Model-based Kraft Cooking Optimisation

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Summary

A recently proposed model for kraft delignification kinetics is used to generate optimum operating conditions for the production of kraft pulp. In contrast to previous models, the optimal profiles for temperature, [OH\textsuperscript{-}] and [HS\textsuperscript{-}] support the current operating practice in mill digesters. The optimisation results suggest coupling as high a [HS\textsuperscript{-}] as possible with a low [OH\textsuperscript{-}] but not below 0.2 M, at a low temperature for as long a cooking time as practical. It is also shown that the optimal [OH\textsuperscript{-}] conditions depend on whether the [HS\textsuperscript{-}] or the sulfidity is kept constant. These optimisation findings are summarised in a set of updated recommended procedures for industrial digester operation in order to maximise yield and selectivity.

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Introduction

The kraft cooking process has experienced a surge in development during the last few decades. Early results from a series of experiments performed in the 1970’s and 1980’s at STFI and the Royal Institute of Technology in Stockholm, Sweden (Carnó and Hartler 1976; Nordén and Teder 1979; Teder and Olm 1981; Johansson et al. 1984), culminated in a set of operational guidelines known as the modified cooking rules, given that they modify the conventional scheme of a relatively short cooking time at high temperature and a single initial alkali charge. Kovasin and Tikka (1993) and Sjöblom (1997) summarise these general rules which have been a driving force for the development of subsequent modified kraft cooking schemes with commercial names like MCC, EMCC, ITC, LoSolids, Compact Cooking, RDH and SuperBatch. The rules are as follows:

1. The concentration of effective alkali should be low and uniform, i.e. decreased at the beginning and increased at the end of the cook.
2. The concentration of hydrogen sulfide ions should be as high as possible, especially at the beginning of the cook.
3. The concentration of dissolved lignin and the ionic strength should be low, especially in the later part of the cook.
4. The cooking temperature should be as low as possible.

However while the rules are supported by industrial experience, current kraft models are unable to adequately reproduce these results. In a representative selection of previously published kinetic models, Andersson et al. (2002a) shows that they yield very diverse results, and that they do not predict cooking data when following modern cooking procedures even after re-fitting key parameters using modern experimental data. In a subsequent publication, Andersson et al. (2002b) also show that these models are not consistent with accepted practice and modern findings in terms of operational conditions for optimal selectivity, and for some cases are unsuitable for optimisation tasks due to deficiencies in model structure. The importance of reliable models for process optimisation thus gives the motivation to explore the improved kinetic model proposed by Andersson et al. (2003). A successful validation of the optimisation results, ensuring consistency with current knowledge and industrial practice would give an upper limit to any expected performance gains. The model by Andersson et al. (2003) includes expressions for reaction rates for the wood components and a sub-model for the amounts of medium and low-reactive lignin and carbohydrate species depending upon the cooking conditions. The interplay of the kinetic and distribution models, combined with the high dimensionality of the problem makes establishing optimal conditions by pure analytical techniques impractical. Consequently the optimisation potential is explored numerically using the model subjected to a number of operation scenarios.

The important quality parameters for kraft pulp are intrinsic viscosity and pulp yield and these are partly correlated. The intrinsic viscosity gives an indication to the degree of polymerisation (DP) of the cellulose chain. During kraft cooking the chain length is reduced both by peeling reactions that initiate early in the cook from about 100°C and alkaline hydrolysis that requires a higher temperature, about 130°C. The yield loss is due to the degradation of lignin, cellulose and hemicellulose. The cellulose fraction yield loss is principally due to peeling reactions, but parallel alkaline hydrolysis opens up the cellulose chain for additional peeling and therefore both mechanisms are of importance for the resulting pulp yield.

