilibrium is reached, the content of xylan in the drained liquor will be 2% (based on wood). It can thus be claimed that the xylan content in the drained liquor after recirculation five times has almost reached the equilibrium level described. Consequently it can be stated that the recirculation of the drained liquor from impregnation in our modified vapor-phase cooking process will have no significant effect on pulp yield even when equilibrium is reached in the impregnation loop. This expectation is in agreement with the study carried out by Dillén and Noréus *(10)*. According to their study, the increase in yield as a result of recirculation of cooking liquor containing hemicellulose seemed to level out after a five-fold recirculation. In their study, the yield increase at a level of 0.5–1% (lignin-free yield calculated on wood) was obviously due to the fact that the drained liquor in their study (pine wood being first cooked from



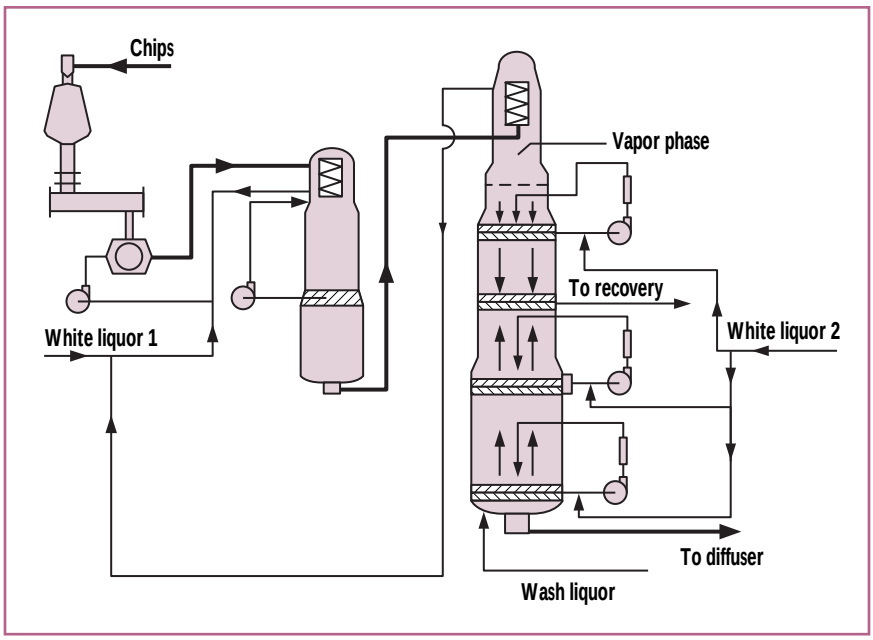
8. Effect of recycling the drained liquor on pulp yield in the modified vapor-phase cook

Cook type	Pulp viscosity, mL/g	Pulp yield, %
Without recycling	995	47.0
With recycling	994	47.0

I. Pulp viscosity and yield at kappa number 30 for the conventional cooks without any addition of the drained liquor and with the addition of the drained liquor

Cook type	Pulp viscosity, mL/g	Pulp yield, %
Without recycling	1007	45.8
With recycling	1000	45.9

II. Pulp viscosity and yield at kappa number 22 for the modified vapor-phase cooks without any recycling of the drained liquor and with a recycling of the drained liquor



9. Sketch of a conceivable continuous industrial system for the modified vapor-phase kraft process

70°C to 170°C within 100 min and the free liquor then being drained off and recirculated) contained much more hemicellulose than in our case when the mixture of pine and spruce was impregnated at 90°C. As shown in the study by Aurell and Hartler *(12)*, about 20% of xylan in pinewood was lost when cooking was performed from 70°C to 170°C within 100 min.

All these results indicate that the recycled drained liquor from impregnation in the modified vapor-phase process has the same cooking effect as the fresh cooking liquor in both the modified vapor phase and conventional kraft cooks.

INDUSTRIAL APPLICATION OF THE MODIFIED VAPOR-PHASE PROCESS

In our previous studies, the modified vapor-phase process either in two-stage or in three-stage has been reported *(1, 13–15)*. A significant improvement in cooking selectivity has been obtained compared to that in a two-stage modified reference with a split charge of white liquor and an exchange of cooking liquor toward the end of the cook. The calculated chemicals and water balances presented here are for simplicity based on a two-stage process. With regard to the industrial application of the process, today's most developed system must be used. In order to elucidate the ways of applying the process on a large scale, a sketch of a conceivable continuous industrial process is shown (Fig. 9). After being presteamed, chips pass through a tramp material separator and a high-pressure feeder, and are first impregnated in a preimpregnation vessel. In this vessel, white liquor 1, either sulfide-rich or with a normal sulfidity, is mixed with the chips. After impregnation, the excess white liquor, after being separated in the top separator in the digester, goes back to mix with fresh white liquor 1. The impregnated chips go to a vapor/liquid phase digester and are subjected to cooking in the vapor phase co-currently followed by two successive co-current liquid-phase cooking zones. The pulp is then cooked and washed simultaneously in the counter-current zones. White liquor 2, either sulfide-free (probably "sulfide-poor" in an industrial application) or with a normal sulfidity, is added to the co-current zone and the counter-current liquid-phase cooking zones. The black liquor after the co-current liquid-phase zones is extracted and goes to the recovery system. The washed pulps go to the diffuser for further washing and then to the bleach plant. As reported earlier *(16–17)*, the temperature in the digester should be kept constant (around 160°C) in order to achieve the best cooking selectivity.

Obviously, the process can also easily be adapted to a modern batch cooking system. The application of the process using divided white liquors on a large-scale relies upon the necessary development in the chemical recovery system.

CONCLUSION

From the chemicals and water balances presented, it can be concluded that when conventional white liquor is used, it is fully possible to supply the various cooking stages with chemicals at the required concentration and it is feasible to apply the modified vapor-phase process on an industrial scale. If divided white liquors are used, necessary developments in the chemical recovery system must be brought to a successful result before a final judgment can be reached.

The recycled drained liquor that will be used in the impregnation stage together with fresh regenerated chemicals has no negative effect on delignification rate, pulp yield, or viscosity in the subsequent cooking. TJ

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