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RECOVERY OF BIOMASS-DERIVED VALUABLE COMPOUNDS USING CHROMATOGRAPHIC AND MEMBRANE SEPARATIONS

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ABSTRACT

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Utilization of biomass-based raw materials for the production of chemicals and materials is gaining an increasing interest. Due to the complex nature of biomass, a major challenge in its refining is the development of efficient fractionation and purification processes.

Preparative chromatography and membrane filtration are selective, energy-efficient separation techniques which offer a great potential for biorefinery applications. Both of these techniques have been widely studied. On the other hand, only few process concepts that combine the two methods have been presented in the literature. The aim of this thesis was to find the possible synergetic effects provided by combining chromatographic and membrane separations, with a particular interest in biorefinery separation processes. Such knowledge could be used in the development of new, more efficient separation processes for isolating valuable compounds from complex feed solutions that are typical for the biorefinery environment.

Separation techniques can be combined in various ways, from simple sequential coupling arrangements to fully-integrated hybrid processes. In this work, different types of combined separation processes as well as conventional chromatographic separation processes were studied for separating small molecules such as sugars and acids from biomass hydrolysates and spent pulping liquors.

The combination of chromatographic and membrane separation was found capable of recovering high-purity products from complex solutions. For example, hydroxy acids of black liquor were successfully recovered using a novel multistep process based on ultrafiltration and size-exclusion chromatography. Unlike any other separation process earlier suggested for this challenging separation task, the new process concept does not require acidification pre-treatment, and thus it could be more readily integrated into a pulp-mill biorefinery.

In addition to the combined separation processes, steady-state recycling chromatography, which has earlier been studied for small-scale separations of high-value compounds only, was found a promising process alternative for biorefinery applications. In comparison to conventional batch chromatography, recycling chromatography provided higher product purity, increased the production rate and reduced the chemical consumption in the separation of monosaccharides from biomass hydrolysates. In addition, a significant further improvement in the process performance was obtained when a membrane filtration unit was integrated with recycling chromatography.

In the light of the results of this work, separation processes based on combining membrane and chromatographic separations could be effectively applied for different biorefinery

applications. The main challenge remains in the development of inexpensive separation materials which are resistant towards harsh process conditions and fouling.

Keywords: preparative chromatography, membrane filtration, biorefinery, recycling chromatography, hydroxy acids

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Lappeenranta, December 2013

Sanna Hellsten

LIST OF PUBLICATIONS

This thesis is based on the following peer-reviewed scientific journal articles, which are referred to in the text by the Roman numerals I-IV.

I **Hellstén, S.**, Sainio, T., Steady state recycling chromatography in acid–sugar separation on an ion-exchange resin, *Sep. Sci. Technol.*, 47 (2012) 2358–2365.

II **Hellstén, S.**, Siitonen, J., Mänttäri, M., Sainio, T., Steady state recycling chromatography with an integrated solvent removal unit – Separation of glucose and galactose, *J. Chromatogr. A*, 1251 (2012) 122–133.

III **Hellstén, S.**, Heinonen, J., Sainio, T., Size-exclusion chromatographic separation of hydroxy acids and sodium hydroxide in spent pulping liquor, *Sep. Purif. Technol.*, 118 (2013) 234–241.

IV **Hellstén, S.**, Lahti, J. Heinonen, J., Kallioinen, M., Mänttäri, M., Sainio, T., Purification process for recovering hydroxy acids from soda black liquor, *Chem. Eng. Res. Des.*, in press, http://dx.doi.org/10.1016/j.cherd.2013.06.001.

The author's contribution in the publications

I The author analysed the experimental data and conducted the numerical simulation study. The manuscript was written together with the co-author.

II The author made the numerical simulation study. The manuscript was written together with the co-authors.

III The author planned the laboratory experiments together with the co-authors, carried out the experiments and analysed the data. The capillary electrophoresis (CE) analyses were done by collaborators. The manuscript was written together with the co-authors.

IV The author planned and carried out the experiments with the help of an assistant (except the UF experiments which were carried out by a co-author), analysed the data and wrote the manuscript together with the co-authors. The CE analyses were done by collaborators.

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SYMBOLS AND ABBREVIATIONS

Symbols

a	Langmuir isotherm constant	-
b	Langmuir isotherm constant	L/mol
c	concentration	mol/L
D	diffusivity	m^2/s
d	diameter	m
EC	eluent consumption	L/mol
F	phase ratio	-
H	Henry constant of adsorption	-
J	flux	$L/(m^2 \cdot h)$
n	amount	mol
N	number of compounds	-
NTP	number of theoretical plates	-
t	time	s
t_0	dead time of the column	s
p	pressure	Pa
Pe	Péclet number	-
PR	productivity	$mol/(m^3 \cdot h)$
PU	purity	-
q	concentration in solid phase	mol/L
R	retention	-
Re	Reynolds number	-
u	linear velocity	m/s
V	volume	m^3
VRF	volume reduction factor	-
Y	yield	-
α	separation factor	-
ε	porosity	-
η	dynamic viscosity	$Pa \cdot s$
π	osmotic pressure	Pa
ρ	density	kg/m^3
τ	time from the feed injection	s

Superscripts

A	first fraction
B	second fraction
F	feed
FF	fresh feed
m	membrane
P	permeate
R	recycle fraction

Subscripts

1	first eluting component
2	second eluting component
b	bed
i	*i*:th component
p	particle
tot	total

Acronyms

2,5-DHPA	2,5-dihydroxy pentanoic acid
2-HBA	2-hydroxy butanoic acid
CA	cellulose acetate
CE	capillary electrophoresis
DVB	divinylbenzene
ECH	epichlorohydrin
GISA	glucoisosaccharinic acid
HPLC	high-performance liquid chromatography
ISPR	*in-situ* product recovery
MF	microfiltration
MWCO	molecular weight cut-off
n.a.	not applicable
NF	nanofiltration
PA	polyamide
PES	polyether sulphone
PS	polystyrene
PSu	polysulphone
RC	regenerated cellulose
RO	reverse osmosis
SAC	strong acid cation-exchange resin
SBA	strong base anion-exchange resin
SEC	size-exclusion chromatography
SMB	simulated moving bed chromatography
SSR	steady-state recycling chromatography
SSR-SR	steady-state recycling chromatography with solvent removal
TDS	total dry solids
UF	ultrafiltration
UV	ultraviolet
WAC	weak acid cation-exchange resin
WBA	weak base anion-exchange resin
XISA	xyloisosaccharinic acid

1 INTRODUCTION

Biomass is defined as bio-degradable material originated from plants, animals and micro-organisms. Today, biomass is widely utilized as a renewable energy source: it accounts for approximately 75% of the world's renewable energy production [1]. Considering that up to 97% of this bioenergy is produced by direct combustion [2], it can be concluded that the degree of refining in biomass utilization is low. Biomass is, however, a versatile resource with various potential applications. Biomass could be converted to value-added products such as liquid fuels, polymeric materials, or fine chemicals. While fossil resources are diminishing, major efforts are made to intensify the utilization of the inexhaustible biomass feedstocks, aiming to replace petroleum-based products by biomass-based alternatives. Motivation to promote the use of biomass may arise from the unstable oil price, from the willingness to improve national energy security, from the need to reduce greenhouse gas emissions in order to mitigate climate change, or from the possible job creation effect related to the implementation of a new technology [1, 3, 4]. Biomass refining has also been seen as a way to improve the competence of forest industry [3]. Intensification of biomass usage has, thus, environmental, economic, social and political impacts.

A biorefinery is a facility for converting biomass to various products. The so-called first generation biorefineries exploit dedicated energy crops such as corn, oil palm, or sugar cane. However, the utilization of fertile land for the production of bioenergy may threaten food security and biodiversity. To avoid the competition for arable land between biomass production and food cultivation and to prevent other adverse effects of energy crop plantations, special interest should be paid to the refining of secondary biomass, i.e., the waste produced in the processing of biomass, e.g. forestry and agricultural residues, side streams of pulp and paper or food industry, and municipal biowaste [5]. In future biorefineries, this low-value biomass could be converted to fuels, materials and fine chemicals in a sustainable manner.

Biorefineries can be established in different sizes. Sometimes it may be favourable to treat the biomass on-site in small units to minimize storage and transportation costs [6-8]. In that case, the process should be simple to keep the investment costs low. Since the composition and availability of biomass may have large seasonal variations, biorefining processes should be

somewhat flexible. On the other hand, a major challenge may be the integration of biorefinery operations to an existing process. For example, integrated pulp mill biorefineries should be developed so that the biorefinery operations will not affect the quality of the pulp and no drastic changes in the pulping process are required.

As the current technology allows transformation of biomass to numerous different biochemicals [9], selection of the product portfolio may be a major challenge in the implementation of biorefineries. Low-price products such as fuel bioethanol might not be sufficiently profitable. On the other hand, the market for high-value specialty products, such as pharmaceuticals, is small. One promising strategy is to mimic petroleum refineries which produce intermediate products that can be further converted to various value-added products [10].

U.S. Department of Energy has established a list of 12 building block chemicals that can be produced from biomass and used as a raw material for various chemicals [11]. The building block chemicals possess multiple functional groups that make their use in chemical syntheses versatile. However, simpler compounds such as bioethanol and other biofuels can also be converted to value-added bioproducts to improve their profitability [12]. These bioproducts may include common chemicals and materials which are currently produced by petrochemical industry as well as completely new, biodegradable products [10]. Manufacturing of polymeric materials is currently considered among the most promising uses for the building block chemicals. To avoid problems in the polymerization processes, high purity of the intermediate products is necessary.

An ideal biorefinery produces multiple products in order to fully exploit the biomass raw material. The versatility of biomass arises from the fact that it is inherently a complex matrix. For example, lignocellulosic biomass consists of lignin, cellulose, hemicelluloses and various minor components (non-structural components such as extractives). All these compounds may go through depolymerisation and participate in different types of other reactions during the processing of biomass, resulting in an even more complex multicomponent mixture. Consequently, the solutions treated in biorefineries, e.g. lignocellulosic hydrolysates, waste waters or fermentation broths, are very complex mixtures. Therefore, separation technology plays a key role in biorefining processes.

Biomass-derived solutions often contain many components which have similar physical properties and molecular structures, and are therefore difficult to separate from each other. For example, purification of acids produced by fermentation is challenging due to side-products with related structures [13]. Therefore, highly selective separation methods are required for recovering the compounds of interest in a satisfactory purity. Moreover, the raw material may contain numerous components with unknown properties, as well as components which cause problems such as fouling [14] or pitch deposits [15]. Furthermore, the processing conditions may be harsh, e.g. when treating acid hydrolysates [16] or highly alkaline black liquor from pulping [15].

The above mentioned issues relating to the feedstock composition together with the objective of recovering multiple products simultaneously make the design and optimization of a biomass fractionation process challenging. Though aiming to keep the process simple, multiple fractionation and purification steps are often required. As a major concern in the development of biorefinery processes is their economic viability [17], it is essential to reduce the separation costs by process optimization. Cost-effectiveness of a separation process can be improved, for example, by combining different unit operations to a hybrid process, which is a well-known process intensification method. However, better knowledge is needed in order to find the most advantageous process concept for different biorefinery separations and how to optimize the process to provide the best performance.

2 OBJECTIVES AND STRUCTURE OF THE WORK

2.1 Aims and scope of the study

The aim of this work is to introduce and investigate new separation process concepts for recovering valuable compounds in biorefineries based on chromatographic and membrane separations. The main research question is whether it is possible to gain advantage in challenging biomass fractionation tasks by combining these two separation techniques.

The separation methods applied in this work, chromatography and membrane filtration, were chosen because they are selective, well-suitable for continuous processes, and less energy-consuming than the conventional separation techniques. Furthermore, both of these separation methods have been found very useful in manufacturing of biomass-based products such as xylitol [18] and high-fructose corn syrup [19]. Several potential applications of membrane technology in biorefineries have also been proposed, as recently reviewed by He et al. [20] and Abels et al. [21].

Chromatographic and membrane separations are traditionally studied separately. However, these two separation unit operations can be readily coupled together. In this work, different ways to combine the separation unit operations in the field of biorefining are investigated. The holistic approach may improve the process performance in terms of productivity and chemical consumption, facilitate the treatment of complex mixtures (e.g. by removing problematic compounds in a separate process step) and increase the product purity.

A special attention has also been paid to steady-state recycling chromatography (SSR). Currently it is not a routinely employed technique. Based on theoretical studies [22, 23] it can, however, improve separation performance. It has also been suggested that a further improvement in the process performance could be achieved using a hybrid separation process in which internal process streams are concentrated by removing solvent in a membrane filtration unit coupled with SSR [24]. The performance of SSR and the new hybrid process in the recovery of monosaccharides from biomass hydrolysates is investigated in this work. In addition, a systematic study on the effects of column efficiency and separation factor on the performance of SSR and a comparison with batch chromatography is presented, because the results of earlier studies on the topic have been contradictory.

This work is limited to the recovery of small molecules (such as sugars and carboxylic acids) from biomass hydrolysates and spent pulping liquors. Three case studies are included: recovery of fermentable monosaccharides from concentrated-acid hydrolysate of wood (Paper I), separation of glucose and galactose of lactose hydrolysate (Paper II), and recovery, purification and fractionation of hydroxy acids of black liquor (Papers III and IV). The aim is to select the most suitable separation process alternative for each of these separation tasks based on understanding of the separation mechanisms.

The framework of this thesis and the separation methods used in Papers I–IV are illustrated in Fig. 1. The focus in papers I and II is on recycling chromatography. Combining of pressure-driven membrane filtration processes with chromatographic separation is discussed in Papers II–IV. Separation processes based on using membrane filtration only are excluded from the work. Evaluation of the economic feasibility of the separation process concepts is also left beyond the scope of the work.

2.2 Outline

A deep understanding of the individual separation techniques applied is of major importance when designing combined separation processes. Therefore, this thesis begins with an introduction to the principles of chromatographic and membrane separations, including a review of the separation mechanisms and the most common separation materials and process modes. Chromatographic separation and membrane filtration are discussed separately in Chapters 3 and 4, respectively. Each of these chapters ends with a brief literature review of the potential biorefinery applications of the separation method under discussion.

In Chapter 5, different approaches to combining separation techniques are presented. The focus is on the combinations of chromatographic and membrane separations.

In Chapter 6, the special challenges related to the stability of separation materials during long-term use are discussed. The stability issue is addressed because fouling and degradation of separation materials under extreme conditions typical for biorefinery environment can be major obstacles for implementation of chromatographic and membrane separations in biorefineries.

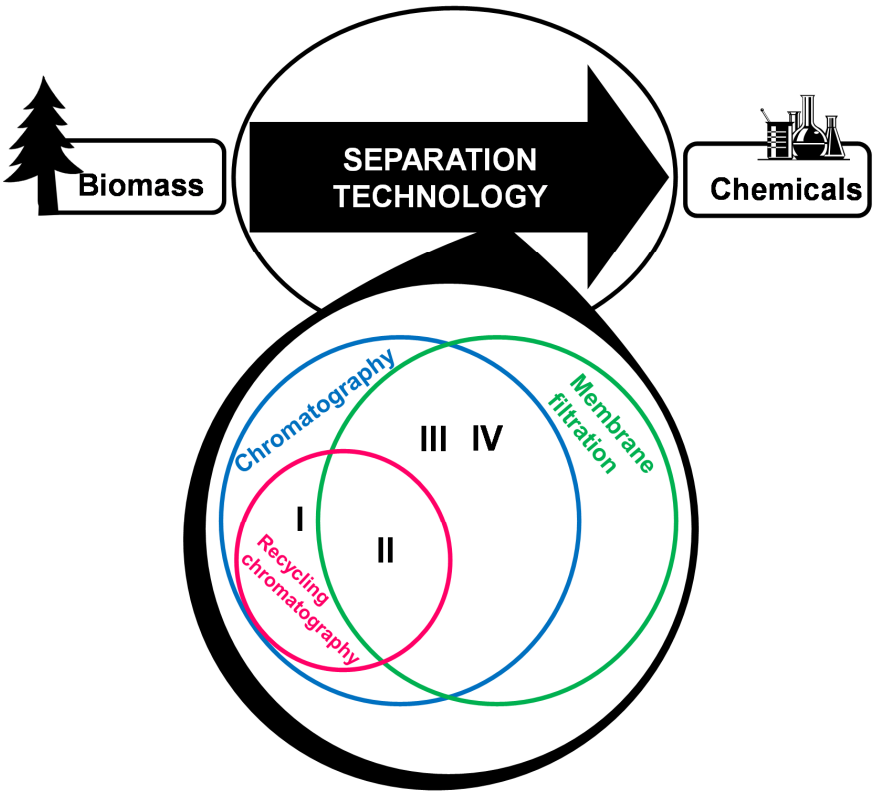

Fig. 1 The framework of the study and the separation methods applied in Papers I-IV.

The experimental part and Papers I-IV give the details of the work carried out, ending with the results and conclusions. In addition to a summary of the work carried out in Papers I-IV, the experimental part of the thesis contains earlier unpublished results of the use of SMB chromatography for separating the hydroxy acids of black liquor. An earlier unpublished comparative study of recycling chromatography and batch chromatography based on a systematic simulation work is presented in Appendix 1.

3 PREPARATIVE CHROMATOGRAPHY

Chromatographic separation phenomenon was first investigated by Tswett in 1906. Today, chromatography is widely utilized both as an analysis technique and in industrial separation processes, e.g. in the purification of active pharmaceutical ingredients and in the production of sugars. This thesis is focused on the application of chromatography at production scale, i.e. preparative liquid chromatography.

The principles of chromatographic separation are discussed in this chapter, starting with the different separation mechanisms and materials employed in chromatography (Section 3.1). In addition, the different operation modes of preparative chromatography are described. The most common process modes of chromatographic separation are batch chromatography and continuous simulated moving bed chromatography. These modes are briefly described in Sections 3.2 and 3.4. Section 3.3 discusses different recycling schemes that can be applied to improve the performance of batch chromatography.

As chromatography was originally designed for isolation of natural products from complex mixtures of vegetal origin [25], its application in biorefineries is a natural choice. The potential biorefinery applications of preparative chromatography are reviewed in Section 3.5.

3.1 Separation materials and mechanisms

Chromatographic separation is based on differences in the migration velocities of components (molecules or ions) of a mixture passing through a stationary material that typically consists of solid particles packed as a bed in a chromatography column. The velocity differences among the components are due to their different partitioning behaviour between the mobile and stationary phases. The partitioning may be affected by attraction forces between the solutes the solid phase (adsorption or complex formation), ion-exchange or ligand-exchange, electrostatic effects (ion-exclusion), steric effects (size-exclusion), or interaction between the solutes (salting-out). The most important of these retention mechanisms (i.e. the separation mechanisms of chromatography) are illustrated in Fig. 2. Often several different mechanisms account for the retention of a component.

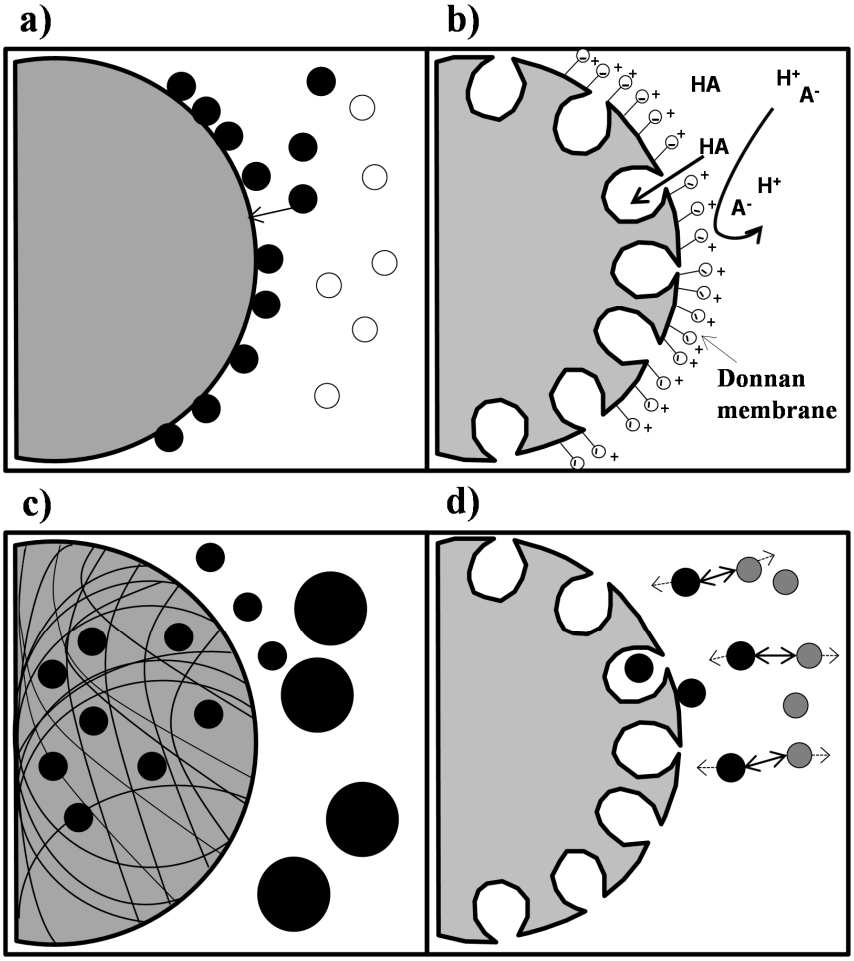

Figure 2 Examples of separation mechanisms in chromatography: a) adsorption, b) ion-exclusion, c) size-exclusion, d) salting out.