**A new model for kraft cooking kinetics**

An improved model description of the kraft cooking kinetics is presented in Andersson et al. (2003) which in turn owes much to both the Purdue (e.g. Christensen et al. 1983) and the 3-stage (e.g. Gustafson et al. 1983) models. Due to the important role of the model for the ensuring development, a brief summary follows here. The model predicts pulp composition, yield, and pulp viscosity data as a function of time and external cooking conditions. The kernel of the model are the kinetic expressions for lignin, L, cellulose, C, glucomannan, G, and xylan, X. These four components are further divided into three species each, with high, medium and low reaction rates. In total there are twelve reacting species. The model additionally includes a distribution function for the split between the medium and the low-reactive lignin and carbohydrate species. In contrast to earlier models, this model satisfactorily explains laboratory autoclave and circulation cooking data using industrial relevant cooking conditions, as well as the phenomena observed by Lindgren and Lindström (1996) for alkali step changes. The
viscosity model was adopted from Lindgren (1997). Consistency is secured since the pulp composition model partly stems from the same experiments as the viscosity model. The generic structure for the kinetics employed for all species, \( j = 1–3 \), of the four components, \( i = L, C, G, X \), is

\[
\frac{dW_j}{dt} = -k_1 \left( [\text{OH}^-]^a [\text{HS}^-]^b + k_2 \right) W_j
\]

(1)

with \( k_1 = Ae^{-Ea/RT} \). A distribution model gives the proportions of species 2 and 3, which in turn is a function of the current alkali concentrations and temperature. The reasoning behind the proposed mechanism in the distribution model to incorporate varying cooking conditions is the observation that the level at the intersection of the asymptotic data for species 2 and 3 depends on the cooking conditions. For lignin, the intersection is the level where \( L_2 = L_3 \) (termed \( L^* \)) and it is at the same level of lignin for the same cooking condition, irrespective of when it occurs in the cook. The value of \( L^* \) depends on the surrounding conditions according to

\[
L^* = 0.49 \left( [\text{OH}^-] + 0.01 \right)^{-0.65} \left( [\text{HS}^-] + 0.01 \right)^{-0.19} \left( 1.83 - 2.91 \cdot 10^{-5} (T - 273.15)^2 \right)
\]

(2)

The carbohydrates follow the same algorithm, with the corresponding expression for \( CH^* \) given by

\[
CH^* = 42.3 + 3.65 \left( [\text{OH}^-] + 0.05 \right)^{-0.54}
\]

(3)

**Results and discussion**

The remainder of this work uses the model of Andersson et al (2003) summarised in the previous section to generate optimal cooking profiles and compare these quantitative results with the qualitative “modified cooking rules” that are currently in vogue. Formally, the optimisation task involves the selection of the time-varying quantities temperature, \( T(t) \), concentration of hydroxide ions, \( [\text{OH}^-](t) \), and the concentration of hydrogen sulfide ions, \( [\text{HS}^-](t) \), to maximise pulp yield or viscosity given a final kappa number constraint of \( \kappa = 30 \) and cooking time of 300 minutes. This can be written as

\[
\max \left( J_{\text{yield}} = f(T(t),[\text{OH}^-](t),[\text{HS}^-](t)) \right), \text{ subject to } \kappa = 30 \text{ and } t_{\text{final}} = 300
\]

(3)

where the kappa number is related to the lignin content of the pulp according to

\[
\kappa = 500 \cdot \frac{L}{L + CH} + 5
\]

(4)

Some optimisation scenarios considered constant sulfidity as an optimisation parameter where the \( [\text{HS}^-] \) was ratioed to the \( [\text{OH}^-] \), according to

\[
\text{sulfidity} = \frac{2 \cdot [\text{HS}^-]}{[\text{HS}^-] + [\text{OH}^-]} \cdot 100\%
\]

(5)

Since the time-varying nature of the decision variables in Eqn. 3 implies that the optimisation problem is infinite-dimensional, the decision variables were coarsely discretised in time where necessary. As a consequence of the discretisation these optimisations correspond to constant composition cooks or cooks employing very high liquor to wood ratios. Such an optimal profile
will naturally be impractical to implement on a real digester, both since there will be differences in concentration between the bound and the free liquor and due to the excessive number of circulations. Still, the optimal profiles would constitute a theoretical upper limit of the performance gain to be expected.

