Understanding the Foaming and Dynamic Behavior of Black Liquor Components

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Key words:
Pulp washing, black liquor, foaming, surface tension, foam control, antifoam, silicone

Abstract

Model black liquor systems have been studied using the Design of Experiments methodology (see “Materials and methods”) to identify the relationship between the key constituents and the foaming characteristics of black liquor. A clear relationship has been established between the foaming tendency and the dynamic surface tension at appropriate time scales. The study showed that fatty acids content was the key influencing factor. The effect of neutral components was observed only in more highly dynamic conditions and at a low level of fatty acids. The influence of resin acids level may be significant in extreme dynamic conditions but was not observed in the foaming conditions. Lignin and sugar had no influence on the foaming behavior of black liquor. The results from this study may be used to accelerate the development of foam control agents for specific black liquors based on their unique compositions and surface active properties.

Introduction

Unwanted foaming at various locations in the pulp washing line and black liquor processing causes costly production disturbances and chemical consumption in pulp mills. The economical importance of efficient foam control has caused increasing interest in studying the role of process conditions in foaming. While commercially available foam-controlling additives are widely used in kraft pulp mills, little is known about the roles of various chemical components of black liquor in forming and stabilizing foam in various process stages.

Black liquor is a very complex and versatile system. It is composed of soluble and colloidal organic and inorganic components coming from the digestion of wood and extracted in the aqueous media from the cellulose fibers during the washing process. The following families of substances compose black liquor: degraded lignin, extractable soap or tall oil, hemicellulose and hydroxyl acids, and many species of inorganic components such as NaOH, Na₂CO₃, Na₂SO₄, Na₂S, and small amounts of Ca, Mg, Si, etc. Depending on the type, age, and season of the wood feedstock, the digestion and washing process, and the location on the washing line, the composition of black liquor can vary considerably. Extensive work has been carried out to characterize strong black liquor, primarily to optimize the recovery of cooking chemicals and combustion properties. The extractives in black liquor have also been well described. Their solubility behavior in black liquor in relation to pulp-fiber washing efficiency has been the object of many studies. These extractives, more commonly described as crude tall soap-forming micelles, are composed of mixtures of fatty acids, resin acids, and what have been referred to as neutral components. Fatty acids are a mixture of saturated and unsaturated straight 16- to 24-carbon chains with a predominance of C₁₈ acids such as linoleic and oleic. Resin acids are present in relatively higher amounts and also larger numbers in softwood black liquor; abietic, dehydroabiatic, isopimaric, and palustric acids are the most representative. The neutral components are also a mixture of a large variety and number of sterols and di- and tri-terpenyl alcohols. In many hardwoods, sistosterol is the major sterol. These extractives are an important part of the surface-active components in the liquor and generate and stabilize foam. However, it is less clear which part of the soap provides the most relevant effect on foam stabilization. Also, the influence of the lignin- and carbohydrate-based components on black liquor foaming is not clearly understood. These macromolecules can, similar to proteins, be adsorbed at the foam interface to stabilize it, increasing surface viscosity.

This study is part of a larger research project to characterize and understand the relationship between black liquor composition with its foaming characteristics, and the performance of foam control agents. The ultimate aim is to develop tools to predict the foaming characteristics of black liquor coming from various geographic areas based on simple analysis and to be able to select the most suitable foam control agent for a specific system. The present paper discusses the first part of the study, which relates the variation of black liquor composition to the dynamic surface properties and foaming characteristics. A subsequent study on the influence on black liquor composition

* Foam Control R&D project leader, Dow Corning Europe S.A. BELGIUM (email: chamee.chao@dowcorning.com)
** Foam Control Technologist, Dow Corning Europe S.A. BELGIUM (email: laurent.vermeire@dowcorning.com)
*** Senior Consultant, SciTech-Service Oy Ltd., FINLAND (email: torolf.laxen@scitechservice.com)
on the performance of foam control agents, in particular silicone antifoams, will be published in due course.