3.1.1 Adsorption

Adsorption is adhesion of molecules on a solid surface. Adsorption can be reversible or irreversible. Chromatographic separation exploits reversible adsorption. It is favourable that the interactions between the solute and the solid phase are weak; otherwise large volumes of eluent are required to elute the adsorbed component. Adsorption typically occurs due to weak van der Waals interactions. Other adsorption mechanisms are also known: hydrogen bonding,

hydrophobic-hydrophilic interactions, complex formation, ligand exchange, and ion-exchange.

The driving force of adsorption is the chemical potential difference across the phase boundary. Therefore, adsorption of a solute may depend on its co-solutes, i.e. the other compounds present in the liquid phase. These co-solutes can be other eluates or components of the eluent. As illustrated in Fig. 2d, repulsive interactions between the solutes may strengthen the adsorption of a solute due to phenomenon analogous to the salting-out effect exploited in crystallization. This effect may be beneficial to chromatographic separation, which has been observed e.g. in the separation of monosaccharides and sulphuric acid [26]. On the other hand, if the separation of compounds occurs rapidly, the solute interactions can be neglected.

3.1.2 Ion-exclusion

Ion-exclusion (Fig. 2b) occurs due to the electrostatic repulsion between ions of the solution and the charged functional groups of the solid surface. In Fig. 2b, the A^- anions cannot pass into the pores of the particle because of the repulsion caused by the negative charge on the particle surface. When the negative ions are repelled, the H^+ cations must also remain in the bulk solution to maintain electroneutrality. This phenomenon is known as Donnan effect. The negative charge on the particle surface forms a Donnan "membrane", which can be permeated only by non-charged molecules (unless charged compounds are moving to the opposite direction as in ion-exchange). Only the non-ionised HA molecules can, therefore, enter the pores in the example of Fig. 2b. In practise, the rejection of charged compounds is, however, incomplete, and depends on the ionic strength of the solution. Ion-exclusion is utilized in the separation of electrolytes from non-electrolytes using an ion-exchange resin or other charged separation material.

Ion-exchange resins are widely used as separation material in chromatography. When ion-exchange resins are applied in chromatography, the separation is typically not based on interchange of ions between the mobile phase and the stationary resin phase but on partition of the compounds between the two phases due to ion-exclusion and other phenomena [27].

Ion-exchange resins are typically polymeric beads, which can be either non-porous or macroporous. The non-porous, gel-type resins have a higher capacity and a lower price than the macroporous resins [28]. On the other hand, macroporous resins are less sensitive towards fouling [28]. Inorganic materials, e.g. zeolites and silicates, may also have ion-exchange properties [29].

Ion-exchange resins are typically classified into four groups based on their functional groups: strong-acid cation (SAC), weak-acid cation (WAC), strong-base anion (SBA), and weak-base anion (WBA) exchange resins.

The functional group in SAC resins is sulphonic acid, and the most common polymer backbone structure is polystyrene (PS) cross-linked with divinyl benzene (DVB) [30]. The DVB content varies among resins from 2 up to 20 % and even higher [28]. The amount of cross-linking affects the capacity and the shrinking and swelling behaviour of the resin. It should be noted that the separation using a SAC resin occurs not solely by ion-exclusion but it is also affected by size-exclusion. Therefore, the degree of cross-linking, which affects the resin structure, can have a substantial impact on the separation selectivity.

SAC resins are the most common type of ion-exchange resins because they are relatively inexpensive and suitable for many purposes. For example, SAC resins in calcium form are typically applied in sugar separations, because calcium forms complexes of different strength with sugars [31]. One drawback of PS-DVB resins, especially the ones with a low degree of cross-linking, is that they are susceptible to degradation by oxidizing compounds [28].

WAC resins contain a carboxylic functional group. The polymer skeleton of the resin is commonly acrylic or methacrylic cross-linked with DVB. Like styrene resins, acrylic resins are also sensitive towards oxidation [28].

Anion-exchange resins have a basic functional group instead of an acid group. SBA resins typically possess quaternary ammonium functionality [28]. For WBA resins, a polyamine group is typical. The skeletal structure may be either styrene-based or acrylic.

3.1.3 Size-exclusion

Size-exclusion (Fig. 2 c) is based on the differences in the hydrodynamic radii of molecules. Small molecules enter the pores of the separation material while the large molecules are excluded due to steric effects. Consequently, large molecules have a shorter pathway through the bed and thus they elute faster. Size-exclusion chromatography (SEC) is widely applied in desalting of proteins [32]. SEC is also known as gel permeation chromatography or gel-filtration chromatography, because the stationary phase is often a gel.

One of the most common size-exclusion gels is a dextran polymer cross-linked with epichlorohydrin (ECH), which has been commercially available with the trademark Sephadex since 1950s. Dextran forms a three-dimensional swollen polymer network, in which the degree of swelling, and thus the pore size, depends on the cross-linking [33]. Sephadex is thermally stable up to 120 °C and has relatively good chemical resistance [34]. However, exposure to very alkaline or acidic conditions may cause hydrolysis of the polymer [34]. Dextran gel materials are not completely neutral due to a small number of carboxylic acid groups in their structure, and ion-exclusion may, therefore, take place in addition to size-exclusion [35, 36]. The effect of ion-exclusion can be supressed using an eluent with a moderate ionic strength [35].

Another well-established polysaccharide-based size-exclusion gel material is agarose, which is commercially available e.g. with trademark Sepharose. Whereas dextran polymer is branched, agarose is a linear polymer which forms a double-helical structure. To improve their thermal and pH stability, agarose gels are often cross-linked [34]. Composites containing both dextran and agarose are also available [34].

Cross-linked polyacrylamide is also a common material for size-exclusion gels [34]. The operating pH range of the polyacrylamide-based gels is limited, because the amine side groups are susceptible to hydrolysis under extreme pH conditions. On the other hand, polyacrylamide is less sensitive to microbial growth than polysaccharide-based size-exclusion gels.

Other neutral chromatographic stationary phase materials which mainly exploit the size-exclusion mechanism include neutral PS-DVB resins and silica. PS-DVB resins are widely

applied and can be functionalized to improve selectivity [37]. Recently a lot of interest has been paid especially to hypercrosslinked PS-DVB resins [38]. Considering inorganic alternatives, silica is a versatile material often used in analytical chromatography. However, it has a limited pH range and the residual silanol groups in the structure may show strong interactions with some compounds [38].

3.2 Principles of batch chromatography

In batch elution chromatography, a pulse injection of the solution to be treated is introduced into the chromatography column, which is continuously flushed with eluent. The separation procedure for a mixture of two components is illustrated in Fig. 3. The processing of large amounts of feed solution is possible using successive pulse injections. Time interval between two pulses has to be long enough to avoid overlapping of the peaks with the ones from the previous pulse. The main advantages of batch chromatography are that it is simple to operate and relatively easy to scale-up.

Separation efficiency depends on the column loading, i.e. on the size of the feed pulse. In Fig. 3, the feed injection is small enough for achieving a complete resolution of A and B, which is typical for analytical chromatography. In preparative chromatography, larger injection volumes are applied. In the so-called operation with touching bands, the injection volume is increased so that B elutes immediately after A, but both compounds can be recovered with a purity of 100%. If the injection volume is further increased, A and B will not be fully resolved. This operation is known as column overloading, and it is commonly used to improve production rate and reduces eluent consumption and the dilution of the products.

Water is a favourable and commonly used eluent, since it is an environmentally benign, non-hazardous, inexpensive and relatively easy to separate from most products. However, in some applications it is necessary to use eluent other than pure water, e.g. a pH buffer or organic solvent. If some of the components have significantly longer retention times than the others, it is possible to use a solvent gradient to accelerate the elution of the last components. The disadvantage is that the solvent recycling procedure becomes difficult.

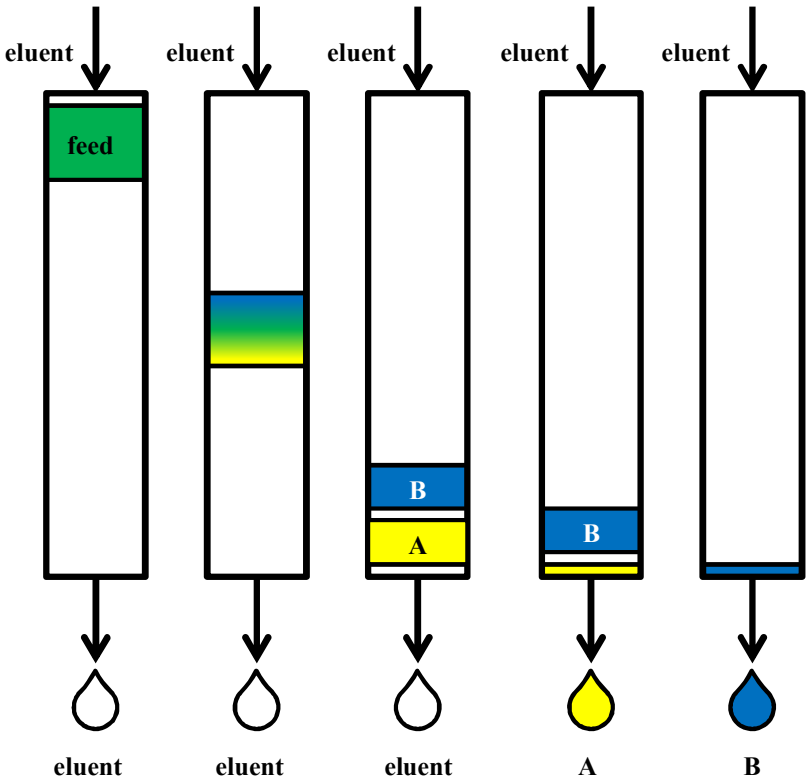

Figure 3 Chromatographic separation of a binary mixture of compounds A and B in batch mode. Separation occurs at ideal conditions and both components possess linear isotherms.

3.2.1 Quantitative description of phase equilibria in chromatographic separation

Chromatographic separation is based on differences in partitioning of compounds between the stationary phase and the mobile phase. The equilibrium of the partition of compounds between the phases is typically described using adsorption isotherms. The most simple isotherm model is the linear isotherm, which is expressed in Eq. (1)

$$q_i = H_i \cdot c_i \qquad (1)$$

where q_i is the concentration of compound i in equilibrium with c_i, its concentration in the liquid phase and H_i is the Henry constant of adsorption.

In linear chromatography, the retention of a compound is independent on its concentration. The linear isotherm model is applicable when the separation is solely based on size-exclusion, since in that case the number of adsorption sites does not set limitations on the partitioning of solutes [39]. It is also valid in analytical liquid chromatography, where concentrations are low. On the other hand, the linear isotherm model often fails to describe the behaviour of compounds in preparative chromatography, because the effect of isotherm curvature is more pronounced at high concentrations. There are, however, exceptions in which a linear isotherm model gives a good estimate on the sorption behaviour; for example, the sorption isotherms of sugars on ion-exchange resins are quite linear up to relatively high concentrations [27].

Non-linear adsorption isotherms are typical in preparative chromatography. Langmuir isotherm is a classic example of a non-linear isotherm. It is written as follows:

$$q_i = \frac{a_i c_i}{1 + b_i c_i} \qquad (2)$$

where a_i and b_i are the isotherm parameters for compound i. In a multicomponent mixture, the solutes compete for the adsorption sites. For compounds with Langmuir-type isotherms this competition leads to the following isotherm equation:

$$q_i = \frac{a_i c_i}{1 + \sum_{j=1}^{N} b_j c_j} \qquad (3)$$

where N is the number of compounds in the mixture. The Langmuir isotherm is an example of a convex upward isotherm. Convex downward known as anti-Langmuir isotherms isotherms also exist. They are observed when electrolyte exclusion takes place, e.g. for electrolytes on SAC resins [40]. The Donnan phenomenon that causes anti-Langmuir isotherms was already discussed in Section 3.1.2.

Because the adsorption behaviour of compounds differs a lot, numerous isotherm models have been developed, and they will not be reviewed herein. Especially if the interactions between solutes affect the sorption equilibrium, rather complex isotherm equations are needed.

The type of the isotherm affects the shape of the elution band in the chromatogram. Whereas a linear isotherm leads to a symmetric elution profile, this is not the case for non-linear isotherms. For Langmuir isotherms, the front of the elution profiles is sharp and the rear is elongated, because small concentrations migrate slower in the column. For an anti-Langmuir isotherm, the front is elongated and the rear is sharp, because small concentrations move faster but cannot pass the large concentrations.

The success of the separation of two compounds depends on the difference of their retention factors, which is typically expressed as separation factor α. For a binary separation of compounds with linear isotherms, α is defined as

$$\alpha = \frac{H_2}{H_1} \qquad (4)$$

Similarly, the separation factor for Langmuir isotherms can be calculated as

$$\alpha = \frac{a_2}{a_1} \qquad (5)$$

3.2.2 Mass transfer in a chromatography column

If chromatographic separation is assumed to take place under ideal conditions, which means that the rate of mass transfer kinetics is infinite and no axial dispersion occurs, the compounds elute as sharp bands, the shape of which is controlled by thermodynamics only. In this situation, column efficiency is infinite. In reality, the elution profiles are often somewhat broadened because of the limited column efficiency. The column efficiency depends on kinetic effects, diffusion, and mass transfer resistances. Since adsorption–desorption kinetics are usually very fast, mass transfer rate is the dominating issue.

Mass transfer can be divided into three steps: mass transfer in the bulk phase via convection and diffusion, film diffusion near the particle surface, and intraparticle diffusion. Intraparticle diffusion is often the rate limiting step. For porous materials, intraparticle diffusion occurs via different mechanisms: molecular diffusion in the large pores, Knudsen diffusion in the vicinity of pore walls, and surface diffusion of the adsorbed molecules.

Liquid flow in a packed bed is not homogeneous because of the tortuosity of the packing. Diffusion in the interparticle pores and eddy diffusion cause dispersion in the bed. These dispersion effects are typically lumped to axial dispersion coefficient D_L [25]. D_L can be estimated, for example, using the correlation by Chung and Wen [41]:

$$Pe = \frac{L}{\varepsilon_b d_p}\left[0.2 + 0.011 Re^{0.48}\right] \tag{6}$$

$$Re = \frac{u\rho\varepsilon_b d_p}{\eta} \tag{7}$$

$$D_L = \frac{uL}{Pe} \tag{8}$$

Pe is the Péclet number, L is the bed height, ε_b is the bed porosity, d_p is the particle diameter, Re is the Reynolds number, u is the linear velocity, ρ is the density, and η is the dynamic viscosity. As indicated by the equations, particle size has a large impact on axial dispersion. Column efficiency is, therefore, strongly affected by the particle size and particle size distribution of the separation material.

Column efficiency is typically reported as number of theoretical plates (*NTP*). The theoretical plates are imaginary fully mixed stages that the column is divided into. *NTP* can be determined from an elution profile by dividing the squared first moment M_1 by the second moment M_2:

$$NTP = M_1^2/M_2 \tag{9}$$

$$M_1 = (1/M_0)\int_0^\infty \tau \cdot h(\tau)d\tau \tag{10}$$

$$M_2 = (1/M_0)\int_0^\infty (\tau - M_1)^2 h(\tau)d\tau \tag{11}$$

where M_0 is the zeroth moment and τ is the time from the feed injection:

$$M_0 = \int_0^\infty h(\tau)d\tau \tag{12}$$

$$\tau = t - \Delta t_{inj}/2 \tag{13}$$

where $h(t)$ is the height of the peak at time t after the start of the injection. Δt_{inj} is the duration of the feed injection. The height of the theoretical plates (*HETP*) can be calculated based on the bed height L.

$$HETP = L / NTP \tag{14}$$

3.2.3 Evaluation of process performance

As for any separation and purification task, the success of a chromatographic separation can be assessed based on the recovery yield of the target compound and its purity. In addition to investment costs, the main factors affecting the economics of the separation process are production rate and consumption of chemicals and energy. These factors should also be used in the evaluation of the process performance.

Typically, a lower limit for either yield or purity is set, and the process is optimized so that the production rate is maximized without failing to fulfil these conditions.

Considering recovery of two product fractions, A and B, the purities of the product fractions can be determined as follows:

$$PU_A = \frac{\sum_{i \in S_A} n_i^A}{\sum_{j=1}^{N} n_j^A} \tag{15}$$

$$PU_B = \frac{\sum_{i \in S_B} n_i^B}{\sum_{j=1}^{N} n_j^B} \tag{16}$$

PU_A and PU_B are purities of product fractions A and B, when S_A is a set of compounds which are desired to be collected in fraction A, and S_B is a corresponding set of target compounds for fraction B. The purity is here expressed as the molar fraction of the target compound in the product fraction. Alternatively, mass fraction can be used.

In the case of a high-value compound, yield is typically used as a constraint instead of purity. The recovery yield of component i is defined as follows:

$$Y_i = \begin{cases} \dfrac{n_i^A}{n_i^F} & i \in S_A \\ \dfrac{n_i^B}{n_i^F} & i \in S_B \end{cases} \tag{17}$$

where n_i^F is the amount of component i in the feed.

Process performance can be assessed based on productivity and eluent consumption. Productivity (PR) is the production rate divided by the volume of stationary phase (V_b). The productivity with respect to target compound i can be calculated using equation

$$PR_i = \frac{Y_i c_i^F V^F}{t_{cycle} V_b} = \frac{Y_i c_i^F \dot{V}^F}{V_b} \tag{18}$$

V^F is the volume of the feed injection and t_{cycle} is the cycle time and $\dot{V}^F$ is the feed flow rate in the case of a continuous process. If multiple products are recovered, the total productivity PR_{tot} is calculated using the equation

$$PR_{tot} = \frac{V^F \left(\sum_{i \in S} Y_i c_i^F \right)}{V_b t_{cycle}} = \frac{\dot{V}^F \left(\sum_{i \in S} Y_i c_i^F \right)}{V_b} \tag{19}$$

Eluent consumption (EC) is here defined as the volume of eluent required per one mol of product.

$$EC_i = \frac{t_{cycle} \dot{V} - V^F}{Y_i c_i^F V^F} \tag{20}$$

If multiple products are collected, the total eluent consumption EC_{tot} can be calculated as follows:

$$EC_{tot} = \frac{EC_1}{1 + \sum_{i=2}^{n} \left(\frac{Y_i}{Y_1} \cdot \frac{c_i^F}{c_1^F} \right)} \tag{21}$$

Productivity can be increased by increasing the column load or by shortening the cycle time by applying a higher flow rate. However, the product purity may decrease if the yield is fixed. In addition to the purity constraints, the applicable flow rate may also be limited by a maximum pressure drop through the column. Furthermore, eluent consumption increases when flow rate is increased, resulting in a more diluted product.

3.3 Recycling chromatography

In preparative chromatography, limited column efficiency and large sample volumes applied often lead to poor resolution of compounds. Consequently, either the product purity or recovery yield must be compromised. Different recycling procedures have been introduced to increase the yield and to improve the product purity in an overloaded chromatography column without increasing the pressure drop. The idea of recycling chromatography is to re-process the partially resolved intermediate in the same chromatography column.