The exact choice of objective function for the optimisation is debatable and clearly influenced by mill-specific external and/or economic circumstances. Plausible candidates in addition to the considered yield and viscosity are to minimise the consumption of cooking chemicals and energy, improve homogeneity, reduce reject content, and increase production rate. Some of those criteria are treated indirectly such as the production rate is linked to the required cooking time, and the alkali consumption is linked to the selectivity. There are also potential decision variables known to affect the process that are not included in the model, such as ion strength and concentrations of dissolved organic matter. The effect of those is however of smaller magnitude as argued by Lindgren and Lindström (1996) and Sjöblom (1997).

Given the multivariable nature of the complete optimisation problem (Eqn. 3) is difficult to graphically depict, and interpret, the following reduced optimisation problems are presented:

- Optimisation of \( T, [\text{OH}^+] \) and \([\text{HS}^-]\) separately in one stage. The cooking time was adjusted to fulfil the kappa number constraint.
- Optimisation of \( T, [\text{OH}^+] \) and \([\text{HS}^-]\) separately in two stages. The condition in the second stage was adjusted to fulfil the kappa number constraint, i.e. the cooking time was set, typically to \( 2 \times 150 \) minutes.
- Combinations of \( T, [\text{OH}^+] \) and \([\text{HS}^-]\) in one stage. The combination of the decision variables was adjusted to fulfil the kappa number constraint. The cooking time was set, typically to \( 300 \) minutes.

Finally some comments regarding the full optimisation problem are given.

**Effects of temperature, \([\text{OH}^+]\) and \([\text{HS}^-]\) for a single stage**

The effects of the decision variables treated individually on pulp yield and viscosity are shown in *Figure 1(a)-(d)*. The final kappa number is constrained to be 30 implying that the required cooking time varies (as noted in the figure). The observed trends are as expected; yield and viscosity increase with decreased temperature, increased \([\text{HS}^-]\) and decreased \([\text{OH}^+]\) (at constant \([\text{HS}^-]\)).

In the temperature interval studied, the yield increase was about 0.5\% while the viscosity increase was about 140 dm\(^3\)/kg, see *Figure 1(a)*. The temperature influence on the selectivity is principally due to the differences in activation energies \( E_a \) for the lignin yield loss as opposed to those for the carbohydrate yield loss and viscosity loss. It should be noted that the temperature effect for viscosity selectivity was greater than that for yield selectivity due to \( E_a = 169 \) and 145 kJ/mol for carbohydrate viscosity loss and carbohydrate yield loss respectively. Still, both are higher than the 127 kJ/mol for lignin, implying that decreasing temperature will always improve selectivity.

From *Figure 1(b)* it is evident that \([\text{HS}^-]\) has the strongest influence for both yield and viscosity resulting in an increase of about 3.5\% yield units and 400 dm\(^3\)/kg viscosity units over the range of \([\text{HS}^-]\) studied. This is due to \([\text{HS}^-]\) affecting only the lignin degradation as expected since given zeroth-order for the \([\text{HS}^-]\) expression for carbohydrates. Consequently significant
optimisation potential is possible by changing only one of the three studied variables. An increase in [HS'] also allows for a drastically decreased coking time (or higher production or smaller cooking vessels), as seen in Figure 1(b).