This study uses the Design of Experiments method to analyze the influence of the level of each selected component in black liquor model systems. The present study has specific relevance for softwood kraft black liquor but could be extrapolated to hardwood liquor as well. More species-specific relevancy needs to be demonstrated, for example, certain eucalyptus or acacia species.

Materials and methods

Design of Experiments (DOE):
Design Expert 6.0.5 software, supplied by Stat-Ease, was used. D-Optimal designs were chosen. Analysis of models providing significant model terms and insignificant lack of fit was used to predict the effect of each factor. The graphs reported in this paper include:

Contour response surface curves (figures 4, 6, and 8), which provide a two-dimensional representation of the response for selected factors, with the DST value displayed on each line of the contour curves, and

Perturbation plots (figures 2 and 3), which show the effect of all the factors at a particular point in the design space. The response was plotted by changing only one factor over its range while holding other factors constant. By default, as in the case shown here, the Design Expert software set the reference point at the midpoint (coded 0) of all the factors. A steep slope or curvature in a factor showed that the response was sensitive to that factor. A relatively flat line showed insensitivity to change in that factor.

Model black liquors:
The components used to prepare model black liquors included:

Fatty acids and resin acids mixtures, supplied from the tall oil distillery of Forchem Oy in Finland. The fatty acids mixtures, named FOR2, was mainly in C₁₈ with 38% linoleic and 32% oleic acids. The resin acids, named FOREXT 35, was a mixture with main components of 39% abietic acid, 20% dehydroabietic acid, and 11% palustriic acid.

In DOE 1, oleic and abietic acids were used as models for the fatty acids and resin acids mixtures respectively. The oleic acid was supplied by VWR and the abietic acid by Sigma Aldrich.

Neutral components, supplied as Neutoil from UPM Kaukas. The main components were sitostereol (26%), sitostanol (6.6%), methylene cycloartanol (6%), and squalene (5.6%).

Lignin was Indulin C, a sodium salt of kraft pine lignin, supplied by MeadWestvaco.

Table sugar (saccharose), supplied from a domestic store.

Sodium hydroxide and sodium carbonate, from VWR.

All model liquor formulations were prepared using 1.3% NaOH, 2.0% Na₂CO₃, and de-ionized water. When neutral components were present, they were pre-dispersed in the fatty acids at 60°C at a weight ratio of neutrals versus fatty acids of 1:1. Each component was then successively dissolved in the alkaline solution at 80°C under vigorous agitation at a level as defined in the design plan. The liquor was kept at 80°C overnight to ensure optimal dissolution.

DOE 1 was a 25-run design with three repeated points and four factors:
A. Oleic acid (0 to 0.2%)
B. Abietic acid (0 to 0.2%)
C. Sugar (0 to 2.6%)
D. Lignin (0 to 10%)

No neutral component was used.

DOE 2 was an 18-run design with three repeated points and three factors:
A. Fatty acids (0.1 to 0.5%)
B. Resin acids (0.1 to 0.3%)
C. Neutrals (0.02 to 0.1%)

The levels of lignin and sugar were kept constant at 5% and 1.3% respectively.

Dynamic surface tension (DST):
A Sita Science Line T60, based on the maximum bubble pressure technique, was used to measure the DST over a bubble life of 30 milliseconds to 30 seconds. All measurements were carried out at 80°C.

Foamability:

Sparge test (figure 5). Using a jacketed glass foam cell at 80°C, 500 milliliters of liquor were sparged using an aquarium diffuser with a controlled air flow rate of 1.6 liters/minute. Foam levels were recorded every 0-second interval. Each experiment was repeated two or three times. The average of foam height versus time was reported. The slope of the linear portion of the curve was used as the foamability response for the design expert analysis, expressed in milliliters/second.

Recirculation pump test (figure 7). 850 grams of liquor were recirculated through a jacketed glass foam cell at 80°C. The recirculation pump frequency was adjusted to study different shear rates. The results discussed were measured at 20 Hertz (1400 grams/minute recirculation rate). The foaming response that was analyzed in the Design Expert software was the foam rising time, which was the time (in seconds) for the foam to reach 28 centimeters in the foam cell column.