3.3.1 Closed-loop recycling and peak-shaving

The simplest recycling procedure is closed-loop recycling, in which the whole separation profile is re-injected back to the column [42, 43]. In other words, the outlet of the column is pumped back to the inlet, and several loops are operated as a closed system. Recycling results in the same improvement in the recovery yield as elongating of the column but without the requirement to increase the column inlet pressure [43]. The resolution of compounds is improved from cycle to cycle, and the product fractions are collected after the desired product purity is achieved. In the so-called peak-shaving mode, a product fraction is (or fractions are) recovered in every cycle, and only the mixed, off-specification zone is recycled back to the column [44]. The injections are smaller than in the closed-loop recycling mode, which improves the efficiency of the separation.

The drawbacks of the closed-loop recycling concepts are that the production rate decreases, and the product becomes very dilute. Furthermore, the achievable product purity may be limited, since there is a limitation for the recycling, which can be no longer continued once the sample has spread over the whole column [44]. Also, it should be noted that extra-column dispersion, e.g. back-mixing due to pumping, partially destroys the obtained resolution as it causes band broadening [43, 45]. A proposed approach to reduce this remixing is the so-called

alternate pumping recycling, where the sample stream is conducted through two columns without passing through a pump in between [46].

3.3.2 Steady-state recycling (SSR) chromatography

Both closed-loop and peak-shaving are batch processes, and since several cycles are required, the productivity of the process is low. To increase the productivity, the batch operation can be substituted with a cyclic process in which fresh feed is injected together with the recycle stream. Since the system reaches a steady state after a few cycles, the method is called steady-state recycling (SSR) chromatography. SSR chromatography was first systematically investigated by Bailly and Tondeur [47]. Since SSR is not a continuous process, the term steady-state in SSR refers always to a periodic steady-state, in which the column outlet profile and the feed composition remain unchanged from cycle to cycle.

A simplified process scheme of SSR is presented in Fig. 4. The unresolved part between the product fractions A and B is the recycle fraction R, which is re-injected to the column together with fresh feed. The fraction cut-times (dashed lines in the figure) are chosen based on the desired purity or yield. The amount of fresh feed that can be treated each cycle depends on the volume of the recycle fraction. As seen in the figure, no waste fraction is collected. Two different types SSR operation modes have been suggested: mixed-feed SSR and segmented-recycle SSR.

In the mixed-feed mode (also known as mixed-recycle) of SSR, the recycle fraction collected from the column outlet is mixed with a suitable amount fresh feed, and the mixture is then injected into the column. At steady-state, the fraction cut-times and the composition of the feed are the same in every cycle.

The drawback of the mixing is that the advantage of the partial separation obtained during the previous cycle is lost. However, the mixed feed mode is more flexible than the modes where the outlet profile is injected to column as such [23]. Since the recycle fraction can be easily collected into a reservoir, the mixed feed mode makes it possible to apply stacked-injections and thus utilize the capacity of the column more effectively [23]. An alternative operation mode of SSR is the segmented-recycle mode (also known as closed-loop SSR), in which the recycle stream is not mixed with the fresh feed but injected as its original profile similarly as

in closed-loop recycling with peak-shaving [48]. Fresh feed is injected before, after, or in the middle of the recycle stream [45].

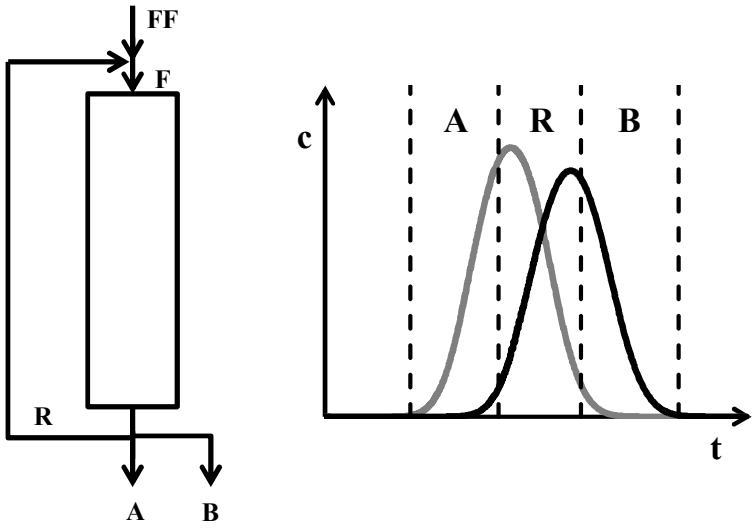

Figure 4 The principle of SSR chromatography. FF = Fresh feed, F = feed to column, A = first product fraction, B = second product fraction, R = recycle fraction.

The main advantage of the segmented-recycle mode in comparison to the mixed-feed is that the partial separation can be exploited. However, the problem is the dispersion in pumps and pipelines. The extra-column effects have to be taken into account also in the process modelling [49].

Another drawback of segmented-recycle operation is that the injection time point is fixed [22]. Therefore, it is not possible to optimize the injection time points so that the column would be effectively used, and the next cycle would elute straight after the previous one. As a result of the above, the segmented-recycle SSR is substantially more complicated to design than the mixed-feed SSR process.

Optimization of the mixed-feed mode in the production of pure compounds from a binary mixture under ideal conditions was first discussed by Bailly and Tondeur [47]. More recently, Sainio and Kaspereit have developed a simplified design-method for mixed-feed SSR with arbitrary purity requirements [22, 23]. Under ideal conditions, the steady-state chromatogram

and the appropriate fraction cut-times of mixed-feed SSR can be predicted based on the isotherm parameters without any dynamic simulations [22, 23]. Using the predicted values for initial injections in the start-up of the SSR process, steady-state can be obtained faster [22].

It is worth mentioning that recycling of the unresolved part in the binary separation as shown in Fig. 4 is not the only way to realize recycling. For example, if strong tailing at the rear or the front of the peak occurs, the dilute part can be recycled. The dilute recycle fraction is injected before the fresh feed [48]. It is also possible to inject dilute fractions of the separation profile as eluent, similarly as has been presented for continuous chromatography [50]. Furthermore, it is possible to recover several recycle fractions in a multicomponent separation. However, optimization of such a recycling process is very complicated, and the literature on the alternative recycling strategies is scarce.

3.4 Continuous chromatography

Continuous separation processes are attractive for large-scale industrial applications. Chromatographic separation can be operated continuously if the solid phase moves to opposite direction than the fluid. Typically, the solid phase flow is counter-current to the direction of liquid flow, but it can be cross-current as well (e.g. in continuous annular chromatography).

A process in which solid phase moves counter-current to the liquid flow is known as true moving bed (TMB) chromatography. A feed stream is introduced into the centre of the column. The more retained compound moves in the same direction as the solid phase whereas the less retained component moves in the direction of the liquid phase, and two product streams are continuously recovered from the ends of the unit. A TMB process is difficult to realize due to several practical problems, including back-mixing and particle attrition and breakage [25]. Therefore, TMB chromatography is in practice substituted with simulated moving bed (SMB) chromatography.

In SMB chromatography, the adsorbent bed is not truly moving but the same effect is achieved by changing the locations of inlet and outlet ports. SMB consists of several sections (typically four) of single or more columns. If the switching time intervals and the columns would be infinitely short, the operation would be identical to a TMB process. A simplified

schematic of the SMB process is shown in Fig. 5. The less adsorbed component is recovered in raffinate stream while the more adsorbed component ends up in the extract stream.

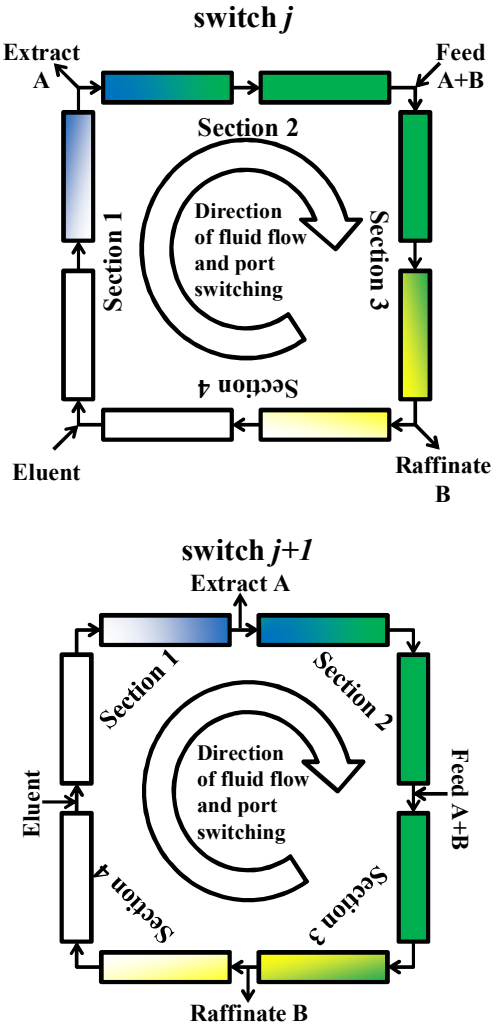

Figure 5 A simplified scheme of a four-zone SMB (adapted from [51]).

The liquid flow rates in different sections and the switch time that corresponds to the solid flow rate are essential parameters in the design of a SMB process [52]. Owing to the complexity and dynamic nature of the process, modelling is an important tool in the design

and control of SMB chromatography. The modelling of SMB has been reviewed e.g. by Guiochon et al. [25] and Rajendran et al. [51]. In addition to the model-based design, short-cut design methods such as triangle theory [52, 53] are widely used. The optimization parameters of the triangle theory, m_j, are calculated as a ratio between the fluid and solid flow rates in section j (for a four-zone SMB j = 1...4) using Eq. (22). In the case of a linear isotherm, a triangle-shaped region in the (m_2, m_3) plane provides pure product streams as presented in Fig. 6. In the areas marked with "No separation", the feed ends up in either extract or raffinate while the other outlet stream contains merely the solvent. The grey area presents the parameter region that is not feasible because at positive feed flow rates $m_3 > m_2$.

$$m_j = \frac{\text{volumetric fluid flow rate}}{\text{volumetric solid flow rate}} \tag{22}$$

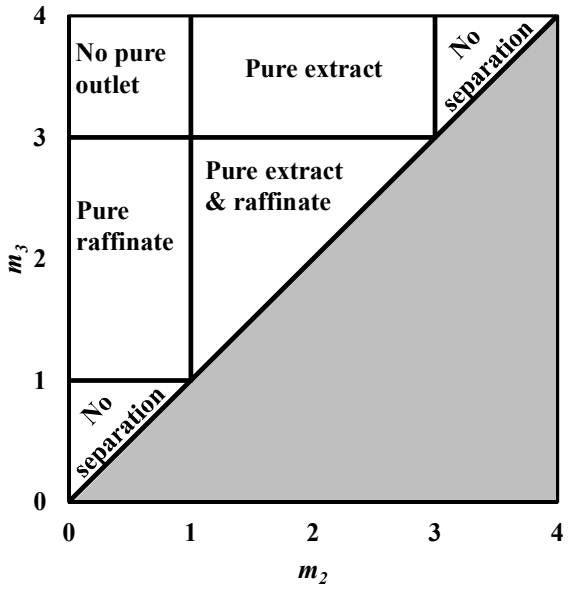

Figure 6 The purities of product streams at different operation region on the (*m2*, *m3*) plane for a system with linear isotherms with H_A = 3 and H_B = 1 (adapted from [52]).

In comparison to batch chromatography, SMB chromatography typically provides higher productivity but is less flexible in operation and more complicated to design. The long time

required to achieve steady-state is one of the drawbacks of SMB [25]. An important advantage of SMB is the less diluted product stream in comparison to the product obtained in batch chromatography. The concentrated product makes the product recovery and downstream processing more efficient [54].

Conventional SMB is inherently a binary separation process [45] and it is thus principally used for binary separations. However, with certain process modifications SMB can also be utilized for ternary and multicomponent separations. A common approach is to apply SMB cascades, in which two or more SMB units are coupled together [55, 56]. Multicomponent separations have been also done in a single device using a nine-zone SMB [57] and a five-zone SMB [58]. As an alternative, a pseudo-SMB process based on the Japan Organo (JO) process of Japan Organo Co. [59] has been found useful for multicomponent separations [60, 61].

3.5 Biorefinery applications of chromatography

Important applications of chromatography in the field of biorefining include various sugar separations (e.g. glucose–fructose separation [62], desugarisation of molasses [62], and xylose recovery from spent sulphite liquor for production of xylitol [63]). Therefore, chromatographic separation would most probably be a useful technique also in a future biorefinery that is based on the sugar platform. Some of the potential applications are reviewed in this section.

3.5.1 Processing of biomass hydrolysates

Biomass is mainly composed of polymers, e.g. cellulose, hemicelluloses, and starch. A common strategy is to carry out a chemical (typically acidic [16]) or enzymatic [64] hydrolysis to decompose these polymers to smaller units such as monosaccharides which are then further refined by fermentation or by other means. After the hydrolysis, the solution typically contains unreacted compounds such as hydrolysis acid and undesired by-products, which may deteriorate the following process step, e.g. by acting as fermentation inhibitors. Common examples of these inhibitory by-products are acetic acid and furfural [65]. Removal of these compounds is called detoxification of the hydrolysate, and chromatographic separation is a suitable purification method for this purpose.

Considering acid hydrolysis, the major impurity in the hydrolysate is the acid applied in the hydrolysis. The hydrolysis acid is traditionally removed by over-liming, i.e. adding an excessive amount of alkali such as $Ca(OH)_2$. If sulphuric acid was used in the hydrolysis, the over-liming results in formation of $CaSO_4$, which precipitates due to its low solubility and can be removed by filtration. The formation of large amounts of sulphates and the fact that the hydrolysis acid cannot be directly re-used are the disadvantages of over-liming. In particular, considering a strong-acid hydrolysis in which a high concentration of acid is applied, the recycling of the hydrolysis acid would be a necessity for the techno-economic feasibility of the process [66]. Chromatographic separation using a SAC resin has been found applicable for the recovery of the products and the acid [26, 66]. The fermentation inhibitors are simultaneously removed, and, therefore, better fermentation yield can be obtained for chromatographically purified than for over-limed hydrolysates [67]. Alternatively, the detoxification of hydrolysates can be performed as a separate process step using adsorption [68].

As an alternative to conventional acid and enzymatic hydrolysis processes, utilization of ionic liquids has been found a promising new technology for biomass conversion processes [69]. However, one of the major challenges is the recycling of the ionic liquid, since its separation may be difficult due to its polarity and non-volatility. Ion-exclusion chromatography is applicable also for fractionation of ionic liquid solutions. For example, Zhou et al. used ionic liquids to aid the hydrolysis of algal biomass, and used Dowex 50WX 4 resin in $[Emim]^+$ form for recovering the solvent and the product, fermentable monosaccharides [70].

In addition to fermentable monosaccharides, rare sugars can also be obtained from biomass hydrolysates. Using chromatographic separation, these high-value products can be recovered in high purity. Saari and Hurme have presented general heuristics for the process synthesis of chromatographic recovery of sugars from biomass hydrolysates [71]. According to them, SAC resins are recommended for these sugar separations. However, because the starting purity is often low, a multistep process using various resin types may be needed.

3.5.2 Product recovery from fermentation broths

The monosaccharides obtained from hydrolysis can be fermented using a suitable micro-organism to obtain products such as bioethanol or carboxylic acids. The micro-organisms

used in fermentation are usually not 100% selective, and by-products may thus be formed. For example, in production of succinic acid, other organic acids such as acetic acid and lactic acid are also typically produced [72]. Chromatographic separation is one option for separating the target compound from the by-products. For example, Nam et al. [73] separated succinic acid from lactic acid in an SMB process using a neutral polymer adsorbent (Amberchrom CG300C).

3.5.3 Fractionation and purification of oligomers and polymers

In some cases it may be preferable to recover the polymeric compounds of biomass as polymers or as oligomers rather than to decompose them into monomers to obtain products with more added value. For example, oligosaccharides obtained from biomass by water or steam treatment have potential applications in food industry as additives and nutraceuticals [74].

Size-exclusion chromatography is a suitable method for fractionation of the recovered polymers and oligomers based on their sizes. It has been applied for purification of oligosaccharides from autohydrolysis of corn cobs [75] and olive tree pruning [76], for fractionation of lignosulphonates [77], and for purification of cellodextrins prepared from microcrystalline cellulose by acid hydrolysis [78].

3.5.4 Desalting

Silage is fermented agricultural biomass, which is rich in lactic acid and amino acids [79]. Recovery of these target compounds in a silage-based biorefinery is challenging, since silage contains high amount of inorganic salts and other impurities. Thang and Novalin [80] found a chromatographic separation using a neutral polymeric resin (Amberlite XAD 1600) suitable for the desalting of silage juice. This chromatographic method was found preferable over electrodialysis with respect to energy consumption when the salt concentration is high [80].

3.5.3 Fractionation of black liquor

Black liquor is the spent pulping liquor, obtained as a side-product from alkaline pulping of wood. It is an important energy source for a pulp mill but also a potential source of different biomass-based chemicals. Special interest has been paid to the recovery of hydroxy carboxylic acids, which are formed during alkaline degradation of the carbohydrates of wood

and have potential applications, e.g. as chelating agents [81] or as precursors for different polymeric materials [82].

Chromatographic separation may be a useful technique for the fractionation of black liquor. For example, Alén et al. [83] used ion-exclusion chromatography for the separation of the inorganic chemicals from the hydroxy acids of black liquor. The application of SEC for fractionation of black liquor is discussed in Papers III and IV. However, chromatographic processing of black liquor is challenging because black liquor is highly alkaline (pH about 13.5) and contains large amounts of lignin and other compounds which may cause fouling and precipitation problems. Therefore, different pre-treatment methods are needed.

4 MEMBRANE FILTRATION

Membrane filtration utilizes a semi-permeable membrane for separation: some components of the treated mixture are able pass through the membrane to the permeate side, while the others are retained. Unlike conventional filtration, membrane filtration is not primarily a solid–liquid separation process but all the compounds are typically in the fluid phase. During the filtration, the feed is divided into two fluid streams: retentate and permeate. Depending on the process, the product may be the permeate (e.g. purified water), the retentate (e.g. juice concentrate), or both.

Different membrane separation processes and operation modes as well as the most important phenomena related to membrane separation are reviewed in this chapter. In the end, applications of membrane technology in biorefineries are discussed. The focus is on pressure-driven membrane filtration, which is the most common type of membrane separation process in industry.

4.1 Classification of membrane separation processes

Membrane separation processes are typically classified based on the driving force. The driving force is a difference in either electrical or chemical potential [84]. The difference in the chemical potential may be induced by concentration, temperature, or pressure.

Electrically driven membrane processes such as electrodialysis can be employed for separating electrically charged components from uncharged ones. Pervaporation and dialysis are examples of concentration driven membrane processes, in which mass transfer occurs via diffusion. In thermally driven membrane processes, temperatures on each side of the membrane are different, and mass flow through the membrane occur because of this temperature difference. The mass transfer may be related to the heat flow (phenomenon known as thermo-diffusion), or it can be caused by the differences in the vapour pressures as in membrane distillation [84]. In the pressure-driven membrane processes, pressure is applied to overcome the osmotic pressure and to induce flux through the membrane.

Pressure-driven membrane separation processes are divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) based on the membrane pore sizes as presented in Table 1. MF is typically applied for separation of bacteria or small

particles, e.g. in clarification processes. UF is capable for separating macromolecules. NF is used, e.g. in separation of small molecules and multivalent ions. RO utilizes non-porous membranes, which are essentially permeable to the solvent (water) only. The main application area of RO is desalination and production of ultrapure water. As seen in Table 1, the operating pressures vary depending on the type of the membrane process: the denser the membrane, the higher the pressure required. In MF and UF, a relatively high permeate flux can be obtained with moderate pressures, whereas high pressures need to be employed in NF and RO.

Table 1 Pressure-driven membrane filtration processes (adapted from [85]).

