Determination of Molecular Mass Dependent Retention of Caustic Hemicellulose Solution by Nanofiltration

R. Schlesinger[1], W. Milacher[2], G. Götzinger[2], H. Sixta[2], M. Net[3], A. Friedl[3], M. Harasek[3]

[1]Wood Kplus, A-4860 Lenzing, Austria, r.schlesinger@kplus-wood.at
[2]Lenzing AG, A-4860 Lenzing, Austria
[3]Vienna University of Technology, Institute of Chemical Engineering, A-1060 Vienna

Introduction

The production of viscose-type textile fibres from wood generates waste streams containing hemicellulose dissolved in strong caustic soda (20 wt% NaOH). Hemicellulose is a technical term for polysaccharides (mainly xylan) originating from raw materials and their degradation products like sugar acids and hydroxy-carboxylic acids [1].

Nanofiltration (NF) is proposed for the separation of hemicellulose and sodium hydroxide because sodium hydroxide passes the nanofiltration membrane whereas most of the hemicellulose is retained.

The present work characterizes nanofiltration membranes by evaluation of size exclusion chromatography (SEC) data and by calculation of molecular mass dependent retentions for the substrate under study. A similar procedure that uses dextran standards instead of a real substrate has been described by Mulder [2]. The molecular mass distribution of hemicellulose is closely related to properties like solubility, osmotic pressure and fouling potential that affect the separation process.

Experimental

Nanofiltration Experiments

Stirred Cell:	3.8 cm^2 active membrane area (Membrane Products, Inc.)
Membranes:	Nanofiltration (NF) and tight ultrafiltration (UF) membranes, thermally and chemically stable in highly alkaline process media (pH 14+)
Pressure:	20 - 35 bar (NF); 5 - 10 bar (tight UF)
Temperature:	20 - 50°C
Stirrer speed:	400 rpm
Volume reduction:	factor 1.4

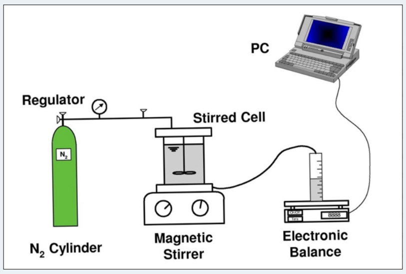

Fig. 1 Nanofiltration experimental setup.

Size exclusion chromatography

Sample preparation:	Dilution 1:20 with 0,5M NaOH
Stationary phase:	2 MCX columns, 1000 Å, 300*8 mm (PSS)
Mobile phase:	0,5M NaOH at 1 ml/min
Injection volume:	80 µl
Run time:	25 min
Detection:	Refractive index (RI) detection
Calibration:	carried out with a set of cello-oligomers, pullulan and dextran standards [3]

Results and Discussion

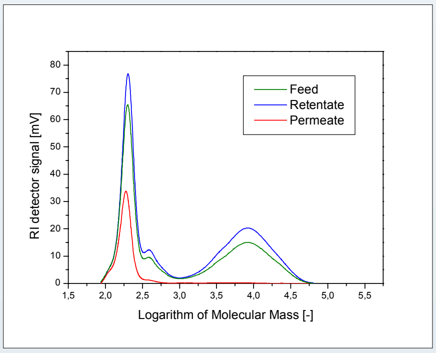

Fig. 2 Size exclusion chromatogram of feed and Koch MPF-34 retentate and permeate.

Only a small portion of solutes in the region below 1,000 g/mol can pass the membrane (Fig. 2). Feed and retentate show similar molecular mass distributions due to the low volume reduction factor used. Molecules with a higher mass are nearly completely retained by the Koch MPF-34 membrane.

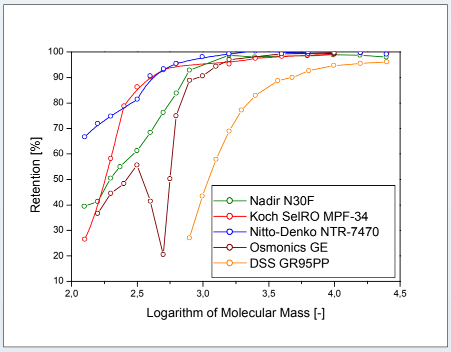

Fig. 3 Retention plotted as a function of the logarithm of molecular mass. Operating conditions: 35 bar, 49°C, 400 rpm.

The Koch and Nitto-Denko membranes feature the highest rejection for hemicellulose (Fig. 3). Both have a molecular weight cut-off (MWCO, defined as the molecular mass retained by 90 %) of about 380 g/mol. The Koch membrane has a very sharp cut-off with low rejections below 300 g/mol and very high rejection above.

	MWCO [g/mol]	R (M = 150) [%]	R (M = 282) [%]
Nadir N30F	710	40,8	58,1
Koch SelRO MPF-34	390	35,4	82,5
Nitto-Denko NTR-7470	380	71,5	74,1
Osmonics GE	840	35,4	52,2
DSS GR95PP	6.120	n.d.	n.d.

Tab. 1 Characteristic membrane parameters at p = 35 bar, T = 49°C, 400 rpm.

The Nadir membrane features, like the Koch membrane, a rejection of about 40 % for solutes with 150 g/mol, a molecular mass that corresponds to that of monosaccharides. However, the Nadir membrane has a rather diffuse cut-off resulting in lower retention at higher molecular mass and a significantly higher MWCO of 710 g/mol.

A clear and reproducible minimum of rejection can be seen from the Osmonics membrane close to 500 g/mol which corresponds to the shoulder of the low molecular mass peak in Fig. 1. Above this molecular mass the rejection increases drastically and reaches 90 % at about 840 g/mol. The DSS ultrafiltration membrane is not suitable for removing hemicellulose efficiently. Additionally, the fact that large molecules can penetrate the membrane pores increases fouling propensity [4]. The molecular weight cut-off and the calculated retention for mono- and disaccharides are presented in Tab. 1.

Conclusions

Size exclusion chromatography data can be used for the determination of molecular mass dependent retention even in the very low molecular mass region between 150 and 1,000 g/mol.

The experimental data show that hemicellulose is almost quantitatively retained at molecular masses above 1,000 g/mol by the membranes studied. MWCOs of the membranes at 49°C are between 380 and 840 g/mol. As retention is satisfactory in the region far below 1,000 g/mol, nanofiltration membranes can be applied successfully to the separation task investigated. The selection of an appropriate membrane and the optimization of process conditions can be considerably enhanced on the basis of known molecular mass dependent retentions.

Literature

[1] U. Mais, H. Sixta, *ACS book on Xylans, Mannans and other Hemicelluloses*, accepted 2002.

[2] M. Mulder, *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, Dordrecht 1991.

[3] H. Sixta, N. Schelosky, W. Milacher, T. Baldinger, T. Röder, *Proceedings of the 11th International Symposium on Wood and Pulping Chemistry*, June 2001, Nice, France.

[4] M. Nyström, L. Kaipia, S. Luque, Fouling and retention of nanofiltration membranes, *Journal of Membrane Science*, 98 (1995), 249-262.