A NEW APPROACH TO DEWATERING BLACK LIQUOR

1. **Sujit Banerjee,** , School of Chemical & Biomolecular Engineering, Georgia Tech, Atlanta, GA 30332

2. **Bhima Sastri,** US Department of Energy, 19901 Germantown Road, Germantown, MD 20874

3. **Osei Asafu-Adjaye,** Forest Products Development Center, Auburn University, Auburn, AL 36849

4. **Brian Via,** Forest Products Development Center, Auburn University, Auburn, AL 36849

Abstract:

Currently black liquor in a pulp mill is concentrated to high solids using multiple effect evaporators. This work reviews a new technique whereby the black liquor is exposed to supercritical CO_2 which deposits solids from the liquor and creates a porous liquid/solid matrix. The CO_2 then displaces water from the matrix at sub-boiling temperatures, thereby saving substantial energy. Thus, the supercritical CO_2 performs a dual role of generating a porous matrix from black liquor and then dewatering it. The amount of water removed is proportional to the boiling point rise of black liquor. This opens the possibility of replacing one or more later stages of a multiple effect evaporator with a supercritical CO_2 dewatering unit. A similar approach applies to lignin deposited from black liquor for use as biofuel. Porosity appears to control displacement efficiency, with the process being more facile for open structures.

Keywords: Black liquor, Lignin, Supercritical CO_2, Evaporators, Dewatering

Introduction:

Black liquor must be concentrated to over 65% solids prior to combustion and its concentration in multiple effect evaporators is an integral part of pulp mill operations. Energy-efficient dewatering of black liquor is, therefore, an industry priority. Non-evaporative techniques such as membrane separation have been studied [1] but have yet to find commercial acceptance. This paper provides a mini review of a new approach where a part of the water in strong black liquor is simply pushed out by supercritical (sCO_2) at sub-boiling temperatures.

Recent work has shown that sCO_2 can displace water from porous structures such as wood, coal, and sludge, thereby conserving the cost of evaporation [2-6]. Water is displaced by sCO_2 through viscous fingering, which is caused by the viscosity difference between sCO_2 and water [7]. This difference causes "fingers" of sCO_2 to enter the porous structure and displace the water. Much work on the process has been spurred by current activity in enhanced oil recovery, where sCO_2 is injected into subterranean water-saturated porous rock to displace oil.

Experimental

As this is a review, detailed experimental details are not provided, but can be found in references 2-5. Briefly, a sample of black liquor is placed inside a lab-scale sCO_2 extraction unit. The chamber is charged with sCO_2 at 90°C and 8.3 MPa (optimum) for about 20 minutes and the moisture content of the sample determined before and after measurement. The decrease in moisture content is sensitive to temperature, but not as much to pressure.

Results and Discussion

Black liquor is not intrinsically a porous structure, but solids separate out when the pH is taken below the pKa values of some of the phenolic groups of lignin. Zhu and Theliander have shown that reducing the pH from 11 to 9.5 raised filtered black liquor solids from 34 to 78% [8]. Hence, the sCO_2 performs two functions: it first generates solids thereby creating a porous matrix, which it then dewaters.

The efficiency of sCO_2 dewatering efficiency is relatively insensitive

to pressure, and the 8.3 MPa value is just above the supercritical pressure. Higher values would raise capital costs without an equivalent benefit. Increasing the temperature increases dewatering efficiency. A value of 90°C was chosen to be below the boiling point of water under standard conditions. However, this value could be raised for strong black liquor, which boils at higher temperatures. Typical results from dewatering black liquor are illustrated in Figure 1. Experimental details are found in Asafu-Adjaye et al. [9]. The term x represents the nominal (both dissolved and entrained) mole fraction concentration of water in sCO_2 under the conditions used. The mole fraction solubility limit of water in sCO_2 at 8.3 MPa and 90 °C is 0.023 [10], so the 90 °C values in Figure 1 are well above the solubility limit. The range of water removal is broadly consistent with those obtained with sludge, wood, and coal. As before, an increase in temperature improved extraction efficiency because it reduces sCO_2 viscosity and increases the viscosity difference between sCO_2 and water [7].
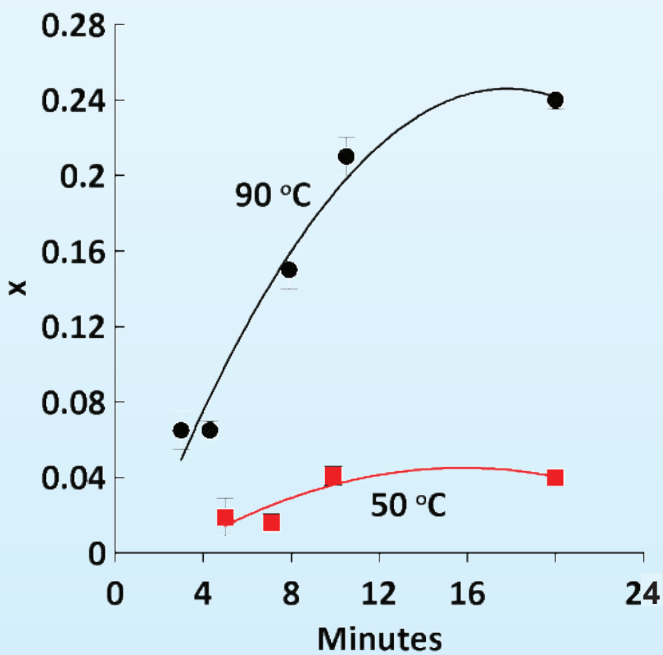