Black liquor from mill:
Analysis of the black liquors was carried out by Nablabs of Finland, using their laboratory testing methods.
Table 1: Analysis of various samples of black liquor first and second washer filtrate tanks of various mills

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Dry Solid, %</th>
<th>Lignin, %</th>
<th>Tall Oil, %</th>
<th>Fatty Acids, %</th>
<th>Resin Acids, %</th>
<th>Neutrals, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood superbatch mill – 1st washer filtrate - sample 1</td>
<td>11.72</td>
<td>4.83</td>
<td>0.51</td>
<td>0.32</td>
<td>0.13</td>
<td>0.07</td>
</tr>
<tr>
<td>Softwood superbatch mill – 1st washer filtrate - sample 2</td>
<td>12.8</td>
<td>4.73</td>
<td>0.38</td>
<td>0.20</td>
<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td>Softwood superbatch mill – 1st washer filtrate - sample 3</td>
<td>11.8</td>
<td>5.00</td>
<td>0.68</td>
<td>0.44</td>
<td>0.21</td>
<td>0.02</td>
</tr>
<tr>
<td>Softwood superbatch mill – 1st washer filtrate - sample 4</td>
<td>13.5</td>
<td>N.A.</td>
<td>0.65</td>
<td>0.26</td>
<td>0.33</td>
<td>0.07</td>
</tr>
<tr>
<td>Softwood superbatch mill – 1st washer filtrate - sample 5</td>
<td>11.8</td>
<td>N.A.</td>
<td>0.68</td>
<td>0.44</td>
<td>0.21</td>
<td>0.02</td>
</tr>
<tr>
<td>Softwood superbatch mill – 2nd washer filtrate - sample 2B</td>
<td>7.26</td>
<td>2.38</td>
<td>0.64</td>
<td>0.42</td>
<td>0.16</td>
<td>0.07</td>
</tr>
<tr>
<td>Softwood superbatch mill – 2nd washer filtrate - sample 1B</td>
<td>6.31</td>
<td>2.17</td>
<td>0.30</td>
<td>0.18</td>
<td>0.07</td>
<td>0.06</td>
</tr>
<tr>
<td>Birch superbatch mill – 1st washer</td>
<td>12.2</td>
<td>4.74</td>
<td>0.25</td>
<td>0.16</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>Birch continuous mill – 1st washer</td>
<td>5.1</td>
<td>1.69</td>
<td>0.31</td>
<td>0.18</td>
<td>0.08</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Results and discussion

Selection of the components and concentration variations.

The following components were selected for this study:

Fatty acids and resin acids of the extractive components are surface-active components and could play an important role in the foaming of black liquor.

The neutral components are described to interact with the fatty acids and resin acids and could also influence the foaming.

The lignin and soluble carbon hydrates could also contribute to the black liquor foaming properties by increasing the surface viscosity.

Foam issues appeared more severe in stage 1 or 2 of the washing process. Table 1 shows the analysis of various black liquors from real mills.

The analytic results were used to define the respective concentration levels used in the DOE:

A. Fatty acids from 0.1 to 0.5%
B. Resin acids from 0.1 to 0.3%
C. Neutral components from 0.02 to 0.1%
D. Lignin from 0 to 10%
E. Sugar from 0 to 2.6% (estimation based on literature data)

The level of alkali and ionic strength was kept constant, using 1.3% NaOH and 2.0% Na₂CO₃ across all the design experiments. This level was selected to represent the ionic strength commonly encountered between washers 1 and 2 in real mill conditions and to provide good soap solubility.

Various DOE methods were conducted and showed consistent trends.

Dynamic surface tension (DST).

Previous studies to characterize the black liquor air-liquid interface were in most cases conducted under equilibrium conditions (giving static surface tensions). The washing process, foaming, and foam control in the washing line are very dynamic processes; therefore, it was very important to characterize the system in a dynamic mode as well. The principle of maximum bubble pressure to measure DST in various bubble formation time scales was used.