The largest yield and viscosity differences for [OH'] at constant [HS'] were about 1.5% yield and 100 dm³/kg viscosity units in the studied interval, see Figure 1(c). Note that an optimum for [OH'] was found at about 0.2 M, i.e. about 8 g/l NaOH, for both yield and viscosity. The decrease in selectivity at too low or too high [OH'] can be traced from the kinetic model structure and parameters. At high [OH'], the carbohydrate degradation was greater than the lignin degradation according to the powers, $a = 1$ for the medium and low-reactive carbohydrate species, i.e. $CH_2$ and $CH_3$, and $a = 0.48$ and 0.2 for the medium and low-reactive lignin species, i.e. $L_2$ and $L_3$, in Eqn. 1. Thus, it is favourable to decrease [OH']. However, at low [OH'], the importance of the constant $k_2 = 0.22$ and 0.42 for $CH_2$ and $CH_3$ while $k_2 = 0$ for $L_2$ and $L_3$ outweigh the effect of the difference in the power $a$. This is explained by the observation that the carbohydrate degradation continues at very low [OH'], while the lignin degradation does not. It should be noted that the mechanisms proposed are somewhat simplified partly due to the complexity arising from the co-existence of the distribution and reaction models. In Figure 1(d) the effect of [OH'] at constant sulfidity (33%) is shown. Obviously, the positive effect of increasing [HS'] accompanying increasing [OH'] even outbalances the harmful effect of using high [OH'] for this case.
Effects of temperature, [OH⁻] and [HS⁻] for multiple stages

The first step towards finding the true time-varying optimal temperature and concentration profiles was made by dividing the cook into just two stages. Andersson et al. (2002b) shows how such a scheme can be extended to multiple stages, thereby approximating the infinitely discretised optimum profile. The result for the 2-stage case for temperature is shown in Figure 2, and for [OH⁻] at constant [HS⁻] in Figure 3 and [OH⁻] at constant sulfidity in Figure 4. The cooking time was 2 × 150 minutes and the kappa number was constrained to \( \kappa = 30 \) by using proper combinations in the first and the second stage. The pulp yield (solid line) and the viscosity (dashed line) against the conditions in the first stage are plotted, augmented with the required conditions in the second stage (dashed-dotted line).

From Figure 2 it can be seen that the highest viscosity was obtained for an even temperature profile, i.e. for \( T_1 \approx T_2 \). However the resulting flat optimum indicates that the potential yield and viscosity gains are small when considering temperature changes alone. It can also be seen that
the temperature dependence of viscosity was marginally larger than that for yield, as expected given the activation energy values. These results indicate that deviations in temperature, provided that they are consistent throughout the vessel, have little influence on the quality of the final pulp.

In contrast to temperature, deviations in [OH\(^-\)] profiling at constant [HS\(^-\)] in two stages as illustrated in Figure 3 was substantial, 1.5% yield units and about 100 dm\(^3\)/kg in viscosity. At the given conditions, optimum yield is where [OH\(^-\)] = 0.30 M and 0.42 M in the first and second stages respectively, while other conditions suggested similar ratios. The steep optimum is obvious from the observations in Figure 1(b), i.e. primarily due to the negative effect of using too high [OH\(^-\)]. If the sulfidity is held constant, the effect on yield and viscosity of profiling the [OH\(^-\)] in two stages is minor as seen in Figure 4. Obviously, when the [HS\(^-\)] also gets involved in the profiling, the effect of alkali profiling is very small.

Figure 2. Yield and viscosity vs. temperature (T) in the first stage for a two stage case (temperature in the second stage is not constant). Kappa number \(\kappa = 30\). Dashed-dotted line is the corresponding temperature in the second stage. Cooking time 2×150 minutes, [OH\(^-\)] = 0.6 M and [HS\(^-\)] = 0.15 M.

Figure 3. Yield and viscosity vs. [OH\(^-\)] in the first stage for a two stage case ([OH\(^-\)] in the second stage is not constant). Kappa number \(\kappa = 30\). Dashed-dotted line is the corresponding [OH\(^-\)] in the second stage. Cooking time 2×150 minutes, \(T = 157^\circ C\) and [HS\(^-\)] = 0.15 M.
Figure 4. Yield and viscosity vs. [OH\(^-\)] in the first stage for a two stage case ([OH\(^-\)] in the second stage is not constant). Kappa number \(\kappa = 30\). Cooking time 2\(\times\)150 minutes, \(T = 152^\circ\text{C}\) and sulfidity = 33%.