Figure 1. Dewatering black liquor (dry basis moisture content of 61-74%) by sCO_2 at 8.3 MPa.

CO_2-induced precipitation of lignin from black liquor has been studied extensively [11, 12] as a part of the LignoBoost process. The onset of precipitation is rapid, followed by agglomeration into larger particles, with the particle size increasing with time [13, 14]. The process described here combines several steps that must occur during the time frame of the extraction, namely the precipitation of solids, their aggregation into a floc of suitable porosity, and its subsequent dewatering by sCO_2. While each of these steps have been described before, their combination in a single operation is unique.

The viscosity of black liquor rises sharply above 50% solids. This leads to an increase in the boiling point rise (BPR) because of the increased concentration of organic material and salts. The relationship between BPR and the dry solids fraction (S) in the liquor is given by eq. 1 [15]

$$BPR = \frac{(68.3\ S)}{(8.1 - 7.1\ S)} \qquad [1]$$

The water removed (x) is linearly related to BPR as illustrated in Figure 2. BPR increases linearly with solids [15], which suggests that the drop in x with rising BPR is caused by the additional solids present. Inorganic salts comprise 30-45% of black liquor solids [15] and they tend to de-posit out as the liquor concentrates. These results are consistent with the fact that the sCO_2 displaces the free water and dissolves out the bound water. In previous work [2, 5] exposing the same sample to multiple pulses of sCO_2 progressively increased the amount of water removed. The same effect was seen with black liquor. Treating samples (60% dry basis MC) with a second cycle of sCO_2 increased x by an additional 37%.

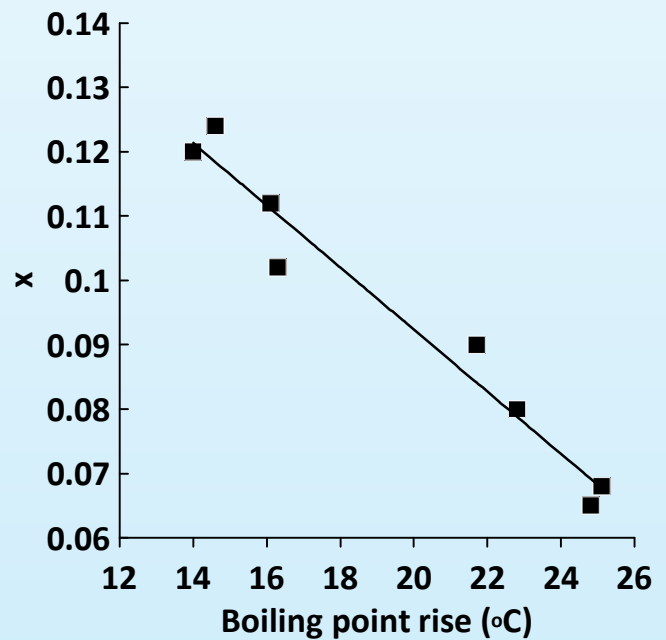Figure 2. Effect of boiling point rise on water removal by sCO_2 at 8.3 MPa and 90°C over 20 min.

In order to factor out the effect of salts contained in black liquor on the degree of dewatering, the effect of sCO_2 on lignin redissolved in water was investigated. The results are illustrated in Figure 3 along with corresponding values for black liquor. Comparatively more water is removed from the black liquor than from lignin as indicated by the higher values of x at similar solids levels. The black liquor trace appears to curve at higher MC, but it was not possible to extend the curve to higher moisture because the 90 µm filter at the exit end

