

A model black liquor formulation for use in development and evaluation of membranes for concentrating weak black liquor

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ABSTRACT: As part of a larger program to develop robust membranes for concentrating weak black liquor prior to the evaporation step, several commercially available membranes were tested for suitability in this application. Given the variation in kraft black liquor for various wood species, the mill-to-mill variations, and the challenges of obtaining fresh samples, the need became apparent for a synthetic reference black liquor that would allow any membrane developer to test a new prototype membrane and compare the results with others.

We present a formulation for a model black liquor (MBL) similar to real kraft black liquor in the composition of the major species that can be formulated from readily available reagents. The MBL was tested with two commercial membranes and resulted in similar levels of lignin retention as the real black liquor. It also showed similar viscosity behavior to real black liquor as a function of solids content.

Application: A recipe for a model black liquor is presented for use in developing and testing robust membranes for concentrating black liquor. The use of a common reference liquor allows developers to directly compare prototype membrane performance to that of other commercial or prototype membranes.

In 2016, Agenda 2020 (now APPTI) [1] identified kraft black liquor (BL) evaporation alternatives as one of five research areas of greatest potential benefit to the industry. APPTI identified membrane-based concentration as the most viable approach [1]. If the weak black liquor leaving the digester could be dewatered from nominally 15 wt% solids to 30 wt% solids before the evaporators, the industry-wide savings are estimated at 23 trillion BTU/year [1]. The remaining water would then be removed with existing evaporators to bring the BL to the 65%–85% solids specification for the given mill.

Beyond the immediate goal of reducing the energy required to concentrate BL, advanced robust membranes would have the potential to fractionate the constituents of BL to produce streams that can be used as feedstocks for production of value-added products. For example, a stream rich in hydroxy acids, resin acids, and lower molecular weight (acetic and formic) acids

could be catalytically deoxygenated and converted to higher-molecular weight products such as biofuels, lubricants, and other products. Lignin and hemicellulose could also be fractionated into ranges of molecular weight that are more suitable for producing high-value nanomaterials. Membrane-based BL concentration has been considered since the 1980s [2]. However, the high solids content, pH, and temperature of BL present a very harsh environment for the commercially available nanofiltration and reverse osmosis membranes.

Weak BL enters the evaporators at 90°C and pH from 11.5–13. While some advanced polymer-based nanofiltration membranes are rated for higher pH, it usually limits them to temperatures well below 70°C. There are ceramic membranes rated for 200°C and above, but their high capital cost and lower solute rejection makes them unsuitable for this application. Furthermore, simply rejecting lignin is not enough: any viable membrane pro-

cess should also reject most of the smaller species (hydroxy acids, salts) at the pH and temperature ranges of BL. These limitations notwithstanding, a market search was done to identify robust commercial membranes for potential use with black liquor, albeit at temperatures below 70°C. A number of candidate commercial membranes were tested with a softwood black liquor using a smaller-scale pilot membrane test facility housed at Georgia Institute of Technology's Renewable Bioproducts Institute (RBI) in Atlanta, GA, USA. Typically, in all types of BL-related research, the BL samples are obtained from a kraft mill. However, shipping restrictions on hazardous materials have grown more stringent over the years, making acquisition of fresh samples a challenge. There is also the issue of considerable BL variation between mills, since there are different wood feedstocks and pulping process variants in use. Thus, it would be useful to have a reference model black liquor that could be easily pre-

pared in-house by any membrane developer or testing laboratory, and then used extensively in the early stages of development and evaluation of candidate membranes. This would also allow direct performance comparisons between different membranes to be tested by different laboratories. If a new membrane performs well with the MBL, it could move on to subsequent testing with real black liquor in laboratory and mill environments.

METHODS

Our goal is to create a MBL that can be made in a laboratory without extensive experience with BL and using easily available constituents. There are many organic reagents that are only sold in gram-sized amounts for analytical calibration, and they usually come at a very high price per gram. The MBL presented here is made from readily available and reasonably priced components. Adams [3] gives the overall solids composition of black liquor shown in **Table I**.