Since the carbohydrate (yield and viscosity) degradation is unaffected by [HS\(^-\)], two-stage scenarios at given cooking times employing various combinations of [HS\(^-\)] in the first and second stage will not affect pulp yield and viscosity. However, also pointed out in Andersson et al. (2003) and Lindgren and Lindström (1996), the importance of the [HS\(^-\)] decreases when \(L_3\) becomes larger than \(L_2\). This can be seen in Figure 5 which illustrates the effect of step decreases of [HS\(^-\)] from 0.3 M to 0.1 M at five different times during the cook, ([OH\(^-\)] = 0.15 M, \(T = 170^\circ\text{C}\)). The kappa number constraint (\(\kappa = 20\)) implies that the earlier the step change was performed, the larger becomes the cooking time required. For [HS\(^-\)] step decreases after around 250 minutes, the effect was insignificant, which can also be seen from the yield levelling out. It can therefore be concluded that the [HS\(^-\)] should be kept as high as possible in the initial and bulk periods of the cook, while it is largely irrelevant during the residual period when \(L_3\) is much larger than \(L_2\). This is in agreement with the general rules for improved cooking conditions. Furthermore, since [OH\(^-\)] strongly affects \(L^*\) through the distribution model, it is reasonable to state that maintaining a high [HS\(^-\)] is especially beneficial as long as the [OH\(^-\)] is also kept high.

Figure 5. Left subplot: Lignin vs. cooking time for step decreases in [HS\(^-\)] from 0.3 M to 0.1 M (bold line = no change, thin lines = changes, dashed lines = \(L_2\) and \(L_3\) for no change). Right subplot: Pulp yield vs. time for step change in [HS\(^-\)]. \(T = 168^\circ\text{C}, [OH^-] = 0.1\) M, target kappa number \(\kappa = 20\).
Multiparameter optimisation

Contour plots are a convenient graphical method to visualise two-variable optimisation scenarios. In figures 6-9, the two optimisation decision variables are plotted on each axis with the cooking time constraint superimposed, while the kappa number constraint is fulfilled in the whole domain. In addition the third variable is held constant for each figure. The optima are the values of the two variables under consideration that deliver the highest (yield or viscosity) point on the constraint path.

Figure 6 shows the pulp yield and viscosity for different combinations of [OH⁻] and temperature at constant [HS⁻]. The upper subplots show yield and viscosity for kappa number 30 in the whole domain. This implies that the cooking time required to reach kappa 30 depended on the cooking conditions. It can be seen that, without considering the time constraint, using as low temperature as possible and approximately [OH⁻] = 0.25 M delivered the highest yield and viscosity in the considered variable domain. However when introducing the 300 minute cooking time constraint (dashed line), the optimal solution changes. This is clarified in the lower subplot which replots the yield and viscosity vs. [OH⁻] along the cooking time constraint, augmented with the corresponding temperature. Now the optimum is at [OH⁻] = 0.2 M and $T = 163^\circ C$, which was about 1.5 units higher than the unconstrained yield minimum. For viscosity, the optimum was found at approximately [OH⁻] = 0.4 M and $T = 155^\circ C$, though it was not at all as clear as the optimum observed for yield. However, a significant viscosity loss was observed for [OH⁻] below 0.2 M. Furthermore, the yield loss observed at high [OH⁻] (corresponding to low temperature given a time constraint) was not found for viscosity, primarily due to the differences in activation energy discussed earlier.