Figure 1 shows some examples of DST curves measured for bubble life, with time going from 30 milliseconds to 30 seconds. The surface tensions near to the equilibrium are very similar for all samples. The fact that some curves cross suggest that variation of the surface tensions is dependant on the bubble lifetime scale, a reflection of the adsorption rate of the surface-active molecules present in the system.

Questions raised include:

- How do the black liquor components influence the DST at the various time scales?
- Which time scales are relevant for the washing application and for the lab testing that are used to assess the foaming characteristics and foam control chemical performance?
In DOE 1, the influence of the levels of oleic acid (factor A, varying from 0 to 0.2%), abietic acid (factor B, varying from 0 to 2.6%), sugar (factor C, from 0 to 0.2%), and lignin (factor D, from 0 to 10%) on the DST were found to be similar. In this experiment, no neutral component was evaluated. In DOE 2, more representative component mixtures, coming from a tall oil distillery, were used. The levels of fatty and resin acids and neutral components were evaluated. The levels of fatty and resin acids evaluated were increased versus those in DOE 1; however, as can be seen in figure 3, the dependency of the time scale of the effects of a fatty acids and resin acids mixture on the DST were found to be similar.

Figure 2 shows the influence of each factor separately on the DST at 50 milliseconds, 110 milliseconds, and 500 milliseconds of bubble life. In DOE 1, the abietic acid (factor B) shows strong influence at a short time scale (50 milliseconds), while the effect of oleic acid (factor A) became more pronounced at longer time scales and predominant as the time scale moved closer to equilibrium (from 500 milliseconds and above). In all cases, no major influence of the sugar (factor C) and of the lignin (factor D) was observed.

In DOE 2, more representative component mixtures, coming from a tall oil distillery, were used. The levels of fatty and resin acids and neutral components were evaluated. The levels of fatty and resin acids evaluated were increased versus those in DOE 1; however, as can be seen in figure 3, the dependency of the time scale of the effects of a fatty acids and resin acids mixture on the DST were found to be similar.

Figure 2: Perturbation curves calculated by the Design Expert software from the DOE 1 experiment, showing the influence of variation of levels of oleic acid (factor A), abietic acid (factor B), sugar (factor C), and lignin (factor D) on the DST at 50, 110, and 500 milliseconds.

Figure 3: Perturbation curves calculated by the Design Expert software from the DOE 2 experiment showing the influence of variation of levels of fatty acids (factor A), resin acids (factor B), and neutrals (factor C) on the DST at 50, 110, and 500 ms.
Figure 4: Contour response surface curves for prediction of the DST at 50, 110, and 500 milliseconds: A. Influence of the fatty and resin acids; B. Influence of the fatty acids and neutrals

The contour response curves in figure 4A more clearly show that the influence of resin acids on DST is significant at a short time scale and becomes less significant at longer time scales.

Figure 4B shows that the neutral components level has some significant influence on the DST. The increase of neutrals increases the surface tension, but this effect is pronounced only at a short time scale and becomes less significant at longer time scales. Indeed, only a small effect is observed at 550 milliseconds and above.

Influence on foaming formation rate.

Foaming tendencies of model black liquor systems were measured by two methods: one for low-shear conditions using a sparging (bubbling) method; the second for higher-shear conditions using the liquor recirculation method.

Sparging (bubbling) method. Figure 5 shows the foam increase rates of some model systems using the sparging method.

For this experiment, the slope of the linear domain of each curve illustrates the response to foamability or foam formation rate in the design analysis with the higher slope corresponding to a faster foam formation rate. The response curves in figure 6 (page 8) show the limited influence of resin acids level variation on the foambility, the main factor being the level of fatty acids present.

The level of neutral components appears to have little impact on the foam formation rate.

Figure 5: Foam formation rate using the sparge test for DOE 2
Relationship between foam formation rates and DST.