	Pore size, nm	**Pressure, bar**	**Permeability, L/(h m^2 bar)**
MF	100–10,000	0.1–2	> 1,000
UF	2–100	0.1–5	10–1,000
NF	0.5–2	3–20	1.5–30
RO	< 0.5	5–120	0.05–1.5

4.2 Membrane materials and separation mechanisms

Separation of compounds in a membrane filtration process may occur via different separation mechanisms. In pressure-driven membrane processes, the most important mechanisms are size-exclusion (sieving), electrostatic exclusion and solution–diffusion. The separation mechanism and a suitable membrane material are key to the membrane filtration process and the specific application. The separation mechanisms in the different pressure-driven membrane filtration processes and the most common membrane materials used are briefly described herein.

Membranes are typically made of organic polymeric or inorganic ceramic materials. Polymeric membranes are more widely applied because of their low price in comparison to ceramic membranes. Another advantage of polymeric membranes over ceramic membranes is that they may provide a higher permeate flux as the membrane resistance is typically smaller due to a thinner membrane layer. This is because manufacturing of thin ceramic membranes is difficult due to the brittleness of the material [86]. On the other hand, the chemical and

thermal stability of polymeric materials is often relatively poor. Therefore, there is a growing interest towards ceramic membranes. In addition, organic–inorganic hybrid membranes with unique properties have been developed [87].

Chemical and thermal stability is an important factor in the selection of a membrane material. However, other properties, especially fouling tendency (see Chapter 6.1), have to be also taken into account. For example, despite their excellent stability, hydrophobic materials such as polytetrafluoroethylene (PTFE) or polypropylene (PP) are often not favoured as membrane materials due to their high fouling tendency and wetting problems in the treatment of aqueous solutions [84].

4.2.1 MF and UF membranes: Sieving effect

In MF and UF, the separation is often solely based on the sieving effect. The mechanism is simple: molecules larger than the membrane pore size cannot permeate the membrane due to steric hindrance. Since the size of a molecule is related to its molecular weight, the membrane pore size is often expressed as molecular weight cut-off (MWCO), which can be useful for estimating whether a certain compound is retained by the membrane. MWCO is determined by measuring the retention of uncharged molecules with similar structure but different molecular weight. Because membranes may possess relatively wide pore size distributions, the MWCO of the membrane is defined as the molecular weight of the compound with a retention of 90% [88].

Polysulphone (PSu) and polyethersulphone (PES) are currently among the most common materials used for manufacturing MF and UF membranes. PSu and PES membranes possess good thermal stability and tolerate a wide range of pH. The drawback of these materials is that they are susceptible to fouling due to their hydrophobic nature, which can, however, be controlled by different surface modifications [89].

Ceramic membranes are also widely used in MF and UF [85]. The most common materials for ceramic membranes are alumina, titania and zirconia [86, 90]. Ceramic membranes are typically composite membranes consisting of membrane layers with different pore sizes [86]. The macroporous support layer can be made of either ceramic or metallic material, e.g. alumina or stainless steel [86]. The thermal stability of ceramic materials is outstanding.

Therefore, they can be utilized in gas separations [84]. In addition, ceramic membranes have high resistance towards organic solvents [90]. On the other hand, the pH stability of ceramic membranes varies depending on the material and crystallinity [90]. The fouling behaviour of ceramic membranes is less studied than that of polymeric membranes. The results of a recent study suggest that for ceramic membranes fouling problems are less severe than for polymeric membranes [91]. Being both more stable and less prone to fouling, ceramic membranes may have a substantially longer service life time than polymeric membranes. However, it should be noted that the fouling behaviour of a membrane is case-dependent and needs to be tested to find the most advantageous membrane for a specific application.

4.2.2 NF membranes: Electrostatic exclusion

The sieving effect discussed above is also the major mechanism in NF [92]. Similarly as in MF and UF, the membrane rejects molecules larger than its MWCO. However, the rejection may also be based on other mechanisms such as electrostatic exclusion.

NF membranes often have charged surface groups similarly to ion-exchange resins. For example, poly(piperazine amide)-based NF membranes have carboxylic acid groups on their surface [93]. Therefore, electrostatic exclusion and Donnan effect (see Section 3.1.2) often occur in NF and sometimes also in UF [94]. In a typical case, the membrane is negatively charged, and an electrostatic repulsion increases the retention of negatively charged solutes. To maintain the electrostatic equilibrium, the solutes with a positive charge cannot permeate either, and thus only the uncharged molecules can permeate. On the other hand, the negatively charged membrane surface attracts the positively charged cations, which are accumulated near the membrane surface, accompanied with negative anions. While the permeation of large, multivalent anions is restricted by the membrane charge and pore size, the permeation of ions of smaller size and charge may be strong due to the high local concentration. Even negative retentions may sometimes be observed. This is how the Donnan effect makes the separation of monovalent and divalent ions using NF possible.

The separation mechanism of NF may vary depending on pH and salt concentration, because these factors may affect, for example, on the swelling or the surface charge of the membrane [95]. The properties of the solutes may also depend on the conditions. For example, the

charge of ionisable compounds such as weak acids changes with pH, and the hydratation radii of saccharides are affected by the presence of other compounds such as salts [96].

Thin film composite membranes represent the highest share of the world market for RO and NF membranes [97]. One of the most important materials for manufacturing the active barrier layer of thin film composite membranes for NF is aromatic polyamide (PA) [98]. The surface layer of a composite membrane is often supported by a microporous sublayer, e.g. of PSu, and a support web, e.g. of polyester.

Aromatic polyamides are applied for NF membranes due to their good chemical stability in comparison to aliphatic polyamides [84]. PA membranes can be used at pH range of 3 to 11. Since NF is an attractive method also for fractionating of highly alkaline and acidic mixtures, and acidic or alkaline membrane cleaning solutions are often required, a lot of effort has recently been put on developing chemically resistant NF membranes. For example, sulphonated poly(ether ether ketone) membranes on a PES support has been found to provide an excellent pH stability [99]. In addition, ceramic membranes for NF are available.

4.2.3 RO membranes: Solution–diffusion

In non-porous RO membranes, permeability is mainly determined by the diffusivity and solubility of the components in the membrane. The same solution–diffusion mechanism is typical in membrane separation of gases, and is sometimes also important in NF [88].

The development of RO membranes has been reviewed by Lee et al. [98]. As already mentioned, thin-film composite membranes of PA are most common in RO. Cellulose acetate (CA) membranes are also widely used in RO processes. CA membranes are manufactured from renewable raw material, cellulose, and they typically have better salt retention than PA membranes. The major drawbacks of CA are its limited temperature resistance (maximum temperature of 30 °C) and a narrow pH range of 2-8, preferably 3-6 [100]. In addition, the biodegradability of CA combined with a poor chemical resistance may reduce the membrane lifetime. CA membranes may possess a fixed charge due to the presence of carboxyl groups [101]. Therefore, electrostatic exclusion may occur also in RO processes [102].

4.3 Concentration polarisation

During membrane filtration, the retained solutes are typically accumulated near the membrane surface in a pseudo-stagnant boundary layer; this is known as concentration polarisation. Concentration polarisation affects both retention and flux, and may lead to fouling of the membrane (see Chapter 6.1 for more discussion on fouling).

The concentration polarisation phenomenon is illustrated in Fig. 7. The solutes move from the bulk feed towards the membrane surface by convection (the flux $J \cdot c$ in the figure). The retained solutes flow back towards the bulk solution by diffusion. However, the diffusion is slower than the convective flow, especially in the case of macromolecules. Therefore, the solute accumulates at the boundary layer near the membrane surface.

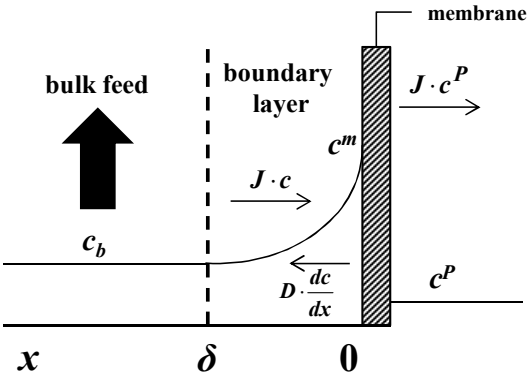

Figure 7 Concentration polarisation in membrane filtration (adapted from [84]).

Concentration polarisation depends on the flux J through membrane and on turbulence, and thus it can be reduced by increasing the cross-flow velocity. Turbulence can also be increased using turbulence promoters (e.g. spacers) or with a special module design (e.g. a vibrating membrane module).

4.4 Design of membrane processes

Membrane processes are typically modular in design, which makes the process flexible so that the production capacity can be adjusted depending on the market demand [103]. Membrane module types include spiral wound, plate and frame, tubular and hollow fibre. The module

configuration depends on the application; for example, the cleaning requirements have to be taken into account.

The membrane modules can be arranged in various different ways. Membrane filtration can be performed as a batch or as a continuous process, and different recycling strategies can be applied to improve the yield. Some of the common system design alternatives are discussed here.

Unlike conventional filtration, membrane filtration is carried out at cross-flow mode rather than as a dead-end filtration. To maintain the cross-flow in batch filtration, the retentate is typically recycled back to the feed tank while the permeate is continuously collected. In this way of operation, the concentration of the solution increases continuously, and the filtration is continued until the desired concentration is reached. If the filtration is performed using a constant pressure, the permeate flux typically decreases with time due to increased osmotic pressure, concentration polarisation and fouling.

Industrial membrane filtration processes are usually continuous. The simplest configuration is a single-pass filtration, in which feed stream is constant and permeate and retentate are continuously collected. Alternatively, part of the retentate can be recycled similarly as in batch operation but diluting it with fresh feed. This recirculation mode is known as feed-and-bleed. It may be used to obtain more concentrated retentate or to improve the yield of a target compound that is recovered in the permeate. The main reason for using recirculation is that it allows using higher flow velocity on the feed channels, which increases turbulence and consequently reduces concentration polarisation.

If high yield of a certain solute that is recovered in the permeate or a high purity of the retentate is required, diafiltration is recommended. In diafiltration, the retentate is diluted by adding solvent (typically water). The addition of the solvent helps to wash the small permeable solute molecules into the permeate.

The desired product purity is seldomly achieved in a single separation step. Therefore, multistep filtration processes known as membrane cascades are commonly used. The separation stages in a membrane cascade can be arranged in numerous different ways. Therefore, the optimization of membrane cascades can be challenging. A common, relatively

simple arrangement is the so-called “Christmas tree” or tapered array illustrated in Figure 8. In a single-pass tapered cascade shown in the figure, the feed volume reduces from stage to stage, and therefore the number of modules is also decreased. Membrane cascades can also be useful in realization of multicomponent separations.

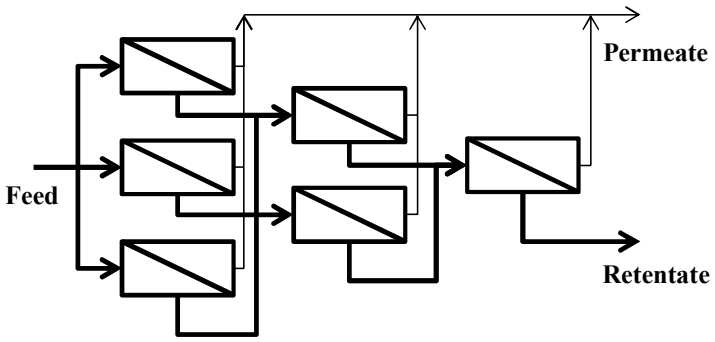

Figure 8 A single-pass membrane cascade with a “Christmas tree” design.

4.5 Evaluation of process performance

The performance of a membrane separation process can be assessed based on flux and retention. Flux corresponds to the production rate and retention affects the product purity.

According to the solution-diffusion model, the flux J depends on the applied pressure as follows [104]:

$$J = A(\Delta p - \Delta \pi) \qquad (23)$$

where A is the permeability of the membrane, Δp is the pressure difference over the membrane and $\Delta \pi$ is the osmotic pressure difference over the membrane. As seen from the equation, the flux increases when the operating pressure is increased.

Retention describes to what extent the solute is rejected by the membrane. Retention R is defined as follows:

$$R = 1 - \frac{c^P}{c^F} \qquad (24)$$

c^P is the concentration in the permeate and c^F is the concentration in the feed. A retention of 100% means that the solute does not permeate at all. Retention may get a negative value due to Donnan effect as described in Section 4.2.2. Retention depends on the process conditions. For example, in NF and RO the retention is often enhanced when the operating pressure is increased.

In processes such as desalination of water, flux and retention are enough for the performance assessment. In fractionation and recovery of components from mixtures, the selectivity of a membrane may be a useful parameter. Considering the separation of two components *i* and *j*, the selectivity, α, can be defined as follows:

$$\alpha = \frac{c_i^P / c_j^P}{c_i^F / c_j^F} = \frac{1 - R_i}{1 - R_j} \qquad (25)$$

When membrane filtration is applied for concentration processes, a suitable process performance parameter is the volume reduction factor (*VRF*):

$$VRF = \frac{V^F}{V^F - V^P} \qquad (26)$$

4.6 Membrane technology in biorefineries

Membrane filtration is an energy-efficient separation method applicable for recovering compounds of different sizes and structures from complex process streams. Membrane processes are flexible in design and also suitable for processing of large volumetric streams such as process waters. Therefore, there is currently a strong interest in the potential applications of membrane technology in biorefineries as recently reviewed by He et al. [20] and Abels et al. [21]. The application range is wide, from water removal from bioethanol using pervaporation to isolation and purification of hemicelluloses using UF.

Here, utilization of membrane technology for processing of biomass hydrolysates, for fractionating spent pulping liquors, and for recovering products from fermentation broths is reviewed. The focus is on recovery and purification of small compounds such as monosaccharides and acids using NF and other membrane processes.

4.6.1 Recovery of sugars from biomass hydrolysates

Membrane filtration is a well-suited method for fractionation and purification of biomass hydrolysates of different origin. Combination of multiple membrane filtration techniques is usually favourable: large molecules such as hemicellulose can be separated by UF, and smaller ones such as monosaccharides by NF. Various examples of utilizing membrane technology in processing of biomass hydrolysates can be found in the literature.

The processing of biomass hydrolysates often involves fermentation. Therefore, an important part in the purification of biomass hydrolysates is detoxification, i.e. the removal of fermentation inhibitors such as acids or furfural. Application of chromatographic separation for this separation task was discussed in Section 3.5.1. Being a simple process capable of separating small molecules such as monosaccharides and acids, NF can be a good alternative to chromatographic separation. For example, Zhou et al. [105] tested NF and RO membranes for separating acetic acid from monosaccharides, and Qi et al. [106] separated furfural from monosaccharides using NF. In addition, a hybrid membrane extraction process has been found efficient for detoxification of dilute acid hydrolysates [107].

NF is also applicable for recovery of individual monosaccharides. For example, the separation of xylose has been investigated intensively. Xylose is a pentose sugar obtained by hydrolysis of xylan, a hemicellulose found in hardwood and various other plants. A typical source of xylose is spent liquor from sulphite pulping [108] which is one type of a biomass hydrolysate. Xylose is used, for example, as a raw material in production of xylitol, a sweetener with various health benefits. Recovery of xylose is conventionally carried out using chromatographic separation. NF has been found a simple yet competitive process alternative for chromatographic separation of xylose from hemicellulose hydrolysates [108, 109].

Membrane technology is also useful in purification of oligosaccharides [74]. Utilizing UF and NF subsequently, both polysaccharide and monosaccharide impurities can be removed. The polysaccharides can be recycled to the hydrolysis stage to improve the yield of oligosaccharides.

Different separation mechanisms including sieving and charge effect play role in the NF of biomass hydrolysates. In addition, intermolecular interactions have been observed e.g.

between xylose and acetic acid [110]. Pursuing for high product purity may be challenging due to the close properties of the components. For example, the separation of lignosulphonates from carbohydrates may be difficult because of the partially overlapping molecular weight ranges of these two types of components [111]. Therefore, other separation methods may be required.

4.6.2 Separation of lignin and hydroxy carboxylic acids of black liquor

Black liquor is the spent pulping liquor of alkaline pulping. Of the pulping processes used in pulp and paper industry, kraft pulping is currently the dominant one. Kraft pulp mills produce tons of black liquor annually. The black liquor is burned in a recovery boiler to produce steam and to recover pulping chemicals, but it is also a potential source of valuable organic compounds such as lignin and hydroxy carboxylic acids. Recovery and refining of these components might improve the materials efficiency and yield new products for the pulp and paper industry.

Recovery of lignin from black liquor has been intensively studied during recent years. Lignin has potential applications in materials engineering. It is also a solid fuel with a high energy value. Recovery of lignin can be profitable, in particular if the recovery boiler is the bottle-neck of the pulping process. Separation of lignin is also an important pre-treatment step for recovering other compounds, e.g. hydroxy acids, because lignin causes fouling and other problems during subtle purification processes [112]. In addition, lignin-derived phenolic compounds may impede the polymerization of hydroxy acids and are, thus, undesired impurities in the final product.

A common approach is to precipitate lignin by decreasing the pH of black liquor by carbonation or using a mineral acid [113, 114]. Carbonation is preferred over acidification as it is a more economic process. In contrast to sulphuric acid precipitation, carbonation does not affect the sulphur-balance of the pulp mill. In addition, the chemical costs are relatively low since flue gases could be possibly applied instead of pure carbon dioxide [115]. A commercial process for recovering lignin from black liquor based on carbonation technique, LignoBoost, is already in use [116].

As an alternative to precipitation, UF can be used for separation of lignin [117, 118]. Providing that a membrane with sufficient pH stability is used, no pH adjustment is required. Lignin separation using UF has several advantages. If membrane cleaning is not taken into account, no chemicals are required in the process. Therefore, the process causes no disturbance on the chemical balances of the pulp mill, which facilitates its integration to an existing pulping process. Furthermore, the lignin product has fewer impurities than precipitated lignin [119]. An economic analysis of the lignin recovery process has been made by Jönsson et al. [120].

Combination of UF and carbonation can be also applied for fractionation of lignin. UF may be useful pre-treatment for carbonation, since it helps to remove hemicellulose, which may hinder filtration of the precipitated lignin and reduce the product quality [121]. Alternatively, carbonation can be used as a pre-treatment for UF [122].

Niemi et al. found UF and NF efficient pre-treatment methods for the purification of hydroxy acids by crystallization [123]. NF may also be applied for the fractionation and purification of hydroxy acids [124]. Another potential technique for downstream processing of hydroxy acids is electrodialysis, which could be applied to remove residual sodium [125]. One of the main drawbacks of electrodialysis is, however, its sensitivity towards fouling [125].

Process conditions in the processing of black liquor are harsh, since black liquor is highly alkaline. Therefore, ceramic membranes are often applied [120]. Polymeric membranes of PES or other material with good chemical resistance can also be used.

4.6.3 Recovery of acids from fermentation broths

As already mentioned, biobased chemicals or their intermediates are often produced by fermentation using sugars obtained from hydrolysis of biomass as substrates. The products of such fermentation processes include alcohols and carboxylic acids, e.g. lactic acid and succinic acid. The applications of membrane technology in the recovery and purification of acids from fermentation broths is discussed in this section.

The micro-organisms exploited in fermentation are typically sensitive to the process conditions such as pH and to the composition of the fermentation broth. For example, in the production of acids, the acid produced and accumulated in the fermentation broth typically

inhibits the fermentation process. Therefore, it is advantageous to recover the product continuously. Different membrane filtration techniques are well-suited for such an integrated product removal processes [103, 126].

Fermentation is often performed at near neutral pH. For example, in the production of lactic acid, the pH is adjusted to 5–6 to obtain the highest productivity [103]. At this high pH, more than 90% of lactic acid occurs in dissociated form. Therefore, the product is more likely collected e.g. as sodium lactate than as free lactic acid. Electrodialysis with bipolar membranes can be used for converting the salts into free acid form [127]. A pre-treatment using MF, UF, or NF is typically required, because the presence of cells of the fermentation broth would impair the performance of electrodialysis [103].

In many cases, the micro-organisms used in a fermentation process are not very selective but produce a mixture of related compounds (e.g. different carboxylic acids). NF is a promising technique for fractionation and purification of carboxylic acids or their salts. For example, Kang and Chang [72] found NF suitable for separation of succinate (a divalent salt) from monovalent organic acid salts.