Assuming constant sulfidity instead of constant [HS⁻] as shown in Figure 7, (following the same formatting as in Figure 6) gives quite different optimisation response surfaces. Now the lower subplot shows that pulp yield and viscosity increases monotonically with increasing [OH⁻] (and decreasing temperature) due to the effect of the [HS⁻], which increases proportionally with increasing [OH⁻]. However this improvement diminishes at high levels of [OH⁻], because the beneficial effect of increasing [HS⁻] levels out balancing the increasingly harmful effect of the high [OH⁻]. Again, the viscosity was more favoured than the yield at high [OH⁻] (corresponding to low temperature given a time constraint). The viscosity increase was 250 dm³/kg for [OH⁻] = 0.30 to 0.85 M ($T = 170$ to $150^\circ C$), at cooking time 300 minutes. In conclusion, the very different optimal results for the case assuming constant [HS⁻] compared to the case assuming constant sulfidity indicates that one must carefully distinguish exactly what is to be held constant in the cook. The jagged contour curves resulted from the discretisation in the numerical calculations. This phenomenon is present in all contour plots, but it is more pronounced in Figure 7 due to its partly relatively flat surface.
Figure 6. Upper plots: Yield (left) and viscosity (right) vs. $[\text{OH}^-]$ and temperature at constant $[\text{HS}] = 0.15 \text{ M}$ and kappa number $\kappa = 30$. Dashed line is cooking time 300 minute constraint. Lower subplot: Yield, viscosity and the corresponding temperature vs. $[\text{OH}^-]$ at cooking time 300 minutes.

Figure 7. Upper plots: Yield (left) and viscosity (right) vs. $[\text{OH}^-]$ and temperature at constant sulfidity $= 33\%$ and kappa number $\kappa = 30$. Dashed line is cooking time 300 minutes. Lower subplot: Yield, viscosity and the corresponding temperature vs. $[\text{OH}^-]$ at cooking time 300 minutes.
Figure 8 shows yield and viscosity vs. \([\text{OH}^-]\) and \([\text{HS}^-]\) at constant temperature and kappa number. It is evident that the \([\text{HS}^-]\) has the largest effect, more than 5% yield in the response surface plot (upper left subplot). It is also seen that, when considering fixed cooking times, there is an optimal choice of cooking time, i.e. between 300 and 400 minutes for the conditions in Figure 8. Furthermore, the optimum for \([\text{OH}^-]\) is around 0.25 M independent from \([\text{HS}^-]\). Along the 300 minute cooking time constraint, the lower subplots show that, using the present ranges, the yield is more than 5% higher using low \([\text{OH}^-]\) and high \([\text{HS}^-]\), while the viscosity is more than 400 dm\(^3\)/kg higher, compared with the worst case.

Figure 8. Upper plots: Yield (left) and viscosity (right) vs. \([\text{OH}^-]\) and \([\text{HS}^-]\). Temperature 155°C and kappa number \(\kappa = 30\). Fat dashed line is cooking time 300 minutes, thin lines are (dashed) 200 minutes and (dashed-dotted) 400 minutes. Lower subplot: Yield, viscosity and the corresponding \([\text{HS}^-]\) vs. \([\text{OH}^-]\) at cooking time 300 minutes.

The yield and viscosity are plotted vs. \([\text{OH}^-]\) and sulfidity in Figure 9. In this case, using constant sulfidity instead of constant \([\text{HS}^-]\) as presented in Figure 7, the optimum yield and viscosity is found at higher \([\text{OH}^-]\), since the \([\text{HS}^-]\) increases with increased \([\text{OH}^-]\). For a time constraint, however, the gain in yield and viscosity is as expected substantial when using low \([\text{OH}^-]\) and high sulfidity, 4% and 300 dm\(^3\)/kg compared with the worst case, respectively. The yield and viscosity vs. sulfidity data extracted (for cooking time 300 minutes) from Figure 9 is shown in Figure 10 indicating explicitly the possible performance gain in increasing the sulfidity is around 3.5% yield units and 300 dm\(^3\)/kg in viscosity in the studied interval. Note that the composition of the cooking liquor is constant throughout the cook, i.e. also the sulfidity.
Figure 9. Upper plots: Yield (left) and viscosity (right) vs. [OH⁻] and sulfidity at temperature 155°C and kappa number κ = 30. Fat dashed line is cooking time 300 minutes, thin lines are (dashed) 200 minutes and (dashed-dotted) 400 minutes. Lower subplot: Yield, viscosity and the corresponding [HS⁻] vs. [OH⁻] at cooking time 300 minutes.