Similar considerations guided the selection of the other chemicals. After considerable experimentation, we have produced the model liquor formulation shown in **Table II**. The source and product code number are listed for each chemical, so that identical chemicals can be purchased or an equivalent option from another source can be determined. The components are mixed with distilled or deionized water to achieve the desired 15%–30% total solids, depending on the final concentration of liquor that is to be used in testing of membranes. Hydrate water should be taken into account. No special procedures are required other than thorough mixing.

Lignin is the organic glue that binds the cellulose fibers together in the wood. It is partially broken down and dissolved in the pulping process but still retains a polymeric structure. It was purchased as a market chemical, also known as Indulin AT (Ingevity; North Charleston, SC, USA). The hydroxy acids category represents many compounds spanning a broad range of

Chemical Species	Wt%	Elemental	Wt%
Alkali lignin	30–45	C	34–39
Hydroxy acids	25–35	H	3–5
Extractives	3–5	O	33–38
Acetic acid	5	Na	17–25
Formic acid	3	S	3–7
Methanol	1	K	0.1–2
Inorganic Sulfur	3–5	Cl	0.04–0.2
Sodium	15–20	Other	0.1–0.3

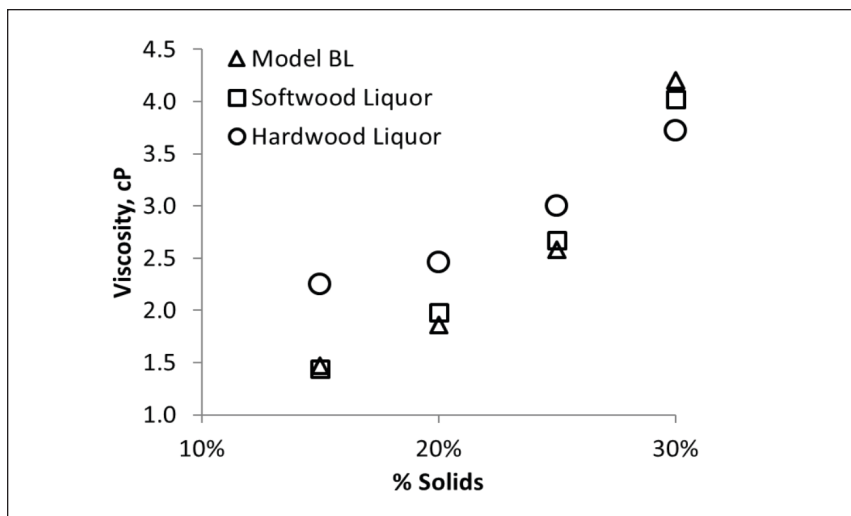
I. Dry-basis composition ranges of softwood black liquor [3].

Chemical	Grams	Wt%	Source	Product Code
NaOH (anhydrous)	8	8.51	EM Chemicals	CAS 1310-73-2
Na ₂ CO ₃ (anhydrous)	10	10.64	Sigma-Aldrich	CAS 6132-02-1
Na ₂ SO ₄ (anhydrous)	10	10.64	Acros	CAS 7757-82-6
KCl (anhydrous)	1	1.06	JT Baker	CAS 7447-40-7
Acetic acid	8	8.51	EM Chemicals	CAS 64-19-7
Abietic acid	2	2.13	Alfa Aesar	CAS 514-10-3
Oleic acid	1	1.06	Fisher	CAS 112-80-1
Galactan (powder)	20	21.27	Premier Research	Galactan
Lignin (powder)	33	35.11	Sigma-Aldrich	CAS 8068-05-1
Methanol	1	1.06	Fisher	CAS 67-56-1
Dry Total	94	100.00		
Water	532.7	to achieve 15% solids liquor		
NaOH = sodium hydroxide; Na ₂ CO ₃ = sodium carbonate; Na ₂ SO ₄ = sodium sulfate; KCl = potassium chloride.				