5 COMBINATIONS OF CHROMATOGRAPHIC AND MEMBRANE SEPARATIONS

Single-step separation processes are commonly preferred due to their simplicity. However, recovery of compounds from complex solutions often requires utilization of several separation techniques. Though it would be possible to perform a multicomponent separation in a single chromatographic separation step using an adequate long column, a multistep separation process may be preferable because it often improves the productivity. For example, combining chromatography with crystallization has been found advantageous for isolating bioactive compounds of natural origin [128]. Furthermore, a multistep separation process can be more robust than a single-step process. For example, a suitable adsorbent can be used for the removal of a foulant component from the solution prior to membrane filtration [129], which not only improves the flux but may also significantly lengthen the membrane lifetime and reduce the downtime due to membrane cleaning.

Membrane filtration can be readily coupled with preparative chromatography, since both methods are typically operated in liquid phase. Different approaches of combining these two separation techniques are discussed in this chapter.

The conventional way of combining different separation methods is the sequential coupling of separate unit operations. The multistep separation processes utilizing this type of coupling are here referred as tandem separation processes, and they are reviewed in Section 5.1.

Considering the design of a tandem separation process, it is common that each of the unit operations is designed and optimized individually. To obtain true synergetic effects, it may be necessary to integrate the different separation techniques more intensively and to optimize the overall process rather than the single process steps. Such integrated processes are known as hybrid separation processes.

The integration of separation processes to a hybrid process can be carried out in different ways. Lipnizki et al. classified hybrid separation processes into separation-type processes which combine only different separation techniques and to reactor-type processes, which combine separation with chemical reaction and can be thus considered as hybrid processes in the meaning of “the offspring of two different processes” [130]. Both of these groups can be further divided into two groups: 1) processes in which the unit operations (and unit processes)

are performed in separate units and 2) processes where the different techniques are integrated in a single unit [131]. The multi-unit and single-unit hybrid separation processes combining membrane separation with chromatography are discussed in Sections 5.2 and 5.3, respectively.

5.1 Tandem separation processes

Tandem processes are the simplest and the most common way to combine different separation techniques. They are suitable for fractionation of multicomponent mixtures. It is also common to apply a different separation technique for pre-treatment or for product concentration, or to handle the waste produced from another separation process.

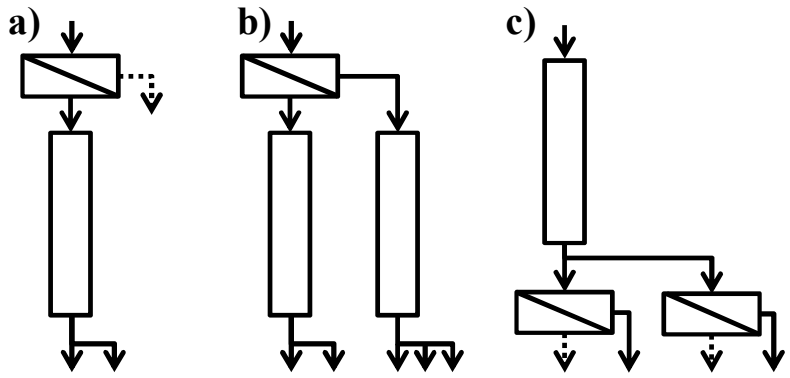

Figure 9 Different ways of combining of chromatographic and membrane separations in a tandem process: a) Pre-treatment using membrane filtration, b) Fractionation of a multicomponent mixture, c) RO for concentration of the products from chromatographic separation.

Some type of a pre-treatment is typically required before membrane filtration or chromatographic separation. Solid particles need to be removed by filtration to prevent blocking of the pores of the membrane or the macroporous resin beads and plugging of the membrane module or the chromatography column. In the case of membrane filtration, MF or UF is often used prior to NF or RO [132]. Similarly, MF or UF can be used prior to chromatography. Schematic of a process where the permeate from membrane filtration is further treated by chromatography is shown in Fig. 9a. Also NF may be useful for removing compounds that would cause disturbance in the chromatographic separation. For example,

Zweckmair et al. [133] applied NF and RO membranes for separating the interfering residual formaldehyde from C_3-carbohydrates.

In Fig. 9a, the retentate from membrane filtration is not processed further. Nevertheless, it is also possible to treat both the retentate and the permeate as shown in Fig. 9b. Such process scheme can be applied in fractionation of complex mixtures. A multicomponent separation using only membrane techniques would require several steps since membrane filtration is inherently a binary separation with limited separation selectivity. Coupling of chromatographic separation with membrane filtration may be an attractive alternative to complex membrane cascade systems. On the other hand, pre-fractionation of the feed using membrane filtration may facilitate the chromatographic separation step. Therefore, the combination of membrane separation with chromatography is also applied in the analysis of complex samples [134].

It is also possible to use chromatography as a pre-treatment for membrane filtration, though it is not common. For example, it may be favourable to reduce the osmotic pressure by separating salt prior to NF, and chromatographic separation is a suitable method for that desalting [80].

The product obtained from chromatographic separation is often too dilute for its end-use, storage, transportation or further processing, and therefore it has to be concentrated. Concentration is conventionally done using evaporation, which is a very energy-intensive process. For example, Thang et al. calculated that 78% of the energy consumed in chromatographic desalting of silage juice is due to concentration by evaporation [80]. RO and NF are less energy-consuming alternatives to evaporation, and they are also applicable for solutions that contain compounds of a limited thermal stability.

Chromatographic separation using an ion-exchange resin may require that the resin is regularly regenerated. Often the regeneration can be avoided by choosing a resin in an ionic form which the ions of feed solution do not convert. If regeneration is needed, the salt solution formed as regeneration waste, has to be taken care of. For example, if sodium-containing solution is treated using a resin that is in H^+ form, the resin has to be regenerated using a mineral acid, e.g. H_2SO_4, and a waste solution containing the corresponding salt, e.g. Na_2SO_4, is produced. Electrodialysis using a bipolar membrane can be applied to convert the

salt to its parent acid and base [135]. For example, it is possible to convert Na_2SO_4 to NaOH and H_2SO_4, and the formed acid can then be re-used in the resin regeneration. Membrane filtration processes can also be applied for recycling of eluent or for concentrating the waste fractions recovered from chromatographic separation prior to their disposal.

5.2 Multi-unit hybrid separation processes

Multi-unit hybrid separation processes utilize a combination of different separation principles by coupling of two or more unit operations so that the internal process streams, e.g. a recycle stream, from one process unit are treated using another separation technique. It is also possible to combine such separation process with a chemical reaction.

One example of a separation-type hybrid process is steady-state recycling chromatography with solvent removal (SSR-SR), where an internal recycle stream of chromatographic separation is treated with another separation method, e.g. RO [24]. SSR-SR process is discussed in Section 5.2.1. Examples of reactor-type processes that utilize both chromatography and membrane filtration are presented in Section 5.2.2.

5.2.1 Steady-state recycling chromatography with solvent removal

Steady-state recycling (SSR) chromatography discussed in Section 3.4 has several advantages over batch chromatography. It allows using a higher column loading and may reduce the overall eluent consumption and provide higher productivity. Nevertheless, the productivity of SSR is limited because the volume of the recycle fraction restrains the amount of fresh feed to be treated per cycle. Since the recycle fraction is more diluted than the fresh feed, the concentration of the feed to the column is lower in SSR chromatography than in batch chromatography.

To overcome the limitation described above, Siitonen et al. suggested that the productivity of SSR can be improved by concentrating the feed in an integrated solvent removal unit [24]. This hybrid separation process is called steady-state recycling chromatography with solvent removal (SSR-SR). The removed solvent can be re-used as eluent. Application of solvent removal is limited to the mixed-feed mode of SSR only, since mixing of the solution can hardly be avoided during the solvent removal.

The solvent can be removed by evaporation or by membrane filtration (NF or RO). Utilization of membrane filtration is more energy-efficient and practical than evaporation since no phase change is involved. The drawback of membrane filtration is that the retention of the target compounds may be limited, which decreases the yield and can make the re-use of the removed solvent difficult.

The solvent removal unit can be situated in different parts of the process. Three alternative locations are illustrated in Fig. 10. It is possible to concentrate the fresh feed before mixing it with the recycle fraction (Fig. 10a), to concentrate the recycle fraction before mixing it with fresh feed (Fig. 10 b), or to mix the recycle feed with the fresh feed prior to concentration (Fig. 10 c). The best configuration depends on the isotherm type, feed concentration and the limitations set on the solvent removal. In the case of Langmuir isotherms and ideal conditions, the configuration shown in Fig. 10c has been found to provide the best productivity [24].

In comparison to SSR process, there is one additional parameter in the design of an SSR-SR process: the amount of solvent to be removed. When membrane filtration is applied for the solvent removal, the volume reduction has some practical limitations, since pursuing for a high volume reduction may be technically challenging and expensive. Therefore, the optimization of an SSR-SR process requires a holistic approach that considers both unit operations. In addition, the solubility of compounds or solution viscosity may set an upper limit for the concentration of the feed to a chromatography column. These restrictions have to be taken into account in the design of the hybrid process.

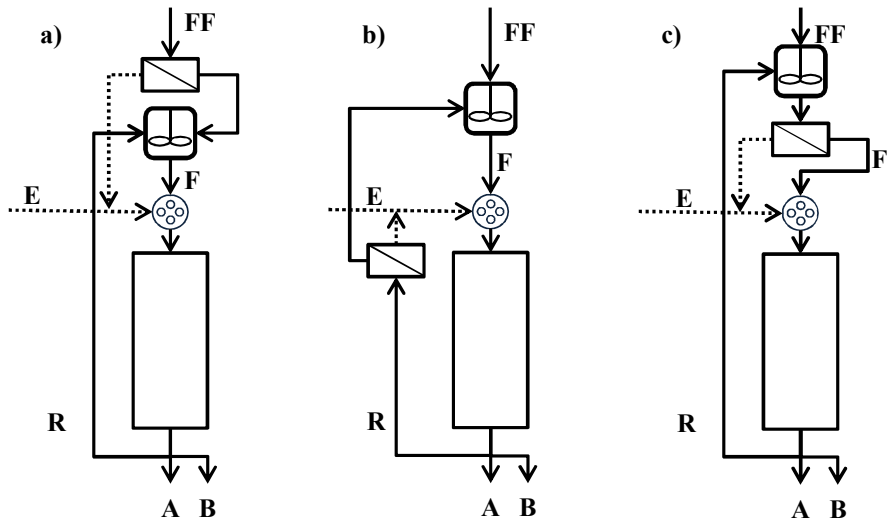

Figure 10 Different positions of the solvent removal unit in an SSR-SR process: a) concentration of fresh feed, b) concentration of recycle fraction, c) concentration of the mixed feed. (Adapted from [24].)

5.2.2 Hybrid separation processes for in-situ product recovery

Continuous processes with *in-situ* product recovery (ISPR) are often preferred over batch processes in chemical industry and are currently attracting interest also in the field of bioprocessing [136]. ISPR can be applied to improve yield by shifting the equilibrium and by removing the inhibitory compounds. However, the selection of a suitable separation method for ISPR may be challenging.

Wagner et al. [137] studied application of SMB chromatography for ISPR in production of rare sugar D-psicose from D-fructose by enzymatic biotransformation. The idea was to recycle the unreacted D-fructose back to the bioreactor so that it is theoretically possible to obtain a yield of 100%. The feasibility of SMB chromatography for the separation of rare sugars is well-established, but the integration of a chromatographic separation process to a bioreactor is not straight-forward because dilution occurs during the separation. To overcome the dilution problem, NF was applied to concentrate the D-fructose stream from the SMB step prior to returning it back to the bioreactor. A similar process where single column chromatography is used instead of SMB was studied by Nimmig and Kaspereit [138]. They

observed that an integrated process can provide higher overall yield even despite the limited retention of the membrane in the solvent removal step.

5.3 Single-unit hybrid separation processes

Membrane chromatography and membrane filtration-cum-chromatography devices are examples of processes where the membrane filtration and chromatography are integrated into a single unit. The idea is either to apply membranes in a chromatography column or resin in a membrane filtration unit.

5.3.1 Membrane chromatography

Membrane chromatography employs stacked membranes instead of adsorbent beads in a chromatography column. The membranes applied are typically MF or UF membranes [139]. Membrane chromatography is used especially in bioseparations, e.g. in protein purification [139].

The main advantage of membrane chromatography over conventional packed-bed operation is the increased mass transfer rate [140]. The mass transfer in the membrane pores occurs mainly by convection, whereas intraparticle mass transfer in adsorbent beads occurs by diffusion. In addition, the cost of membranes is low in comparison to the chromatographic beads, which reduces the separation costs and makes it even possible to omit time-consuming cleaning procedures by disposing the membranes after a single use [140].

The main drawbacks of membrane chromatography are the heterogeneity and low binding-capacities of membranes in comparison to chromatographic resins. These properties may lead to poor resolution. To take the advantage of both the good mass transfer properties of membranes and the high resolution of resin beds, the so-called mixed-matrix membrane chromatography employs resins embedded in a membrane support [140].

5.3.2 Membrane filtration-cum-chromatography device

Hybrid processes combining sorption with membrane filtration have been studied for water purification, e.g. for boron removal [141]. If the adsorbent particles are packed as a bed inside the membrane module, it is possible that chromatographic separation takes place. This kind of

a hybrid process may allow recovery and purification of multiple target compounds, e.g. from a fermentation broth, in a single unit.

Xu et al. [142] developed an integrated separation apparatus that combines membrane and chromatographic separations, a so-called membrane filtration-cum-chromatography device. The device itself is a partially-coated hollow fibre MF module whose shell-side is filled with chromatographic resin beads. The separation process is operated in a cyclic manner so that in each cycle the resin bed is loaded with the MF permeate and then eluted with a buffer solution. The new device was found applicable for recovery and purification of proteins straight from a synthetic fermentation broth. The hollow fibre membrane separates the cellular material that would disturb the chromatographic separation of proteins. In comparison to traditional MF, a membrane filtration-cum-chromatography process was found less prone to fouling because of the self-cleaning of the membrane during elution. The drawbacks of the hybrid process may include the complicity of design and limited productivity.

6 CHALLENGES TO SEPARATION MATERIALS IN BIOREFINERY ENVIRONMENT

Biorefinery environment presents challenges to the selection of separation materials for chromatographic and membrane separation processes. The extreme pH of hydrolysates or spent pulping liquors, especially when combined with an elevated temperature, sets high requirements for the stability of the separation materials applied. Furthermore, the treated solutions contain compounds, e.g. lignin derivatives, which are known to cause fouling [112]. The combined effects of fouling and degradation are often referred as ageing.

The ageing of separation materials is an important topic since it may be a major obstacle for application of membrane technology and chromatography in biorefineries. Therefore, the effects, detection and prevention of fouling and chemical deterioration of membranes and stationary phase of chromatographic separation in long-term use are discussed in this chapter. The focus is on polymeric materials, since they are more susceptible to chemical deterioration than their ceramic alternatives but also very commonly used because of their inexpensive price.

6.1 Fouling

Fouling is defined as the accumulation of undesired material on solid surfaces. The materials and compounds that cause fouling are known as foulants, and they may be organic, inorganic or biological. Fouling may increase mass transfer resistance, block pores, or cause deactivation of the functional groups of the surface. Fouling may occur via various mechanisms, including adsorption, precipitation, and trapping of particles inside the pores of a membrane or an adsorbent bead.

6.1.1 Effects of fouling

In membrane filtration, fouling is typically observed as a flux decline which cannot be eliminated by rinsing with the solvent (in contrast to concentration polarisation discussed in Section 4.3). However, fouling may be reversible so that the flux may be increased partially or up to the initial level after backflushing or cleaning with a suitable chemical. In addition to the flux decline, fouling may also cause changes in the retention of components, as it may change the chemical nature and morphology of the membrane.

Fouling of resins used in chromatography is much less studied than fouling of membranes. It is, however, known that fouling may increase the pressure drop through the bed and reduce the capacity of the resin and thus affect the retention time and resolution of components.

6.1.2 Prevention of fouling

There are four different approaches to reduce fouling: pre-treatment of the feed solution, modification of the separation medium, optimisation of the process conditions, and cleaning [84].

Various pre-treatment methods for the feed solution can be applied to reduce fouling. The fouling components can be eliminated by chemical or physical means. As an example, chemical decomposition by oxidation and physical removal using activated carbon adsorption have been found suitable methods for removing foulants from wood hydrolysates [14]. The challenge in this kind of a feed pre-treatment is how to avoid loss of yield. For example, activated carbon adsorption is usually not selective towards the foulants and thus it may adsorb also valuable target compounds.

Modification of the surface chemistry of the separation material may help to reduce fouling. Several examples can be found on the field of membrane science. Regarding the surface chemistry, usually hydrophilic surfaces are less prone to fouling than hydrophobic ones [84]. However, modification of the membrane to make it more hydrophilic does not always improve the fouling tendency: its success depends on the nature and sometimes even the concentration of the foulant [143]. A favourable membrane pre-treatment might not only reduce the flux decline, but it may also facilitate the cleaning of membranes [144].

The resin beads applied in chromatography can be modified in the same way as membranes. However, the modification also affects the retention of compounds. Therefore, the challenge is to find a modification method that is efficient for reducing fouling without compromising separation selectivity and process performance.

In addition to surface chemistry, the structure of the material also affects the fouling tendency. Non-porous materials, e.g. RO membranes, are typically fouled less than porous ones as the latter allow more mechanisms of fouling. In the case of a porous membrane, a uniform structure with a narrow pore size distribution is somewhat less prone to fouling than a non-

uniform structure [84]. In the case of MF membranes, particle blocking of the membrane pores is a major cause of flux decline, and it may be prevented by choosing a membrane with a smaller pore size.

In membrane filtration, fouling is strongly dependent on concentration polarization (see Chapter 4.3). Fouling can be reduced by increasing turbulence and working at subcritical flux [145]. Other process conditions such as temperature, pH, and salt concentration may also affect the fouling tendency, since they affect the properties of membranes and solutes [95]. Particularly, in the treatment of protein solutions, these factors have a major importance [100].

Severe fouling can be prevented with a regular cleaning procedure. Typically, the cleaning is done using chemicals such as acids, alkalis, organic solvents, or detergents, or sequential combinations of these. Enzymes may also be utilized. The chemical resistance of the separation material has to be taken into account when selecting the cleaning agent. Cleaning with an unsuitable chemical may change the membrane properties and even lead to more severe fouling [146]. Moreover, too harsh cleaning conditions may lead to degradation of the membrane.

6.2 Durability of separation materials under extreme conditions

Separation materials may be exposed to extreme process conditions, e.g. a high temperature or the presence of organic solvents or oxidizing chemicals either during the separation operation or during cleaning. Here extreme conditions are regarded as high and low pH and high temperature. These conditions are typical for biorefineries. For example, the treatment of acidic hydrolysates or black liquor requires separation materials with good chemical durability. Especially the combination of a high temperature with an extreme pH is disastrous for many materials. For example, Zagorodni et al. have found that strong alkali causes degradation of the functional groups of an anion-exchange resin at an elevated temperature [147]. A new challenge to the selection of separation materials is raised by the increasing use of ionic liquids.

Mechanisms of chemical deterioration of membranes and chromatographic beads include dissolution of the material and changes in the chemical nature of functional groups. The

functional groups may also get detached, e.g. due to breaking of covalent bonds between the functional groups and the polymer matrix. Chemical reactions may also result in extra cross-linking of the polymer structure, which can change the mechanical stability and other properties of the material.

6.3 Analysis of fouling and chemical deterioration

The fouling and chemical deterioration of membranes and chromatographic separation materials, e.g. ion-exchange resins, can be examined in various ways. Combination of different techniques is typically required to obtain understanding of the mechanisms of fouling and degradation.

Various imaging techniques including scanning electron microscope and atomic force microscopy [148, 149] have been applied for studying of the morphology of separation materials. These techniques provide information on the swelling, changes in the pore structure and aggregation of precipitates on the surface. Spectroscopic methods, e.g. infrared spectroscopy [147] or surface-enhanced Raman spectroscopy [150], can be useful in the identification of foulants or the mechanisms of chemical deterioration.