Figure 10. Yield (solid line) and viscosity (dashed line) vs. sulfidity at the cooking time 300 minutes constraint path in Figure 9. Kappa number κ = 30.

In summary, a succinct description of the optimisation results is complicated by the multivariable nature of the problem, and consequently the plethora of scenarios that can be considered. However these results suggest that of the design variables, [HS⁻] is more important than [OH⁻] which is more important than temperature to achieve high yield and viscosity in the final pulp. The desired (but perhaps unfeasible) working point would be to select as high [HS⁻] as possible, at least during the initial and bulk period of the cook, while the [OH⁻] should be minimised, but
not below 0.2 M. The temperature should be kept as low as possible by using a long cooking time. Furthermore the [OH] and temperature profiles should be even.

**Comparison of optimisation results with accepted practice**

It is interesting to compare the quantitative optimisation results from the previous section with the four generally accepted operational rules for selective kraft cooking outlined in the introduction.

1. **Rule 1 advises to employ low and uniform [OH] profiles.** The results presented in this study suggest that if the sulfidity is constant throughout the cook, the effect of [OH] levelling out between the first and the second part of the cook is very small. However, it becomes important in the case where [HS] is kept constant. While a direct comparison with industrial practice is perhaps unfair, it is reasonable to believe that it falls somewhere between the two studied scenarios – the white liquor has a given sulfidity, but the actual sulfidity during the cooking stages will increase due to the large consumption of [OH] compared to [HS]. The [HS] profile in a mill digester is therefore likely to be approximately constant. Sandström (2000) postulates that the beneficial effect with respect to selectivity primarily was due to the more even [OH] profile. According to the model simulations, the gain reported is primarily due to the decrease of [OH], combined with a longer cooking time (refer Figure 1c), and not due to the uniformity of [OH] itself. The present results also suggest that the [OH] should not be too low as the selectivity deteriorates for [OH] below 0.2 M.

2. **Rule 2 recommends to use a high [HS] during the initial and bulk stages.** Using the distribution model mechanism in the improved kinetic model by Andersson et al. (2003), this rule can be further expanded by adding that high [HS] is beneficial as long as the amount of $L_2$ is significant compared to $L_3$.

3. **Rule 3 recommends to use a low concentration of dissolved lignin and ionic strength during the final part of the cook.** These phenomena were not modelled, and consequently this rule is not addressed.

4. **Rule 4 recommends to use a low temperature.** The present results suggest that levelling out the temperature has a comparatively small effect on the selectivity, while the gain is larger in the case when the cooking time can be increased in order to decrease the temperature.

Another interesting observation from the present results related to the general cooking rules is that, if the sulfidity is constant, the most selective conditions are obtained at low temperature and high [OH]. However, if the [HS] is constant the opposite is suggested, i.e. high temperature and low [OH]. Thus, the current trend in modern cooking techniques, using high alkali concentration combined with low cooking temperature may partly be an effect of the increase of the [HS] when the effective alkali charge is increased. The present results also emphasises the importance of using black liquor impregnation, exploiting the high sulfidity in spent cooking liquors. Another alternative for achieving a high [HS] in the early stages of the cook is to use a white liquor split into one sulfide-rich and one sulfide-poor white liquor, which is possible using e.g. the Tampella recovery process (Hauki 1982) or the black liquor gasification process for chemical recovery (Stigsson 1994).
The beneficial properties of high sulfidity or high [HS]\(^+\) has long been recognised with respect to cooking selectivity although earlier studies report negligible gains above 45-50% (Hart and Strapp 1948; Rydholm 1965; Annergren and Wilhelmsson 1974; Mao 1995). However, these references only discuss the sulfidity of the white liquor whereas the sulfidity increases substantially during an industrial cook due to the high consumption of OH compared to HS. Thus the present results based on simulations of constant composition cooks in one or several stages, suggesting improved selectivity in cases approaching 100% sulfidity, are not in conflict with earlier findings. The suggested response to very high [HS]\(^+\) (or sulfidity) is also supported by the well-known beneficial effect of black liquor impregnation. Moreover, the earlier studies naturally used conventional cooking schemes when establishing the optimal sulfidity levels, which may also mislead any conclusions considering modern cooking schemes.

