Chemical Engineering Journal 304 (2016) 977–985

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Effect of process variables on the performance of electrochemical acidification of Kraft black liquor by electrodialysis with bipolar membrane

Maryam Haddad [a,*], Raynald Labrecque [b], Laurent Bazinet [c], Oumarou Savadogo [a], Jean Paris [a]

[a] Research Unit on Energy Efficiency and Sustainable Implementation of the Forest Biorefinery (E^2D^2BF), Department of Chemical Engineering, Polytechnique de Montréal, Canada
[b] Laboratoire des technologies de l'énergie d'Hydro-Québec (LTE), Shawinigan, Canada
[c] Institute of Nutrition and Functional Foods (INAF), Laboratory of Food Processing and Electromembrane Processes (LTAPEM), Department of Food Sciences, Université Laval, Canada

HIGHLIGHTS

- Effects of temperature and BL composition on EDBM performance were studied.
- Increasing the operational temperature postponed BPM colloidal fouling.
- BL composition impacted the fouling, system hydrodynamics and process efficiency.
- Improving the operational conditions mitigated the fouling and increased the efficiency.
- EDBM of the BL with 20% TDS content at 55 °C registered the best results.

ARTICLE INFO

Article history:
Received 19 May 2016
Received in revised form 4 July 2016
Accepted 7 July 2016
Available online 9 July 2016

Keywords:
Bipolar membrane
Electrodialysis
Operational conditions
Ion exchange membrane fouling
Lignin extraction

ABSTRACT

Lignin which is dissolved in the residual black liquor stream of Kraft pulping mills can be extracted and converted into a wide range of value-added bio-based products. To this end, design and development of an eco-efficient lignin extraction method is crucial. Electro-membrane technologies and particularly, electrodialysis with bipolar membrane (EDBM) is a promising and green avenue to acidify the black liquor and extract the lignin. Therefore, the aim of this study is to evaluate the performance of the EDBM acidification process in terms of current efficiency and energy consumption. The effect of main process variables such as operational temperature and black liquor chemical composition on the efficiency of the EDBM process have been evaluated. The experimental results demonstrated the substantial influence of these parameters on the EDBM current efficiency, energy consumption and fouling of the ion exchange membranes. Furthermore, it was indicated that promoting the hydrodynamics of the system could delay and mitigate the lignin self-aggregation and precipitation inside the EDBM stack. The highest current efficiency and, subsequently, the lowest energy consumption were achieved when the EDBM process was carried out at 55 °C with the black liquor solution containing 20 (wt.%) total dissolved solids.

1. Introduction

Kraft process is a predominant pulp and paper production method, worldwide. In most of the conventional Kraft pulping mills around 50% of the wood components (mainly hemicellulose and lignin) are dissolved in a residual stream called black liquor (BL) and combusted in the recovery boiler to produce steam, electricity and re-generate the cooking chemicals (A schematic drawing of a Kraft pulping process is presented in Appendix A) [1]. In contrast, in an integrated forest biorefinery (IFBR) concept, wood constituents are separated from the pulp stream and transformed into value-added bio-based products [2]. In particular, extracted lignin can be used as biofuels or as a precursor to a vast phenolic platform of chemical pathways [3]. Furthermore, lignin extraction can increase the capacity of the Kraft mill by decreasing the load of its recovery boiler [1].

Different processes have been proposed for lignin extraction [1,4]. Indeed, lowering the pH of the BL by CO_2 sparging is the most common process to acidify the BL and extract the lignin [1]. However, in recent years, the increasing interests in green products and sustainable technologies encouraged researchers to look for

* Corresponding author.
E-mail address: maryam.haddad@polymtl.ca (M. Haddad).

http://dx.doi.org/10.1016/j.cej.2016.07.030
1385-8947/

eco-efficient pathways to extract the lignin. In particular, acidification by electrodialysis with bipolar membrane (*EDBM*) process leads to lignin extraction and production of caustic soda [5]. However, in the practical EDBM trials, membrane fouling was observed [5–7]. It was found that the protonation of the lignin phenolic groups resulted in formation of destabilized colloidal lignin which eventually formed a layer of lignin on the surface of the IEMs (bipolar and cation exchange membranes) and increased the global system resistance [5,6].

In general, process conditions play an important role in controlling the fouling of the membranes and performance of the membrane-based technologies [8]. The productivity of an EDBM process is governed by various parameters. The nature of the feed solutions and desired quality of the products determine a number of these parameters; while some process variables such as applied current density, electrical conductivity, kinematic viscosity and operational temperature of the feed solutions can be varied in specific ranges based on the stack and IEMs' properties and limitations [8]. However, except for the impact of the applied current density on the performance of the EDBM process (the applied current density equals to 75% of the measured limiting current density value [9]), the influence and interdependencies of the other process variables have never been fully evaluated especially when a complex solution containing polyelectrolyte components like Kraft BL is acidified by means of the EDBM method.