of the extractor began to clog. Clogging did not occur with higher solids. The filters remained unobstructed when liquor with 60% solids was processed because the higher viscosity hindered movement of the entrained solids.
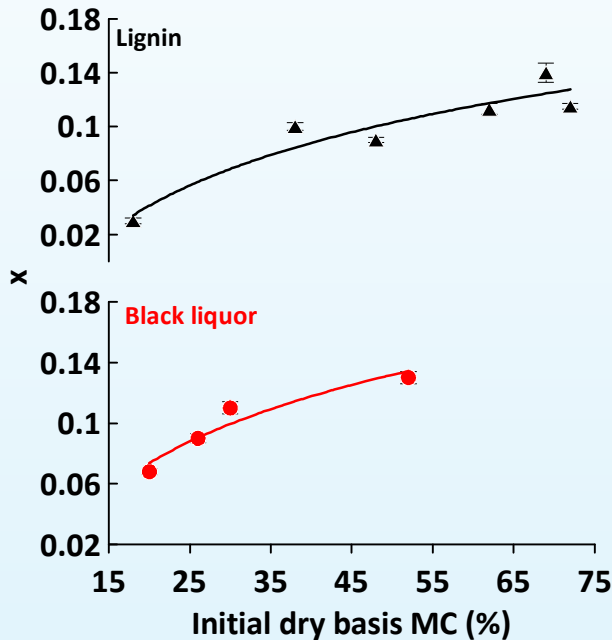

Figure 3. Dependence of water removal on initial dry basis moisture content for lignin and black liquor.

The nature of the solids deposited from black liquor and lignin is different at high solids. In both cases, the lignin should rapidly precipitate upon acidification because the pH drops immediately on CO_2 treatment and deposits about 78% of the dissolved lignin [8]. The precipitation should be largely independent of the concentration of the dissolved lignin because only the difference between pH and pKa controls the degree of deposition. In contrast, the salts in black liquor begin to precipitate beyond a solids level of 50% [15]. Hence, the deposits from black liquor are principally lignin at solids below 50% and a mixture of lignin and salts at higher solids. It is interesting that the lignin-BPR relationship is linear in Figure 2 but shows apparent curvature in Figure 3. This stems from the non-linear relationship between BPR and moisture content.

In order to put the degree of water removal from lignin and black liquor in perspective, wet cotton wool was treated with sCO_2. These results are included in Figure 4. The slope of the line is lower than that of the corresponding values for black liquor and lignin in Figure 3, indicating that black liquor solids express water more readily. The likely reason is that the liquor solids are more porous than cotton wool. The difference in the slopes among the three substrates is within a factor of six of
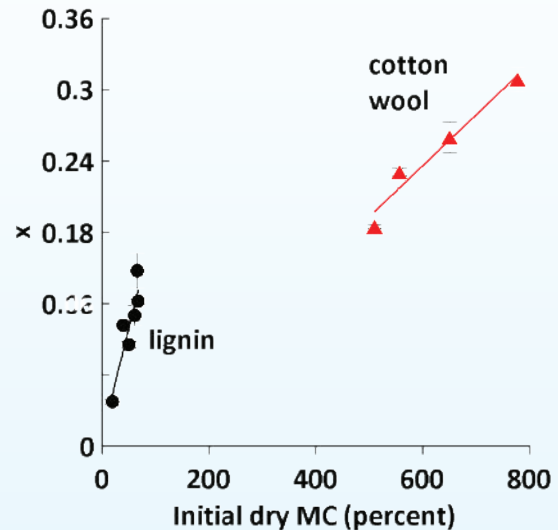

Figure 4. Comparison of water removal from lignin and cotton wool.

one another. If all the substrates share a common mechanism of free water displacement, then the differences are expected to be small, because the structure should have little influence on the properties of free water.

Conclusions

Strong black liquor and lignin concentrates can be dewatered by sCO_2, which separates out solids by acidifying the solution and simultaneously dewatering the wet solids. For example, the solids content of the black liquor can be increased from 66% to 72% solids in one cycle. The novelty of the procedure lies in its ability to combine the steps of precipitation, floc formation and dewatering in a single step. The level of dewatering increases through multiple treatment. For black liquor, the lignin appears to deposit first, followed by the salts. The amount of water re-moved far exceeds its solubility in sCO_2 and is proportional to the boiling point rise of black liquor. Overall, sCO_2 provides a route to non-evaporative dewatering with the potential of substantial energy savings as well as a step towards decarbonizing the pulp mill. The process is best suited for dewatering high-solids liquors, which have the highest energy demand, and where the volume to be dewatered is relatively small. Lignin is currently used as biofuel and drying is an important element of the processing sequence [16]. It is also a source of biomass-derived products and of precursors for the manufacture of carbon fiber used for light-weighting high value products. Dewatering biomass such as bagasse for biorefinery applications is another opportunity.

A potential drawback of the present approach is that a pressurized extractor is required to keep the CO_2 under supercritical conditions. However, pressurized chambers are used for commonplace applications such as dry-cleaning [17]

where the CO_2 is recycled. Pure CO_2 can also be obtained from indirectly heated lime kilns [18]. The sCO_2 dewatering process described here is currently run in a batch mode, which is impractical for a high throughput process such as black liquor dewatering. A Kamyr-style approach where streams of black liquor and sCO_2 are co-currently pumped through a mixing tube is presently being considered for scale-up.

Acknowledgment

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