Changes in a separation material can also be observed by investigating its properties, e.g. the streaming potential of membrane [151]. For resins, the measurement of properties such as water content or ion-exchange capacity (if applicable) may reveal the possible undesired changes that have occurred during their use.

The characterization of separation materials is typically done using off-line analyses, but recently also real-time analysis techniques have been developed. For example, ultrasonic time-domain reflectometry has been found promising method for investigation of membrane fouling [152], and confocal scanning laser microscope for *in situ* monitoring of fouling in packed beds [153].

Another common approach to determine fouling or degradation is to study the performance of the separation material under different process conditions. In the case of membrane filtration, membrane performance can be assessed by examining flux and retention of model compounds. The model compounds used in comparing the performance of a membrane at different pHs have to be uncharged and stable under the whole pH range studied, e.g.

polyethylene glycol [154]. In chromatography, the retention times of model compounds are indicators of the separation selectivity. Long-term performance of the separation material can be studied with successive injections. A faster method may be to compare the separation before and after exposing the bed to the studied solution by running a break-through curve.

7 MATERIALS AND METHODS

The experimental methods applied in this work are summarized here. A more detailed description is given in Papers I-IV.

7.1 Raw materials

The solutions treated in this work were soda-cooked black liquor and different types of synthetic model solutions representing biomass hydrolysates or black liquor.

Fractionation of black liquor was studied using soda black liquor from a laboratory-scale cooking of wood. Softwood (SW) and hardwood (HW) soda black liquors were prepared at VTT (Espoo, Finland) using pine or birch chips as raw material. The cooking temperatures for SW and HW chips were 170 °C or 165 °C, respectively. The liquor to wood ratio (W/D) was 4:1 and the amount of effective alkali was 5.5 mol/kg. The cooking was continued until H-factor [155] of 1936 for SW or 1324 for HW was reached. The total dry solids (TDS) content of the black liquor was approximately 14 wt%.

A synthetic model solution containing sulphuric acid and glucose was used in the wood hydrolysate fractionation study in Paper I. The concentrations of H_2SO_4 and glucose in the solution were chosen to correspond to the composition of a typical lignocellulosic hydrolysate from concentrated acid hydrolysis [26].

Another set of model solutions containing NaOH and sodium L-tartrate dibasic di-hydrate was used in the investigation of the separation mechanism in the chromatographic fractionation of black liquor (see Paper III for details).

7.2 Chromatographic separations

7.2.1 Resins

Different types of resin beads were applied in the chromatographic separation, adsorption and ion-exchange experiments. The resins are listed in Table 2.

Table 2 Resins used in the chromatographic separation experiments.

Resin	Type	Matrix	Ionic form	Application
CS11GC (Finex)	SAC	PS-DVB (5.5% DVB)	H^+	Liberation of hydroxy acids (Paper IV)
CS16GC (Finex)	SAC	PS-DVB (8% DVB)	H^+	Acid–sugar separation (Paper I)
Sephadex G-10 (GE Healthcare)	SEC gel	Dextran–ECH	-	Separation of NaOH and hydroxy acids (Papers III and IV)
Amberlite XAD-16 (Rohm and Haas)	Neutral adsorbent	PS-DVB	-	Adsorptive removal of lignin (Paper IV)

7.2.2 Batch chromatography

Glass columns (Kronlab ECO SR) of three different sizes were used in the experiments: 33 mL (length 20 cm, i.d. 1.5 cm), 100 mL (length 20 cm, i.d. 2.5 cm), and 800 mL (length 40 cm, i.d. 5 cm). The columns were thermostated at constant temperature using water circulation through the column jackets.

The eluent was purified, degassed water in most cases. Eluent and feed were introduced to the column by top down flow using HPLC pumps (Waters 515). The injection valve (a MV-7 motor valve) was controlled using computer software (LabView, National Instruments).

The column outlet was monitored using conductivity, refractive index and UV detectors, and an automated fraction collector was used for collecting samples for off-line analyses. The details are given in Papers I, III and IV.

7.2.3 Recycling chromatography

SSR chromatography experiments were performed using the same equipment as in batch chromatography experiments. The feed was introduced into the column via an injection loop, which also served as a reservoir for the recycle fraction. The fraction cut-times were selected based on simulation results. The experiment was continued until steady-state was reached.

During the last cycle, samples were taken at the column outlet to construct chromatograms corresponding to the steady state. The details are found in Paper I.

7.2.4 SMB separation of hydroxy acids and NaOH

Continuous separation of hydroxy acids and NaOH was carried out using a three-zone open-loop SMB. In an open-loop SMB system, the liquid phase is not recycled. Despite the higher eluent consumption, open-loop SMB is often preferred to conventional closed-loop SMB for separation of complex mixtures containing unknown components, since it reduces the risk of cross-contamination [156].

Five columns (H_{col} = 20 cm; D_{col} = 1.5 cm) packed with Sephadex G-10 were put in three sections in a 2-2-1 configuration as illustrated in Fig. 11. Eluent was fed to zone I. Extract was withdrawn with a pump between zones I and II. The feed solution, SW soda black liquor ultrafiltered with the NP010 membrane, was introduced to zone III. The feed and the columns were thermostated at 50 °C.

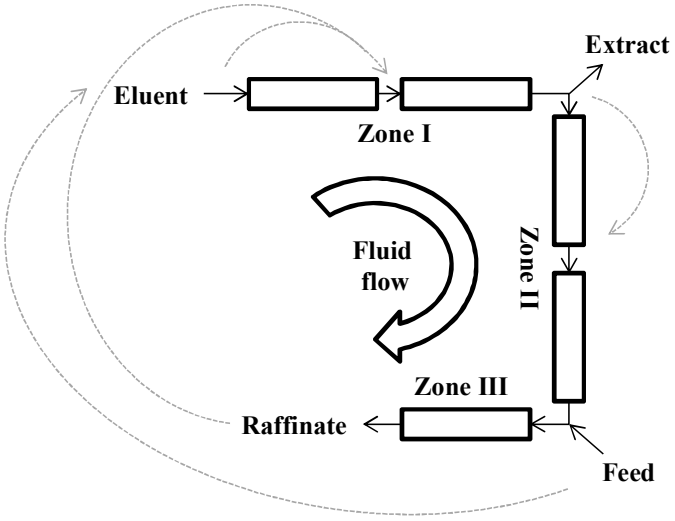

Figure 11 SMB configuration used in the separation of NaOH and hydroxy acids.

Four SMB runs with different liquid flow rates were done. The flow rates of feed and product streams are presented in Table 3. Eluent flow rate was in each run 5.3 mL/min, and the column switch time was 10 minutes.

Table 3 Flow rates in the SMB runs.

Run	Feed, mL/min	Extract, mL/min	Raffinate, mL/min
1	0.63	2.78	3.15
2	0.63	2.38	3.55
3	0.84	2.99	3.15
4	0.84	2.78	3.36

Samples of each switch were analysed for lignin and acids using UV spectroscopy and capillary electrophoresis as described in Papers III and IV. The concentration of NaOH was estimated based on pH, and the results were verified by titration.

7.3 Membrane separations

In this work, UF was used for removing lignin from black liquor (Papers III and IV). In addition, RO was considered for solvent removal in separation of glucose and galactose in Paper II. However, no experimental work but only numerical simulation was included in that study.

7.3.1 Membranes

The membranes applied in the experiments are listed in Table 4. Polyethersulphone (PES) UF membranes with different MWCO values were applied for removing lignin from black liquor. PES membranes were chosen because of their good alkali and temperature resistance. In addition, loose UF membrane UC030 T made of regenerated cellulose (RC) was applied for removing small colloids of precipitated lignin. The membranes were pre-treated by cleaning with a 0.1% solution of Ultrasil 110 (Ecolab Inc.), rinsing with purified water, and compacting at the maximum filtration pressure.

Table 4 Membranes used in the experiments.

Membrane	Manufacturer	Material	MWCO	Application
NP010	Microdyn-Nadir	PES	1,000 Da	Lignin removal (Paper IV)
UP010	Microdyn-Nadir	PES	10,000 Da	Lignin removal (Paper IV)
GR95PP	Alfa-Laval	PES	2,000 Da	Lignin removal (Paper III)
UC030 T	Microdyn-Nadir	RC	30,000 Da	Removal of precipitated lignin residuals

7.3.2 Equipment and filtration procedure

All the filtration experiments were done using a cross-flow module with a membrane area of 0.01 m^2. The retentate was recycled back to the feed tank during the filtration as shown in Fig. 12. As an exception, the UF pre-treatment for the chromatographic separation experiments of Paper III was done at VTT (Espoo, Finland) using a DSS LabStak M20 filter unit. The soda black liquor was ultrafiltered without any pre-treatment.

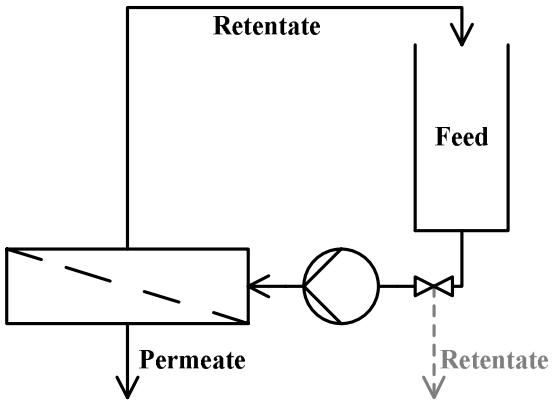

Figure 12 Simplified scheme of the membrane filtration equipment applied.

7.4 Other separation techniques for purification of hydroxy acids

The hydroxy acids fractions recovered using UF and chromatographic separation were purified using ion-exchange, adsorption and evaporation. The details of the purification procedure can be found in Paper III.

The lignin content of black liquor can also be reduced by precipitation. In this work, the residual lignin in the UF permeate was removed by precipitation using carbon dioxide. Carbonation is a commonly used method for recovering lignin from black liquor (process known as LignoBoost).

The precipitation was carried out in a stirred tank reactor (V = 10 L) equipped with four baffles at atmospheric pressure and temperature of 45 °C. This temperature was found suitable for membrane-treated kraft black liquors by Wallmo et al. [21]. Carbon dioxide (purity 95%) was fed to the vessel from a nozzle located below the impeller with a flow rate of 2 L/min. The precipitation was continued for 2 hours to reach the final pH of approximately 9. The suspension was then kept agitated for 30 minutes prior to filtration at temperature of 45 °C to allow completion of the precipitation. The precipitated lignin was separated by vacuum filtration in a Buchner funnel through a filter paper.

More lignin was precipitated by adding concentrated sulphuric acid (95-97 wt%) until a pH of 2.5 was reached. Simultaneously, the carboxylic acids, which still occur in their sodium salt form after the carbonation, were converted into their protonated form. The same equipment was used as in the carbonation. The acid precipitation was performed at 25 °C.

The precipitated lignin was separated by vacuum filtration using a Buchner funnel. The small lignin precipitates remaining after the vacuum filtration were removed by UF using UC030 T membrane (Microdyn-Nadir). The filtration was carried out at the temperature of 45 °C using a constant pressure of 1 bar and the equipment described in Section 7.3.2. The cross-flow velocity was approximately 2.0 m/s. Prior to the filtration, the membrane was compacted using a pressure of 1.5 bar for 15 minutes at 45 °C, cleaned with a 0.1% solution of Ultrasil 110 (Ecolab Inc.) at 40 °C and rinsed with clean water. Pure water flux was measured at 1 bar both before and after the filtration.

7.5 Analyses

The most important analysis techniques used in this work are listed in Table 5. The details are given in the corresponding papers.

Table 5 Analysis techniques applied.

Analysis technique	Compounds analysed	Paper
HPLC	tartrate	III
	glucose	I
Capillary electrophoresis	hydroxy acids	III, IV
Titration	H_2SO_4	I
	NaOH	III, IV
UV-spectroscopy	lignin	III, IV

7.6 Simulation and numerical process optimization

One of the research questions of this work is whether recycling and concentration of recycle streams is beneficial for chromatographic separation in biorefinery environment. In Paper I, the performance of SSR chromatography in fractionation of wood hydrolysate was compared to conventional batch process. In addition, the effects of separation factor and column efficiency on the performance of SSR in comparison to batch chromatography were investigated in a separate study, the results of which are presented in Appendix 1. In Paper II, different configurations of SSR-SR process were compared with each other and with SSR and batch processes. To make the comparison among the different process modes possible, it is necessary to optimize each alternative with respect to adjustable operation parameters such as injection volume. Dynamic simulation was applied as a tool in this optimization work. The details of the simulation are given in Papers I and II.

In all cases, a simulator for single-column chromatographic separation using MATLAB (Mathworks Inc.) interface was applied. The simulation was based on second order partial differential equations solved numerically using the method of lines [157]. The computing was parallelized using commercial grid computing software (Techila, Techila Technologies Ltd.).

The basic assumption in the simulation was that the profiles of subsequent injection pulses will not overlap. The model parameters such as isotherm constants and diffusion coefficient were determined experimentally or taken from the literature. Radial concentration gradients were assumed negligible. Specific purity constraints were set for each case, and the cut-times were optimized to fulfil these constraints. The analytical shortcut method for determination of cut-times in SSR is valid only in ideal conditions [22]. In all cases studied in this work, dispersion was present. The short-cut method was used to obtain an initial value, and the cut-times that provide the target purity were determined from a series of simulation runs using the least-squares method. For optimization of the injection volume and eluent flow rate, the simulation was repeated varying these parameters. The performance was evaluated based on productivity and eluent consumption which were calculated using the equations presented in Chapter 3.2.3.

8 RESULTS AND DISCUSSION

In this work, the feasibility of new separation processes based on chromatographic and membrane separations for fractionation of biomass hydrolysates and black liquor was studied. Three types of separation process concepts were included in this study: recycling chromatography; hybrid SSR-SR process that combines recycling chromatography with membrane filtration; and tandem separation processes based on chromatographic and membrane separations. The results of the work are summarized in this Chapter, and the details can be found in Papers I-IV and in Appendix 1.

8.1 Recycling chromatography for recovering sugars from biomass hydrolysates

Several studies on the performance of recycling chromatography in comparison to conventional batch chromatography [23, 158-160] or SMB processes have been previously published [158, 159]. However, the results are often valid only for the specific separation case studied, and the reported results are in part contradictory. In this work, SSR chromatography was compared with conventional batch chromatography for fractionation of biomass hydrolysates. The results are presented in Papers I and II.

Guiochon has stated that the major advantage of recycling chromatography over batch operation is that wasting the intermediate is avoided without compromising the productivity [161]. In this work, it was, however, assumed that no waste fraction is collected in either process concepts. Consequently, the injection volume used in the batch process was fixed by the purity constraints given and the other process parameters such as eluent flow rate. By contrast, two variables, injection volume and eluent flow rate, were adjusted during the optimization of SSR chromatography.

In Paper I, the use of recycling was found to improve the productivity of chromatographic fractionation of strong-acid hydrolysate of wood by 43%. Similarly, an improvement in productivity due to recycling was also observed in the case of chromatographic separation of the monosaccharides of lactose hydrolysate in Paper II. However, such increase (about 20%) was not as substantial as in the case of strong-acid hydrolysate fractionation. This result is probably due to the different isotherm models and better column efficiency in the lactose hydrolysate fractionation study.

In both cases studied, the maximization of productivity using the recycling mode slightly increased the eluent consumption in comparison to the batch process operated with the parameters that provided the highest possible productivity. The increase in eluent consumption was due to the use of a higher eluent flow rate in the SSR mode compared to that of the batch mode. However, the operating parameters of SSR can also be chosen so that eluent consumption is the same as in the optimized batch process or even lower and a higher productivity can still be obtained than using a batch process.

As a conclusion of both two case studies, SSR was found to outperform batch chromatography in recovery of monosaccharides from biomass hydrolysates. The freedom to choose not only one but two operating parameters (injection volume and eluent flow rate) is a great advantage of SSR chromatography over batch chromatography and makes it possible to obtain higher productivity without compromising the eluent consumption.

Examples in which an SSR process provides higher productivities with lower eluent consumption in comparison to batch chromatography are also found in the literature. For example, in the production of pharmaceutical intermediates it has been shown to increase the productivity up to 10-fold and to reduce the eluent consumption significantly at the same time [160]. The low eluent consumption is one of the main advantages of SSR, since the eluent has often the highest impact on the total costs of chromatographic separation [43]. In addition, the product obtained from an SSR process is typically less diluted than in batch chromatography [47], which may have the advantage of reducing the cost of downstream processing.

As discussed above, two chromatographic separation cases with different isotherm types (anti-Langmuir and linear isotherms) were studied in Papers I and II. In both of these cases, SSR was found preferable over a batch process. However, this ranking of the chromatographic process concepts cannot be generalized and assumed to be valid also for systems with different mass transfer and isotherm models, which may be specific to other separation tasks also in the field of biomass refining.

To obtain further proof of the advantages of SSR, an additional simulation study was performed using isotherm parameter data taken from Schlinge et al. [158], who also made a comparison between different process concepts (batch, SMB, closed-loop recycling and mixed-feed SSR) using dynamic simulation. In their study, binary separations with

competitive Langmuir isotherms were investigated and the effects of isotherm parameters and feed composition on the separation performance were studied. Both closed-loop recycling and mixed-feed SSR were found to improve the productivity in comparison to batch chromatography in most cases, but not always. In particular, when the separation factor was high, a batch process was found to outperform the recycling mode. However, the yields obtained using recycling chromatography were often higher than the target yield set for batch chromatography, and a direct comparison of the productivities may thus be misleading.

In this work, the purity constraints were equal for the different process concepts included in the comparison, which was not the case in the study of Schlinge et al. [158]. The detailed results of the simulation study are presented in Appendix 1. In brief, SSR process always outperformed batch process, and its superiority was even better when the column efficiency or the separation factor was low. These results contradict the findings of Schlinge et al. [158] because the yield constraints were treated in a different manner (here the yield of SSR was always equal to that of batch, not higher). On the other hand, the results are in agreement with the results of a simulation study made by Kaspereit and Sainio [23], which demonstrated that in the presence of dispersion, mixed-feed SSR outperforms batch chromatography with respect to productivity and eluent consumption. Another study shows that at ideal conditions recycling does not cause any improvement in comparison to batch chromatography [22].

The comparison of SSR chromatography with continuous SMB chromatography was excluded from this study. Similar improvements as those that were here achieved by recycling could also be obtained using an SMB process. Indeed, SMB may even be superior to SSR process. For example, in the work of Schlinge et al. [158], SMB was found to outperform all the other process options with respect to productivity. However, it should be noted that the investment costs of SSR are only slightly higher than those of a batch chromatography unit, which is not the case for SMB, which utilizes several columns. According to a study of Grill et al. [159], SMB is superior to SSR in large-scale enantioseparation, but SSR is competitive at moderate production scale. SSR has lower investment costs than SMB chromatography since only single column is required, and still SSR is often capable for similar or better separation efficiency than SMB. One-column recycle chromatography has been shown to be more efficient, regarding both the eluent consumption and the pressure drop, than a four-column SMB for a binary separation [162], for a pseudo-binary separation [163], and for

separating a single component from a ternary mixture [164]. Therefore, SSR chromatography can be considered as a serious alternative to SMB chromatography.

8.2 Hybrid SSR-SR process for sugar separation

Intensification of chromatographic separation by concentrating the processed solutions using membrane separation was the topic of investigation in Paper II. The case study concerned the separation of galactose and glucose from lactose hydrolysate using a SAC resin. As already discussed, the use of SSR instead of batch chromatography was found to increase the productivity and to decrease the specific eluent consumption in this difficult separation task. The next research question was whether substituting the SSR process with of a hybrid SSR-SR process would provide a further improvement in the process performance.

The simulation study of Paper II showed that a major increase in productivity can be obtained using SSR-SR instead of a conventional batch or SSR processes. When the feed solution was dilute, the productivity improved up to 500% in comparison to an SSR process without solvent removal. Simultaneously, the eluent consumption was reduced by 64%. Furthermore, assuming that the removed solvent is utilized as eluent, the eluent consumption would be 85% lower than in the corresponding SSR process. When the concentration of the feed solution was higher, only modest improvements in the process performance were observed. The benefits of solvent removal were found to depend strongly on the concentration limitations set for the solvent removal unit.