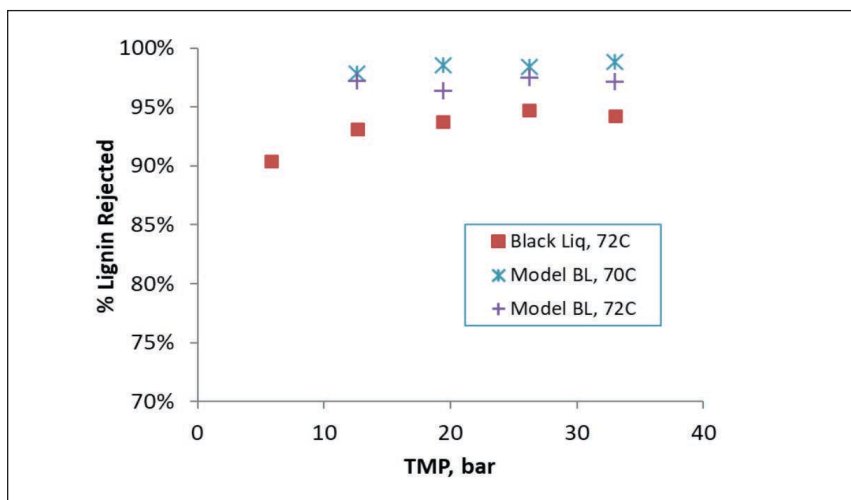
II. Model black liquor composition (dry basis).

molecular weights. They originate from dissolution and degradation of hemicelluloses and some degraded cellulose in the pulping process. The viscosity of the model liquor should be close to that of the real black liquor, as viscosity is expected to affect membrane performance at higher solids content. The most abundant extractive acids in black liquor are steric, oleic, linoleic, and linolenic [4]. For MBL formulation, we use oleic acid, because it is the only one that is commonly avail-

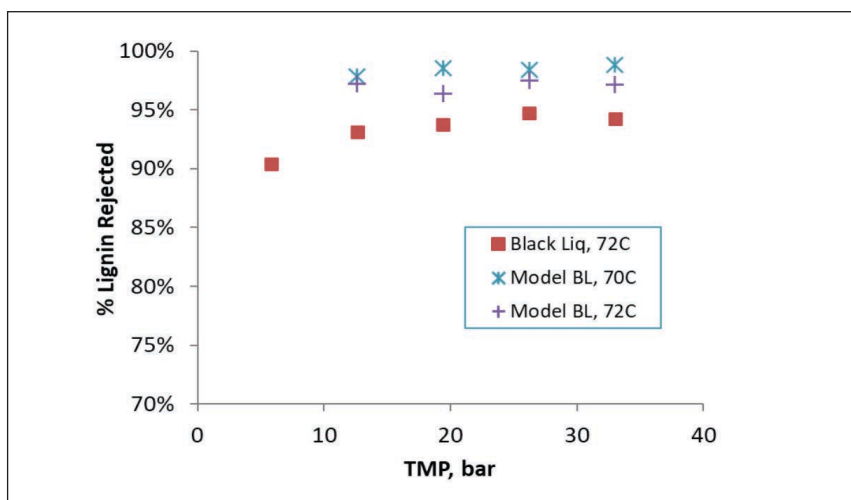
able as a reagent. For softwood liquor, there is also a subset of acids called resin acids, of which the major ones are levopimeric, neoabietic, and abietic. Abietic acid is the most readily available and is used for MBL formulation. Galactan is a polymeric form of galactose found in hemicellulose. It is sold over the counter as a dietary supplement. We use it to model the bulk of the hydroxy acid fraction shown in Table I. Acetic acid was selected to model the lower molecular weight spe-



1. Viscosity behavior of model black liquor (MBL) and real liquors at 50°C.



2. Lignin rejection for model and real black liquor through a Microdyn-Nadir NP030 membrane (TMP = transmembrane pressure). Cross flow velocity = 0.64 m/s.



3. Lignin rejection for model and real black liquor through a Koch SeIRO MPS-36 membrane. Cross flow velocity = 0.64 m/s.

cies. This is in addition to the actual amounts of acetic acid found in black liquor. The lignin fraction was set at about 35%.