Temperature, ionic strength (mineral concentration) and viscosity of a solution can affect its electrical conductivity [10]. In addition, the viscosity of the solution controls the turbulent mixing in the EDBM stack and subsequently, the fouling of the IEMs [11]. A number of parameters can influence the viscosity of a solution containing polyelectrolyte particles (in current study lignin) such as the concentration and molecular weight of the polyelectrolyte, ionic strength (mineral concentration) of the solution, temperature, shear rate and degree of ionization. However, there is no general theory explaining the correlations of these factors [12]. For that reason, it is essential to determine the evolution of the BL viscosity as a function of the temperature and BL chemical composition in order to maintain a high turbulent mixing in the system and minimize the IEMs' fouling [11]. Most of the BL properties have a direct or indirect correlation with its chemical composition. The chemical composition of the Kraft BL is strongly affected by type of the wood chips (softwood vs. hardwood) and the operational conditions of the Kraft mill. To evaluate the trends of the BL properties under different operational conditions its total dissolved solids (TDS) content is considered to be the key influencing factor. Roughly, lignin accounts for 30–45% of the TDS content of a softwood Kraft BL and inorganic matters such as sodium salts comprise of about 30–35% of the BL TDS content [1]. Even though it is well-known that increasing the temperature would improve the dissociation of a large number of salts, there seems to be no common agreement on the impact of the temperature on lignin solubility in the literature: Norgren and co-workers claimed that elevating the BL temperature induced the protonation reaction of the lignin phenolic groups which decreased the lignin solubility and promoted its precipitation [3,13]. On the other hand, some researchers reported that the lignin solubility was improved in an alkaline solution with increasing the temperature [1,14]. In addition, the IEMs and the components of the EDBM stack are mainly made of cost-effective polymers that do not possess a very high level of thermal stability [15]. Thus, screening the most appropriate temperature for the electrochemical acidification of the BL via the EDBM method is crucial.

To this end, the objectives of this study are (1) to investigate the effect of the BL chemical composition and temperature on its electrical conductivity and viscosity and (2) to determine the influence of the operational temperature and BL chemical composition on the performance of the EDBM process and ultimately the efficiency of the electrochemical acidification method. The outcome of this investigation would give a clear and general insight into the effect of the main process variables on the performance of the EDBM process, which has gained less attention in previous studies dealing with the EDBM system. Moreover, the end results of this work would enable us to enhance the process efficiency and mitigate the IEMs' fouling in order to make this eco-efficient electrochemical acidification method one step closer towards its practical implementation in a Kraft mill.

2. Experimental

2.1. Membranes and materials

The membranes used in this study were Fumasep *FBM* bipolar membrane (FuMA-Tech Co., Germany) and *CMB* cation exchange membrane (Neosepta, Japan). Their main properties are given in Table 1. A Canadian Kraft pulping mill provided the softwood black liquor with a TDS content of about 50 ± 2 (wt.%). This liquor was pre-filtered to remove any suspended solid particles larger than 0.010 μm utilizing a simple vacuum filtration apparatus and a filter paper (Whatman Grade 111105, UK). Analytical grade chemicals were purchased from Sigma–Aldrich, Canada and standard solutions were supplied by Fisher Scientific, Canada. Demineralized water was used to prepare all the aqueous solutions.

2.2. Electrochemical acidification apparatus and protocol

As shown in Fig. 1, a two-compartment cell was used. The BPMs and CEMs were placed in an alternating pattern and the EDBM stack was surrounded on one end by the anode compartment and on the other end by the cathode compartment (Fig. 2). The main specifications of the EDBM stack are summarized in Table 2. The stack was hydraulically connected to three holding reservoirs via three pumps (Model: IWAKI Magnetic Drive Pump *MD*.30*R*, Iwaki America Inc., USA). These reservoirs were filled with 2 L of BL, NaOH and electrode rinse solution (Na_2SO_4), respectively. In order to increase the agitation inside the stack and minimize the membrane fouling [11], all the experiments were conducted at the maximum flowrate corresponding to the pumps and stack configuration. A jacket coil heat exchanger was installed in each reservoir to maintain a constant temperature. The driving force of the system was provided by a *DC* power supply (Model: Xantrex *XKW* 40–25, USA) connected to the electrode pair. The main operational conditions are presented in Table 3. These conditions remained unchanged for all the experiments performed during the course of this study. It is noteworthy to mention that to avoid production of H_2S and fouling of anion exchange membrane the two-compartment EDBM stack configuration (BPM-CEM) was chosen for this study [9]. Before starting each experiment, the set-up was rinsed for 30 min with demineralized water to wash any particle that could remain in the apparatus. All the experiments were carried out in batch mode and preliminary measurement of limiting current density was performed based on the Cowan and Brown method [16]. The EDBM stack was operated in a galvanostatic mode in which a constant current was applied and the voltage was allowed to vary during the EDBM process. The applied current, voltage drop as well as conductivity and temperature of each reservoir were monitored and recorded by means of a data acquisition system (Model: Agilent 34970*A*, USA) connected to a data logger software. Every five minutes, a sample of BL was taken for pH measurement using a pH meter (Model: 916 Ti-Touch, Metrohm, Switzerland) equipped with an automatic temperature compensation probe. Three replicates were performed for each operational