The present results indicate that the current industrial practice, typically not employing a white liquor sulfidity above about 40%, appears arguable. In fact, in many cases the pulp mills are significantly below this number. There are several possible more or less well-founded reasons for this, of which the following are considered to be most problematic. (i) increased odor problems, (ii) increased SO\(_2\)-emissions from the recovery boiler, (iii) increased corrosion in the recovery boiler, and (iv) decreased recovery capacity. The environmental aspects (i, ii) as well as the corrosion problem (iii) can be solved using modern technology and equipment, e.g. recovery boilers using high dry solids black liquor, scrubbers decreasing the SO\(_2\)-emissions, and more corrosion resistant material can be used though the material cost is higher. Furthermore, the recovery capacity issue (iv), referring to decreased effective alkali, is probably of minor importance, since an increased [HS]\(^+\) accompanied with a decreased [OH] actually is suggested being more beneficial according to the present results, which is also reported by Rydholm (1965). Using a higher liquor to wood ratio will also prevent the [OH] from dropping too low, which would result in worse selectivity.

When considering the optimisation implications from this work, one should remember that all results are generated from the kinetic model, and therefore will be constrained by its possible limitations. The model was however fitted and validated using various cooking schemes, employing cooking conditions from a large variable space. There are naturally also other objectives than selectivity that must be considered in terms of an optimal cooking process, such as impregnation and homogeneity, and chemical and heat economy. For the case of an existing continuous digester, one would ideally implement the improved kinetic model as part of a complete industrial digester model such as that developed by Kayihan (2002), including mass transfer at the chip scale and the digester scale, for off-line optimisation of liquor charging and circulations, temperature profiling etc.

**Conclusions**

This work explores cooking selectivity optimisation scenarios based on a new kinetic model for kraft cooking. The results were compared, and found consistent to, the generally accepted rules for selective kraft cooking. This work, based on the numerical optimisation, modifies these cooking conditions to be: (i) use as high [HS]\(^+\) as possible, by means of increased sulfidity, extensive black liquor impregnation, and perhaps also split white liquors in order to charge as large part as possible of the HS in the early stages of the cook. (ii), use low [OH], but not below 0.2 M, if the [HS]\(^+\) is constant throughout the cook. However, given a certain sulfidity throughout the cook, the [OH] (and subsequently the [HS]\(^+\)) should be high. The temperature should be as
low as possible, and will in practice be constrained by the available capacity, i.e. size, of the digester, and the demands on the production.

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List of symbols

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<td>$k_1$, $k_2$</td>
<td>rate constants</td>
<td>e.g. M$^{-1}\text{min}^{-1}$</td>
</tr>
<tr>
<td>$A$</td>
<td>pre-exponential factor</td>
<td>e.g. M$^{-1}\text{min}^{-1}$</td>
</tr>
<tr>
<td>$E_a$</td>
<td>activation energy</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
<td>kJ/(mol K)</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>kappa number</td>
<td></td>
</tr>
<tr>
<td>$W_{ij}$</td>
<td>species $j$ of wood component $i$</td>
<td>kg, % on wood</td>
</tr>
<tr>
<td>$L$</td>
<td>lignin</td>
<td>kg, % on wood</td>
</tr>
<tr>
<td>$CH$</td>
<td>carbohydrates</td>
<td>kg, % on wood</td>
</tr>
<tr>
<td>$C$</td>
<td>cellulose</td>
<td>kg, % on wood</td>
</tr>
<tr>
<td>$G$</td>
<td>glucomannan</td>
<td>kg, % on wood</td>
</tr>
<tr>
<td>$X$</td>
<td>xylan</td>
<td>kg, % on wood</td>
</tr>
</tbody>
</table>

References