Black liquor contains organic compounds spanning a wide range of molecular weight, which interact to produce non-Newtonian viscosity behavior. **Figure 1** shows the results of viscosity measurements over the range of solids content that membranes would be expected to operate in. The MBL was tested against a hardwood and a softwood liquor at 50°C using a Brookfield LVDV-I Prime viscometer (Brookfield Engineering; Middleboro, MA, USA). The viscosity vs. solids behavior of the MBL is quite close to that of the real liquors.

A membrane separation system for concentration of weak black liquor prior to evaporation would most likely consist of at least two stages: an initial nanofiltration (NF) stage to retain the heavy and medium weight organic compounds, followed by a tighter NF or reverse osmosis (RO) stage to retain most of the inorganic compounds and the lightest organic compounds [2]. A search of commercial membranes revealed a short list of NF membranes nominally suitable for testing with black liquor. Weak black liquor feeds the evaporators at temperatures as high as 90°C, which would rule out all polymer NF membranes. Therefore, we allow for the possibility of cooling the weak liquor to below 70°C for the membrane concentrators and then reheating the concentrated liquor before sending it the evaporators. Counter-flow heat exchange would allow for much of the lost heat to be recovered if necessary.

No RO membranes were found sufficiently robust to warrant testing with black liquor. Therefore, the MBL was only benchmarked using lignin rejection in NF membranes. Lignin is the largest organic species in BL and also the most abundant. It is also easily detected by ultraviolet-visible (UV-VIS) absorbance spectroscopy, and it is a convenient measure of performance for the initial nanofiltration stage. We

benchmarked the MBL against two of the tested NF membranes. **Figure 2** shows the lignin rejection in a Microdyn-Nadir NP030 flat sheet NF membrane (Microdyn-Nadir; Wiesbaden, Germany), which is a polyethersulfone (PES) membrane on a polyethylene support and has a rated molecular weight cut-off (MWCO) in the range of 500–600 Daltons. The lignin rejection from MBL at 67°C is quite close to that from real BL. **Figure 3** shows similar results using a Koch SelRO flat sheet MPS-36 (Koch Separation Solutions; Wilmington, MA, USA), a proprietary thin film composite membrane that is rated at 1000 Daltons. In this case, the observed lignin rejection for the MBL is slightly higher than for the real liquor, but it is still quite reasonable and follows the same trends with transmembrane pressure (TMP).

We have used only lignin rejections for membrane benchmarking in this work. Rejections of other species were not measured/benchmarked, since the MWCOs of the two membranes (500–1000 Daltons) would lead to a very low rejection of the other species in both MBL and real BL. Thus, the rejections of these species are not meaningful as a benchmark. Nevertheless, these species (Table II) are still important for simulating the other characteristics of real BL (e.g., viscosity, as seen in Fig. 1), and will become more useful in benchmarking when

higher-performance membranes are sought to be tested.

CONCLUSION

The present MBL formulation proposed here exhibits similar viscosity and membrane permeation (e.g., lignin rejection) behavior compared to a real softwood black liquor. The MBL also mimics the pH of real BL. While the exact rejection values for lignin and other species will differ somewhat from real black liquors, the MBL will be a useful tool for initial evaluations of existing and new membranes for suitability in BL concentration applications. The MBL components are readily available and inexpensive and only require mixing together thoroughly with purified water to prepare the MBL, thus eliminating the need to acquire black liquor from a mill for early-stage research and development efforts. **TJ**

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ABOUT THE AUTHOR

This study was part of a larger project funded by a consortium of pulp and paper companies. We found that by defining a reference black liquor, membrane performance can be compared by different research labs or membrane manufacturers.

The most difficult aspect of this research was deciding on a small number of compounds to simulate a substance that is composed of hundreds of compounds. To do so, pulping and recovery experts were consulted.

We propose a tool that allows membrane developers to easily test membranes without having to obtain real black liquor. It was interesting to see the close agreement in viscosity behavior between the model and real liquor.

Mills would benefit from the implementation of robust membranes for concentrating black liquor from 15% to about 35%, as the energy savings is substantial. Our next step is continued development and optimization of the robust membranes for black liquor.

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