Three configurations of SSR-SR process (see Fig. 10) were compared. In each configuration, the solvent removal unit is located in a different place: 1) concentration of fresh feed, 2) concentration of recycle fraction, 3) concentration of the mixed feed. According to an earlier study of Siitonen et al. [24], the third configuration in which the recycle fraction is mixed with fresh feed prior to solvent removal provides best productivity in the absence of concentration constraints. The same configuration was found the most favourable in most cases also in the present study. However, it was observed that when the maximum concentration achievable in the solvent removal unit is lower than the concentration of feed solution, it is favourable to remove the solvent from the recycle fraction before the mixing.

The main limitation of the present study was that the solvent removal unit was assumed to cause no losses in the yield. If membrane filtration is applied for solvent removal, these losses cannot be completely avoided. In practise, the retention of monosaccharides by RO or especially NF membranes is often below 100%, which means that a small fraction of the product ends up in the permeate stream. This leakage of the target molecules not only reduces the yield but also may hamper the re-use of the solvent, since the impurities in the removed solvent would unavoidably reduce the purity of the end products. In the case of treating a multicomponent mixture, the possible effects caused by the presence of other compounds such as inorganic salts on the separation also needs to be studied. For example, the salts of a lactose hydrolysate would probably concentrate in the removed solvent. If the solvent is re-used as eluent, the presence of salts might change the partition of monosaccharides in the chromatographic separation.

It is thus necessary to take into account the retention of the membrane in the design of an SSR-SR process, especially if the re-use of the solvent is considered. Nevertheless, it should be borne in mind that the SSR-SR process could be more profitable than SSR and batch processes even if the removed solvent was disposed. It is also worth noticing that a significant improvement in the productivity was also achieved when the feed to conventional batch chromatography was simply concentrated, especially when the feed solution was dilute. Therefore, a simpler tandem separation process can be used instead of a more complex hybrid process.

8.3 Tandem separation process for fractionation of black liquor

Black liquor is rich in potentially valuable organic compounds such as hydroxy carboxylic acids. However, the recovery of these compounds is challenging due to high lignin content and alkalinity of black liquor, and multiple separation unit operations are, therefore, required. In this work, a tandem separation process based on UF and SEC was found promising for the fractionation of black liquor. The results of each process step are briefly discussed in this chapter. The details can be found in Papers III and IV.

8.3.1 Lignin removal using UF

UF was used as a pre-treatment for recovering hydroxy acids of black liquor. The aim was to reduce the concentration of lignin-derived compounds which may cause various problems in the further processing of black liquor.

A typical example of the flux and pressure profiles during concentration by UF of soda black liquor is presented in Fig. 13. The applied PES membrane with a MWCO of 1 kDa (Microdyn-Nadir NP010) provided a permeate flux of 40 kg/(m^2 h), which is only slightly lower than the flux value reported for a 5-kDa ceramic membrane at the same pressure at 90 °C [165]. With respect to permeate flux, a PES membrane is, thus, competitive to ceramic membranes.

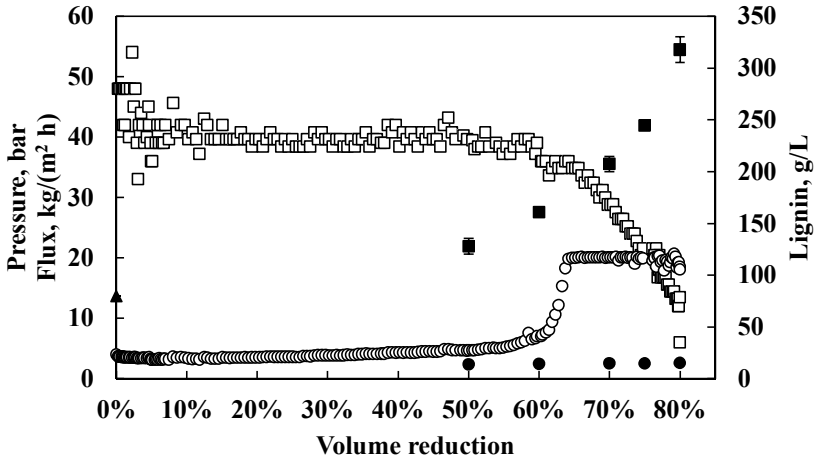

Figure 13 UF of SW soda black liquor using the NP010 membrane. Pressure (○), Flux (□), the concentration of lignin in the feed (▲), permeate (●) and retentate (■). T = 60 °C, cross-flow velocity 2.3 m/s.

In order to achieve a high yield of hydroxy acids, the filtration was continued until a volume reduction of 80% was reached. As a result, the obtained yield of hydroxy acids was 70–90%. As seen in Fig. 13, it was possible to maintain a constant flux only up to a volume reduction of approximately 60%. The concentration of lignin in the feed solution was at this point approximately twice the initial one. The high lignin content and increased viscosity are most

probably the main reasons for the strong flux decline that was observed towards the end of the filtration, as a result of more severe concentration polarization and fouling of the membrane.

Interestingly, the concentration of lignin in the permeate did not significantly increase with increasing volume reduction. Therefore, the product purity might not have to be compromised with the yield. On the other hand, the production rate decreases significantly due to the flux decline when striving for a high volume reduction. Since black liquor is available in large quantities, a maximal yield of hydroxy acids in the first processing step is not necessarily required, and it may, thus, be favourable to run the filtration only until a volume reduction of 50–60%. However, if the lignin is also recovered as a product, it may be attractive to concentrate it further by continuing the UF until a high volume reduction is reached, because UF is less energy-consuming than evaporation and simultaneously increases the yield of hydroxy acids.

Two PES membranes with different MWCO values (1 kDa and 10 kDa) were compared in Paper IV. The rejection of lignin was approximately 80% using a membrane with a MWCO of 1 kDa (NP010 by Microdyn-Nadir). As can be expected, a membrane with MWCO of 10 kDa (UP010 by Microdyn-Nadir) provided lower lignin rejections: 59% for HW soda black liquor and 69% for SW soda black liquor. A lower retention for HW lignin than for SW lignin using membranes with a large MWCO was also reported by Keyomu et al. [166], who studied UF of kraft black liquor using ceramic membranes. The different behaviour of black liquors originated from different wood species may arise from the differences in the molecular structure of lignin.

It was found that the lignin content in the permeate of the 10-kDa membrane was too high considering the further processing. In particular, the ion-exchange step of the multistep process presented in Paper IV was susceptible to problems caused by such lignin concentration. On the other hand, the permeability of the 10-kDa membrane was approximately four times that of the 1-kDa membrane. For comparison, Satyanarayana et al. [167], who also used both 1-kDa and 10-kDa membranes for UF of black liquor, observed only a 95% higher flux with the 10-kDa membrane than with the 1-kDa membrane. If the high yield of hydroxy acids is not the first priority, it might be useful to perform the lignin separation in two steps using a high MWCO membrane and a low MWCO membrane.

As a conclusion, UF using a 1-kDa membrane was found a very effective method for removing lignin from soda black liquor. However, if a further reduction in the lignin concentration is needed, precipitation can be considered. An example of the reduction of lignin concentrations after subsequent membrane filtration and precipitation steps is shown in Fig. 14. Precipitation using carbon dioxide and H_2SO_4 reduced the concentration of lignin in ultrafiltered black liquor by 53%, when the final pH after the acid precipitation was 2.5. By optimizing the precipitation process, the amount of precipitated lignin could be increased. The residual lignin after UF consists of fragments with very small molecular sizes, and it is, therefore, challenging to remove them without causing losses in the yield of hydroxy acids.

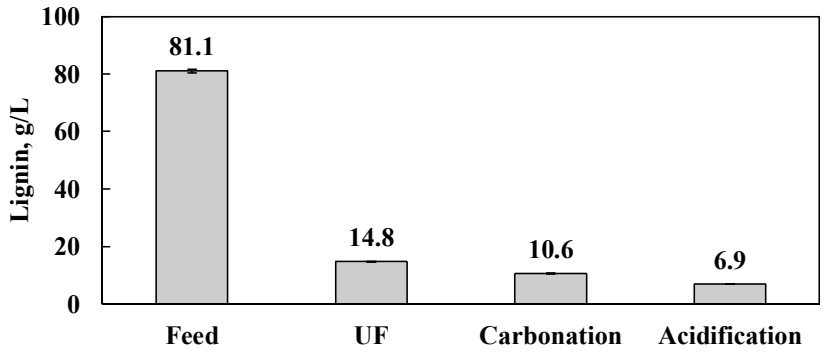

Figure 14 Concentration of lignin in SW soda black liquor after different process steps: UF using the NP010 membrane, carbonation (final pH 9), and sulphuric acid precipitation (final pH 2.5). The error bars show the deviation in the results of parallel samples.

8.3.2 Separation of NaOH and carboxylic acids using batch chromatography

In addition to the lignin removal, the separation of inorganic cooking chemicals is of major importance in the recovery of hydroxy carboxylic acids from black liquor. Regarding the chemical balance of the pulp mill, the cooking chemicals ought to be fully recovered from the hydroxy acid side product stream. Furthermore, inorganics such as NaOH might be problematic impurities in the final products.

In this work, SEC was found suitable for separating NaOH and sodium salts of hydroxy acids. A SEC gel with a small exclusion limit (Sephadex G-10) was used. NaOH was more retained than the salts of hydroxy acids because of its small molecular size. A complete separation

between NaOH and hydroxy acids was achieved. Examples of the chromatograms obtained for SW soda black liquor are presented in Fig. 15. As seen in the figure, a complete separation between hydroxy acids and NaOH can be obtained for the feed solutions containing 10 and 25 wt% TDS. In addition, a partial separation between hydroxy acids and volatile acids was simultaneously obtained.

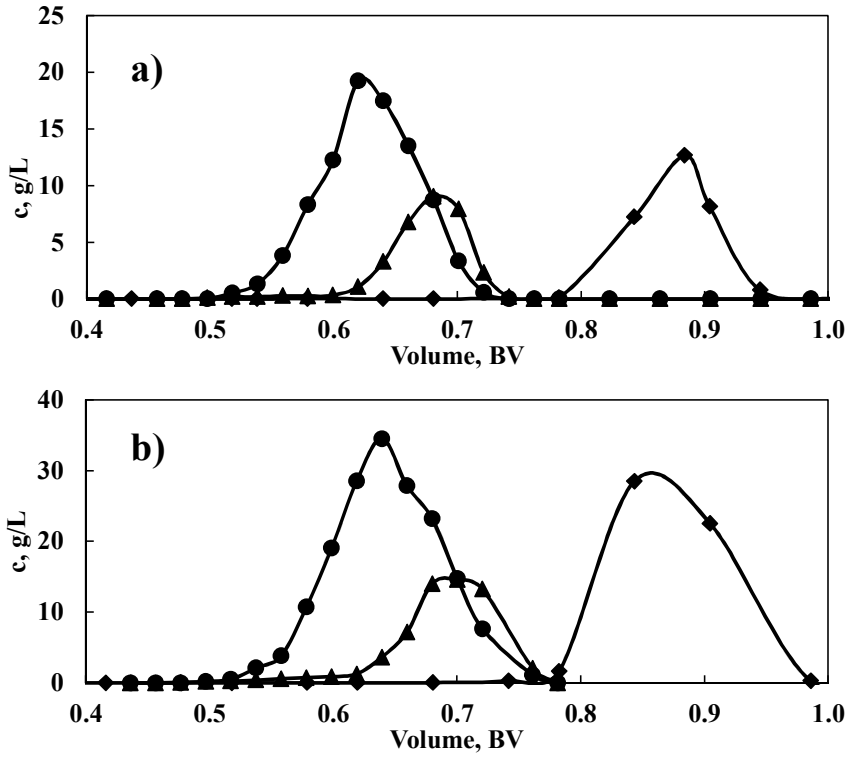

Figure 15 Fractionation of SW soda black liquor using Sephadex G-10 SEC gel. Outlet concentration of hydroxy acids (circles), volatile acids (triangles), and NaOH (diamonds). Feed concentration: a) 10% TDS; b) 25% TDS. V_{inj} = 0.08 BV, eluent flow rate 0.6 BV/h. Lines are to guide the eye.

The injection volume in the fractionation experiment the results of which are shown in Fig. 15 was 8% of the BV. However, a further optimization study showed that the injection volume can be increased up to 25% of the BV without compromising the resolution between hydroxy acids and NaOH. Experiments with model solutions showed that the presence of the sodium salts of hydroxy acids can increase the retention of NaOH. The mechanism is discussed in

detail in Paper III. The same phenomenon in the separation of strong electrolytes using SEC has been intensively studied by Davankov and co-workers [39, 168-171]. This interesting separation mechanism makes it possible to use very large injection volumes and, thus, high productivity can be achieved.

Different methods which have been earlier suggested for separating the inorganics from black liquor include ion-exchange chromatography [83], cooling crystallization [123], and electrodialysis [125]. SEC, which was used in this work, has advantages over all these methods. When recovering hydroxy acids using ion-exchange chromatography, it is necessary to first liberate the acids and convert NaOH to Na_2SO_4 using sulphuric acid, and sodium sulphate can then be separated using chromatography [83]. In the work of Alén et al. [83], two chromatographic separation steps are required because of incomplete separation. Cooling crystallization also requires an acidification pre-treatment, since the method is sensitive towards lignin [123]. Furthermore, about 30% of the inorganics remained in the black liquor after crystallization in the work of Niemi et al. [123]. Electrodialysis suffers from fouling due to lignin [125]. In contrast, SEC chromatography required no acidification of black liquor and complete separation between hydroxy acid salts and NaOH was obtained in a single separation step. Moreover, fouling did not appear to deteriorate the separation in a series of more than 40 successive injections (see Paper III).

8.3.3 Separation of NaOH and carboxylic acids using a continuous SMB process

Separation of NaOH and hydroxy acids of soda black liquor was tested also using a continuous SMB process. Four test runs were performed using the flow parameters presented in Table 3. The corresponding operation parameters m_2 and m_3 (see Eq. 22) for each run are illustrated in Fig. 16.

The average concentrations of NaOH, acids and lignin in the outlet streams during each switch are illustrated in Fig. 17. As seen in the figure, steady-state was reached in each run.

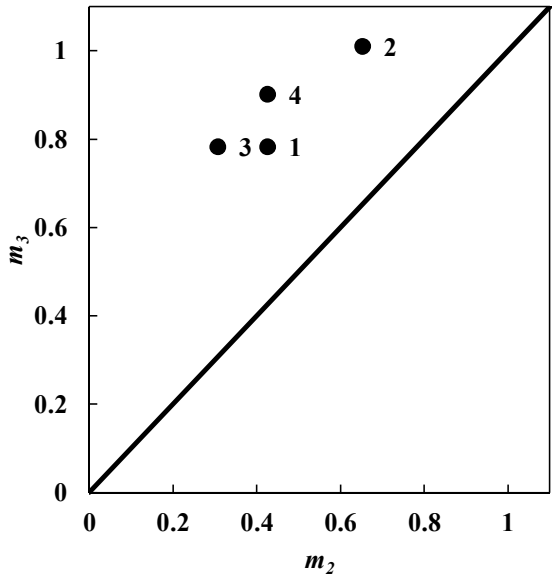

Figure 16 The operating points of the four SMB runs on a (m_2, m_3) plane.

In the first run, the faster moving component, i.e. the sodium salts of hydroxy acids, was recovered in the raffinate and the slower moving component, i.e. NaOH, in the extract. This means that the separation was successful.

In the second run, the aim was to increase the productivity by changing the flow parameters. The feed flow rate was the same as in the first run but the raffinate withdrawal rate was increased by almost 30%. Because of the higher fluid flow rate, NaOH ended up into the raffinate, not into the extract as in the first run. Lignin was also completely collected from the raffinate outlet. No separation was, thus, obtained. The increase in the raffinate withdrawal rate was, therefore, too drastic.

In the third run, the feed flow rate was increased by one third in comparison to the first two runs. The extract withdrawal rate was adjusted so that the ratio of liquid flow rate to solid flow rate in zone III was the same as in the first run, while the corresponding ratio in zone II was decreased. This operating strategy was expected to increase the product concentrations and to avoid the occurrence of NaOH as an impurity in the hydroxy acid product. In

comparison to the first run, the concentrations of extract and raffinate were higher. A small amount of hydroxy acids ended up in the extract, reducing the yield.

In the fourth run, the feed flow rate was the same as in the third run, but the extract flow rate was reduced so that it was equal to that in the first run. The reduced extract withdrawal rate should help to avoid the loss in the yield hydroxy acids. Consequently, the ratio of liquid flow rate to solid flow rate in zone II was the same as in the first run, but the liquid flow rate in zone III was increased. As seen in Fig. 17, a small part of NaOH ended up in the raffinate reducing the purity of hydroxy acids.

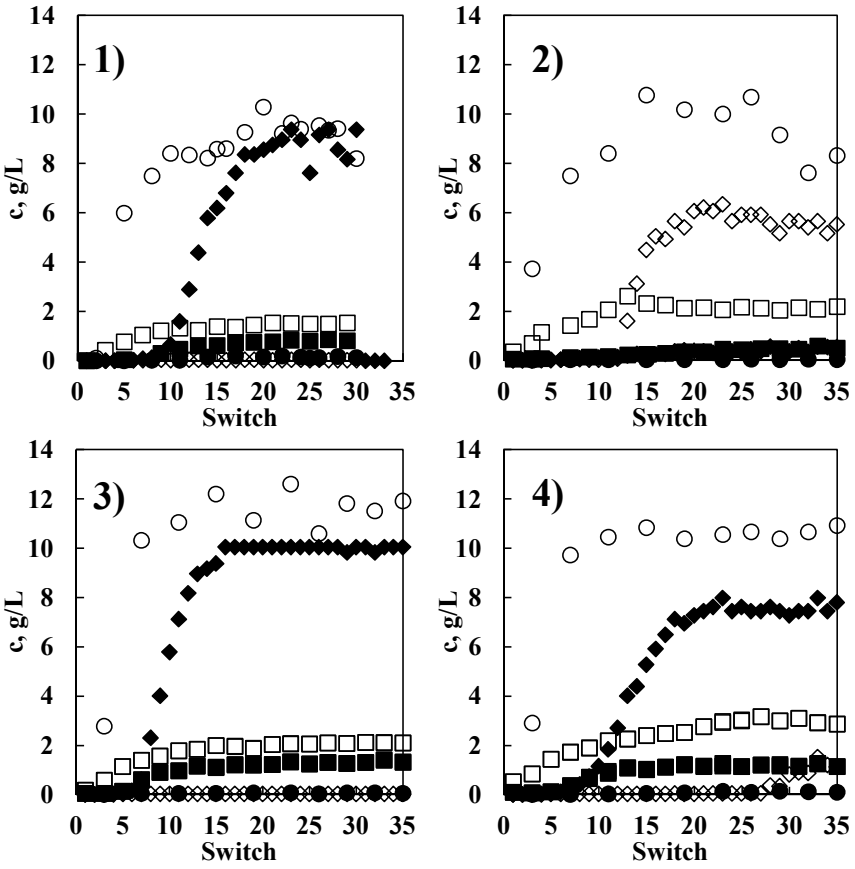

Figure 17 Concentration of NaOH (diamonds), acids (circles), and lignin (squares) in the extract (closed symbols) and raffinate (open symbols). The parameters for each run are presented in Table 3 and Fig. 16.

The product purity, productivity, yield and eluent consumption in the different runs are presented in Table 6. The highest purity of hydroxy acids, 60%, was obtained in runs 1 and 3. As the mass fractions of hydroxy acids and NaOH in the feed were 0.48 and 0.16, respectively, the purity of hydroxy acids was improved by 25% in these two runs. Considering the recovery of all acids including the volatile acids, their purity in the raffinate was approximately 85%. The main impurity in the raffinate was the group of lignin-derived compounds, while the amount of NaOH was negligible. In all of the SMB runs except the second run, lignin-based impurities were distributed in both raffinate and extract so that their concentration in raffinate is somewhat higher than in the extract. Similarly in the batch experiments a major part of lignin-derivatives ended up in the hydroxy acid fraction due to their relatively large molecular size. It is necessary to bear in mind that the purpose of this separation was to remove NaOH, and the other impurities such as residual lignin and volatile acids can be removed using other techniques as described in Paper IV.