Similar trends were observed on the effect of the various components on the foam formation rate using sparging or recirculating methods and on the DST. Indeed, the sparging foaming rate behaved very similarly to the DST at 550 milliseconds, while the trends for the recirculation foaming rate were very similar to the DST at 0 milliseconds. The correlations thereafter confirmed the relationship.

Correlation between DST and foaming. Correlation graphs were plotted between the DST at various bubble lifetimes and the foaming rate of the experimental model systems. Figure 9 shows that the best correlation was obtained for the DST at 500 milliseconds bubble lifetime, which is probably the time scale that equals the dynamic conditions present in the sparging method.

A similar correlation was carried out for the recirculation foaming method. As shown in figure 0, the best correlation was the time found at around the 0-millisecond time scales. This suggests that the recirculation method represents

Recirculation method. The foam formation rates using the recirculation equipment for the DOE 2 model systems are shown in figure 7.

For this series of foaming rates, the time for the foam level to reach 28 centimeters in the glass foam cell column was utilized with shorter times indicating faster foam formation. As shown in figure 8, the response curves analyzed by the Design Expert software showed the same trends as the sparging method. The fatty acids level appeared again to be the key factor influencing the foam formation rate, whereas the resin acids level had little influence on the foam formation rate by recirculation. The increase of the neutral components reduced the foam formation rate, but this effect was more pronounced at a low level of fatty acids. Very similar trends were observed when the time for the foam level to reach 25 centimeters was chosen.

Figure 7: Foam formation rate using the recirculation test for DOE 2 at 20 Hz pump rate
Figure 8: Contour response surface curves for prediction of the foam formation rate (time to reach 28 cm) by the recirculation method at 20 Hz: A. Influence of the fatty and resin acids; B. Influence of the fatty acids and neutrals

Figure 9: Correlation between the foam formation rate by sparging and DST at various time scales

Figure 10: Correlation between the foam formation rate by recirculation and DST at various time scales

Conclusions and future work

DOE analysis using model systems carried out in this study clearly shows the influence of the variation in the black liquor components on its foaming tendencies. This can be directly correlated with the DST, provided that an appropriate range of time scales are used to represent the dynamic conditions of the foaming process.

The sparging method was found to provide a foaming process at a lower dynamic condition than the recirculation method, as would be expected.
method. The sparging foam formation correlated well with the DST at 500 milliseconds, while the recirculation method matched well with DST at 110 milliseconds, with a shorter time scale. The fatty acids were found to be the main factor influencing the foam formation rates of black liquors. The neutral component was found to reduce the foaming tendencies, but this effect was significant only at a higher dynamic foaming condition and at a low level of fatty acids. The influence of resin acids was very low with the two foaming processes evaluated, but based on the DST, it could become significant and even predominant at an extreme dynamic condition. Finally, the variation of the levels of lignin and the sugar showed no significant influence on the black liquor dynamic properties.

These results increase significantly the understanding of the cause of foaming problems in kraft pulp mills and provide a good basis to understand how to solve these challenges in a more cost-effective way. Indeed, the results generated here will be used to evaluate the influence of the dynamic behavior of black liquor components on the performance of foam control agents. The overall work can allow simplified and more effective selection of a foam control agent and reduce costly testing on line.

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Bibliographic references


11 Nablabs Laboratories – Nab labs Process Analytics, Tikkalantie 2 Box 142, FI-26100 Rauma, Finland (www.nablabs.fi).
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Australia & New Zealand
Dow Corning Australia Pty. Ltd.
Tel: +61 1300 360 732

Europe
Dow Corning Europe – Belgium
Tel: +32 64 88 80 00
Dow Corning Ltd. – UK
Tel: +44 1676 528 000

North America
Dow Corning Corporation – USA
World Headquarters
Tel: +1 989 496 7881 (Customer Service)
Tel: +1 989 496 4000 (Corporate Center)

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Dow Corning do Brasil Ltda.
Tel: +55 19 3887 9797

Dow Corning Technical Information Centers

The Americas
+1 989 496 6000, or
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