As seen in Table 6, the productivity was highest in run 3. In addition, the eluent consumption was lowest in run 3, and the product streams were more concentrated than in the other runs. However, the yield of hydroxy acids in run 3 was somewhat lower than in run 1.

Table 6 The separation performance in the four SMB runs.

	Run 1	**Run 2**	**Run 3**	**Run 4**
PU(Raffinate), -	0.60	0.40	0.60	0.56
PU(Extract), -	0.90	0.46	0.87	0.85
PR(OH-acids), kg / (h m^3 resin)	106	120	133	126
PR(NaOH), kg / (h m^3 resin)	125	6	152	107
Y(OH-acids), -	0.94	1	0.88	0.83
Y(NaOH), -	1	0.16	1	1
EC, L/kg (OH-acids)	254	224	204	215

Based on the results, SMB chromatography with a SEC gel was found suitable for separating hydroxy acids and NaOH of soda black liquor. In comparison to batch chromatography, the

drawback is that the partial separation between the acids cannot be exploited. However, a continuous process may be more convenient in processing of large volumes of black liquor, and it may provide higher productivity and more concentrated product. A full optimization of the two process alternatives would be, however, required to quantify the real improvement in the productivity when SMB is used instead of batch chromatography.

8.3.4 Purification of hydroxy acid fractions

In addition to membrane filtration and chromatography, other separation techniques were also utilized for purification of hydroxy acids. Ion-exchange was applied for liberating the acids and removing the residual sodium, adsorption for removing residual lignin and evaporation for the removal of volatile acids. The detailed results are found in Paper IV.

Ion-exchange for was found to be a successful method for the liberation of acids. Alternative techniques for this purpose include electrodialysis and acidification. Acidification is the simplest alternative. The main advantage of ion-exchange over acidification is that the salt concentration of the solution does not increase. Electrodialysis is considered a more expensive but environmentally benign alternative to ion-exchange [172]. The main disadvantage of ion-exchange is the chemical consumption due to the regeneration and cleaning of the resin. Mineral acid is required for regeneration of the resin. For example, if H_2SO_4 is used for regeneration, a waste solution containing Na_2SO_4 is produced. This waste can be converted to NaOH and H_2SO_4 using bipolar electrodialysis [135, 173], and the produced acid can be, for example, re-used for the regeneration of the resin. Lignin adsorbed on the resin or precipitated in the column can be cleaned using alkali or organic solvent.

Adsorptive lignin removal using a neutral polymeric adsorbent (Amberlite XAD-16) was found efficient for removing the residual lignin. A similar type of resins has recently been applied for separating lignin from different wood-derived solutions [174-176]. Though adsorption of the target compounds on the resin may be a serious disadvantage of the purification method [175], no significant loss in the yield of hydroxy acids was observed in this work. The adsorption was carried out as a batch process. However, fixed-bed adsorption, which has been applied by Westerberg et al. [174], may be a good option. As presented by Schwartz and Lawoko [176], the resin can be regenerated using an organic solvent, e.g. acetone.

The concentration of volatile acids in the hydroxy acid fractions was reduced by evaporation. Volatile acids can be removed without losing hydroxy acids, since the difference in the vapour pressures is relatively large (see Table 7). As proposed by Alén and Sjöström [177, 178], distillation is a suitable method for partial fractionation of the acids of black liquor. However, evaporation and distillation are energy-intensive methods, and therefore other methods for removing the volatile acids and fractionating the hydroxy acids may be more attractive. These methods are discussed in the following chapter.

8.4 Prospective advanced separation processes

The separation tasks discussed above are basically pseudo-binary separations, in which one compound was removed or a group of compounds was recovered as a mixture. Combination of membrane filtration with chromatographic separation is, however, an attractive technique also for multicomponent separation. As an example, the possibilities for utilizing these techniques for fractionation of hydroxy acids are discussed in this chapter.

The main carboxylic acids of black liquor from soda or kraft cooking are listed in Table 7. The separation of lignin and inorganics from black liquor using UF and SEC resulted in a mixture of these acids. Hydroxy acid mixtures may be used as such for co-polymerization [82]. Nevertheless, more added value may be gained by isolating single hydroxy acids in high purity. The acids present in black liquor are, however, challenging to fractionate because their properties are very similar with each other (see Table 7). Different separation techniques can be considered.

Alén and Sjöström [177, 178] used distillation to fractionate the hydroxy acids recovered from black liquor. The purities obtained were 73% for xyloisosaccharinic acid (XISA) and about 50% for glucoisosaccharinic acid (GISA). In addition, a mixture of glycolic, lactic and 2-hydroxybutanoic (HBA) acids was obtained. These small hydroxy acids were found difficult to separate by distillation due to their close boiling points and instability during heating. The low purity of the products makes distillation an unfavourable separation technique for the fractionation of hydroxy acids. Furthermore, distillation is an energy-intensive unit operation.

Table 7 Properties of the main carboxylic acids of black liquor*).

Acid	M_w, g/mol	V_m, cm^3/mol	pK_a, -	Vapour pressure, bar (at 25 °C)
GISA	180	113	3.2	$6.1 \cdot 10^{-14}$
XISA	150	150	3.5	$1.9 \cdot 10^{-9}$
2-HBA	104	87.0	3.8	1.0
2,5-DHPA	134	101	3.8	$1.1 \cdot 10^{-3}$
Lactic acid	90	70.5	3.9	2.0
Glycolic acid	76	53.6	3.7	0.17
Oxalic acid	90	50.8	4.1; 1.3	0.33
Acetic acid	60	56.1	4.8	1900
Formic acid	46	39.8	3.7	4900

*) SciFinder, version 2013.1; Chemical Abstracts Service: Columbus, OH, 2013; calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02.

Extraction is another conceivable separation technique for fractionation of multicomponent mixtures. However, conventional extraction gives poor yields because the solubilities of the hydrophilic, ionisable acids in common organic solvents are low. Therefore, Caşcaval et al. [179] used reactive extraction for fractionating mixtures of succinic, acetic and formic acids. The main drawback of extraction is the use of organic solvents, which makes the process less environmentally friendly. In addition, the process is rather complex, since a multi-stage extraction was required already for separating the three acids.

Electrodialysis can also be considered for the purification of hydroxy acids. The advantage of electrodialysis is that it is possible to simultaneously liberate the acids if a bipolar membrane is applied. Electrodialysis has been applied e.g. for recovery of lactic acid from fermentation broths and from grass silage [180, 181]. However, the selectivity of electrodialysis in fractionation of carboxylic acids may be poor. For example, Moon et al. [13] found the separation of succinic acid from acetic acid difficult. In addition, fouling may cause serious problems in the electrodialysis of black liquor [125], and an efficient pre-treatment would, therefore, be required.

Chromatographic separation and NF are potential separation methods also for purification of individual hydroxy acids. Prospective fractionation and purification processes are discussed in this section.

8.4.1 NF for fractionation of hydroxy acids

NF has been found an applicable separation method for fractionation of organic acids including hydroxy acids. For example, Kang and Chang [72] used NF for separating sodium succinate from a mixture containing formate, acetate and lactate. Therefore, it is a promising technique also for the production of pure acids from black liquor.

The separation of acids by NF is based on the differences in molecular sizes and charges. As an assumption, acids with a large molecular size or multiple carboxylic groups are more retained by an NF membrane than small monocarboxylic acids. The selectivity of the separation depends, however, on pH and on the composition of the solution.

Effect of pH on NF is rather complicated. The topic was recently reviewed by Luo and Wan [95]. In summary, the main factors that affect are the charge of membrane, the charge of compounds in the solution, membrane swelling, fouling, and concentration polarisation. In the case of ionisable compounds such as carboxylic acids, the charge effects are of major importance.

Carboxylic acids dissociate as pH increases above their pK_a. Consequently, the osmotic pressure of the solution is higher at high pH and thus a higher pressure is required to obtain the target flux. A change in pH does not affect only the flux but also the rejection of solutes. NF membranes are typically negatively charged in neutral and alkaline conditions. When the pH is above the isoelectric point of the membrane, negative anions will be repelled by the negatively charged membrane. To maintain electroneutrality, cations cannot permeate either if the permeation of anions is restricted. Due to this Donnan effect, the retention of acids is likely to increase with increasing pH. Examples of that can be found in literature. For example, Han and Cheryan [182] showed that the retention of acetate on different NF membranes depends strongly on pH. However, they observed that pH did not affect above pH 5, e.g. when the acid was completely dissociated. More recently, Zhou et al. [105] studied the separation of acetic acid from monosaccharides as a function of pH using Desal 5 DK (GE

Osmonics) membrane. They observed an increase from 2.8% to 95% in the retention of acetic acid when pH increased from 2.9 to 9.9. The increase was linear below pH 7. Freger et al. [183] studied the effect of pH and salt concentration on the retention of lactic acid. They observed the highest rejection of lactic acid at neutral pH.

On the other hand, the Donnan effect may improve the separation selectivity, especially in the separation between monovalent and multivalent ions but also in the separation of ions with different molecular sizes. Therefore, it might be advantageous to carry out the NF of hydroxy acids mixtures at neutral pH rather than under acidic conditions. For example, the selectivity of the Desal 5 DK membrane in the fractionation of hydroxy acids has been found to improve when pH increased from 2 to 6: the retention of XISA increased while the negative retention of formic acid was strengthened [124].

In addition to pH, interactions between different carboxylic acids may affect their retention [184, 185]. Laufenberg et al. [185] found that multicomponent effects may play a major role in the separation of carboxylic acids. Consequently, the feed composition, which is determined by the wood species, pulping process and pre-treatment, may have a substantial influence on fractionation of hydroxy acids by NF.

The NF of hydroxy acids from black liquor most probably requires a pre-treatment to reduce the lignin concentration and to adjust the pH, because most NF membranes are somewhat susceptible to fouling and their pH range may be limited. Removal of inorganic salts may also be necessary, especially if the lignin removal and pH adjustment is done using a mineral acid. This is because the presence of salts increases the osmotic pressure of the solution. Furthermore, a highly concentrated salt may reduce the retention of compounds such as acids and sugars by increasing the membrane pore size and simultaneously decreasing the size of solutes due to their dehydration [96, 183, 186].

When the operating conditions are properly chosen, NF can be a feasible method for the fractionation of hydroxy acids. However, insufficient separation selectivity may be encountered when using NF for separation of compounds with such a small difference in their molecular sizes because the membranes often possess a wide pore-size distribution [124]. Application of NF cascades has been proposed for improving the separation [187]. Since membrane filtration is inherently a binary separation process, the fractionation of

a multicomponent acid mixture using NF might, however, require numerous process steps and complicated cascade arrangements. Therefore, considering the production of hydroxy acids in high purity, a combination of NF and chromatographic purification could be a more attractive alternative than use of NF only.

8.4.2 Chromatographic fractionation of hydroxy acids

Fractionation of hydroxy acids could also be made using chromatography. If SEC is applied for separating NaOH, partial fractionation of hydroxy acids is obtained, as discussed in Papers III–IV. However, the resolution was poor even when a relatively low column loading of 0.08 BV was applied. Therefore, some other chromatographic separation technique might be preferable for the fractionation of hydroxy acids.

Chromatographic separation of hydroxy carboxylic acids using anion-exchange resins has been studied already in the 1960s [188]. Anion-exchange chromatography has also been found applicable for the determination of carboxylic acids in black liquors [189]. The problem with anion-exchange resins is that they are easily fouled by organic matter [190], and thus an effective lignin removal pre-treatment is necessary. In addition, to obtain sufficient separation selectivity, it may be necessary to use a buffer solution with organic modifiers as eluent.

Cation-exchange resins could also be applicable for fractionation of hydroxy acids. In comparison to anion-exchange resins, cation-exchange resins are typically less expensive and more resistant to fouling. Resins with different ionic forms may be considered. For example, Ca^{2+} ions may form weak complexes of different strength with hydroxy acids and thus make their separation possible. However, high sodium content of black liquor makes the use of Ca^{2+} form resins unfavourable. Therefore, it might be necessary to remove the sodium using ion-exchange or electrodialysis prior to the chromatographic separation with a Ca^{2+} form resin. Alternatively, a resin in Na^{+} or H^{+} form could be selected. Alén et al. [83, 191] applied a SAC resin in Na^{+} form for separating hydroxy acids from black liquor. The purpose of their work was, however, to separate hydroxy acids from sodium sulphate rather than to fractionate the acids. Nevertheless, partial separation between hydroxy acids and volatile acids was also obtained.

Neutral polymeric resins can also be applied in chromatographic separation. Recently, Nam et al. [192, 193] studied the adsorption of acids (succinic, lactic, formic and acetic acid) on a neutral PS-DVB resin and found it suitable for the separation of succinic acid from lactic acid using SMB chromatography [73]. Lee et al. [194] separated lactic acid from acetic acid using SMB chromatography with a poly(4-vinylpyridine) resin.

In the preliminary tests done in this work, SAC resins were found promising for fractionating the hydroxy acids of ultrafiltered soda black liquor, whereas the use of WAC resins turned out less successful (see Fig. 18). In particular, when a WAC resin in a monovalent ion form (Na^+) was used, no fractionation occurred. Also neutral Amberlite XAD polymeric resins showed insufficient selectivity (data not shown). It should be noted, however, that the ultrafiltered soda black liquor that was used in the experiments contains lignin and sodium hydroxide as main impurities. Pre-treatment of black liquor to reduce the concentrations of lignin and inorganic salts could possibly improve the separation.

Based on the literature review and the results of the preliminary tests, it is thus concluded that chromatographic separation is a promising technique for fractionation of multicomponent acid mixtures. However, multiple separation steps may be required to obtain a sufficient purity. The drawback of chromatographic separation is dilution of the product, and possibly the need for using eluents other than water. Membrane filtration, RO in particular, may be a useful technique for removing the solvent to obtain a more concentrated end-product.

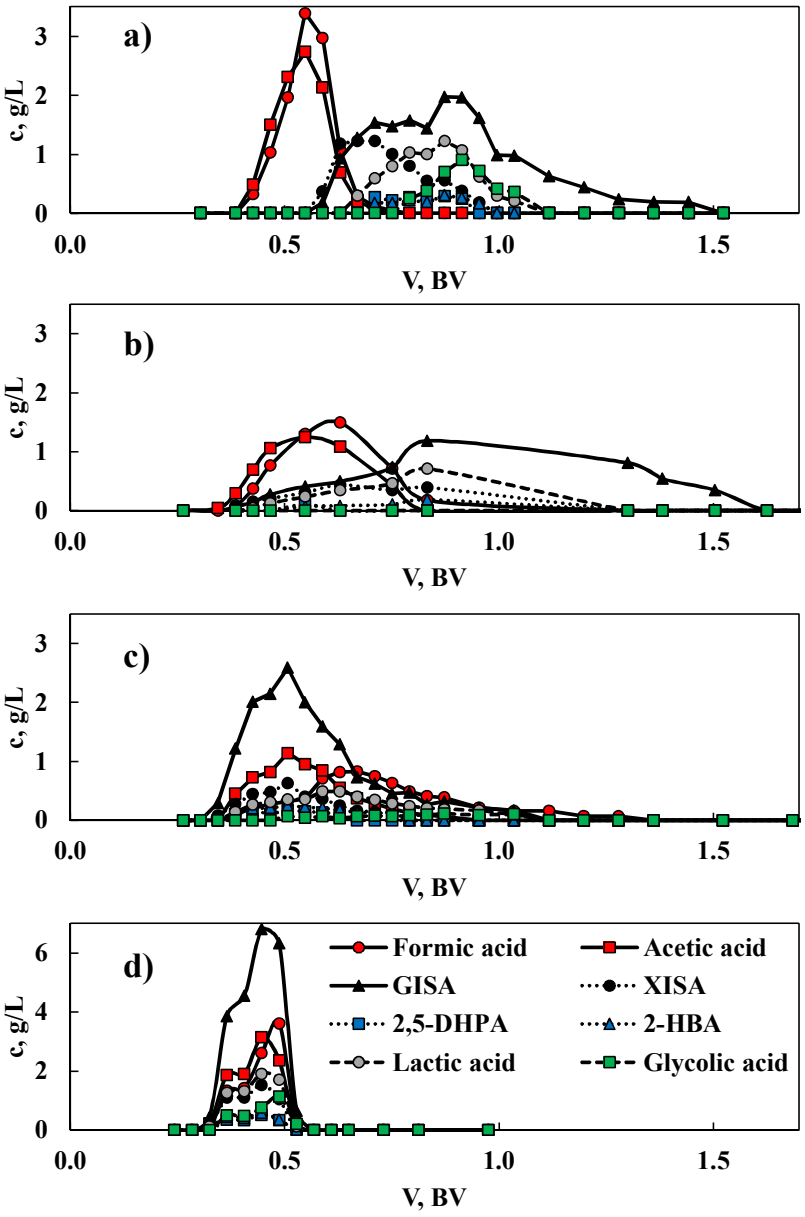

Figure 18 Fractionation of SW soda black liquor (pre-treated by UF, 10% TDS) using a) SAC resin (Finex CS16GC) in Ca^{2+} form, b) SAC resin (Finex CS16GC) in Ba^{2+} form, c) WAC resin (Finex CA16GC) in Ca^{2+} form, d) WAC resin (Finex CA16GC) in Na^{+} form. V_{inj} = 0.08 BV, eluent flow rate 0.6 BV/h. The acids are in their Na salt form.

9 CONCLUSIONS

Combining various separation techniques may be essential in the fractionation of complex multicomponent solutions such as biomass hydrolysates. It is sometimes a requisite for recovering the target compounds in the desired purity, but also in many cases it may improve the production rate and reduce the chemical consumption.

In this work, the potential benefits of combining preparative chromatography with membrane filtration in biorefinery applications were investigated. Based on the results, it can be concluded that the abovementioned combination is beneficial in recovering compounds from biomass hydrolysates or black liquor. Different ways of combining these two separation methods were considered. Firstly, a hybrid separation process, SSR-SR, was found to simultaneously improve the productivity and reduce the eluent consumption in comparison to conventional chromatographic separation processes. Secondly, a tandem separation process based on UF and SEC was found successful for fractionating black liquor without using additional chemicals, which has not been reported before. However, other separation and purification techniques such as adsorption and ion-exchange were also needed to obtain a high-purity product.

Another research question was whether the use of recycling chromatography, mixed-feed SSR chromatography in particular, would be advantageous in comparison to the conventional, widely-applied batch chromatography. Based on the example cases studied, SSR chromatography should be considered as an alternative for a batch process when designing chromatographic separation processes for difficult separation tasks. The benefit brought by recycling depends, however, on the isotherms and column efficiency. When the separation selectivity is good, which was the case in separation of NaOH and hydroxy acids from black liquor, recycling is not necessarily required, since large column loadings can be used and high productivity is obtained also using the simple batch mode. Since the feed volumes treated in the separation of valuable compounds from black liquor can be high, continuous SMB process may be the method of choice. On the other hand, in the recovery of high-value products such as rare sugars at high purity, recycling chromatography can be highly advantageous. One of the main benefits of SSR is that since a high purity can be obtained even when the column efficiency and separation selectivity is low, it is possible to use low-cost separation materials.

As a conclusion, the combining of different separation techniques has been proven to be a highly useful strategy for the development of techno-economically feasible processes for recovering valuable compounds in biorefineries. Membrane filtration and preparative chromatography are promising methods for various biorefinery applications because they offer good separation selectivity with relatively low consumption of energy and chemicals. The selection of the most advantageous process concept, however, requires understanding of the separation mechanisms. In addition, phenomena such as fouling and ageing of separation materials are important topics of research, since new, fouling-resistant and highly stable separation materials may be required in the harsh process conditions which are typical in biorefinery environment.

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Performance of recycling chromatography vs. batch chromatography

1 INTRODUCTION

Steady-state recycling (SSR) chromatography was introduced by Bailly and Tondeur already in the 1980s [1]. However, the true benefit of SSR in comparison to conventional batch process remains still unclear. According to a theoretical work of Kaspereit and Sainio, the performance of optimised SSR chromatography is always better than or as good as that of optimised batch chromatography [2]. On the other hand, contrary results have been reported by Schlinge et al. [3]. In their study, the SSR chromatography provided in some cases lower productivity than conventional batch process. Binary mixtures of compounds with Langmuir-type isotherms were studied, and the effects of different feed composition, retention factor and separation selectivity on the process performance were investigated. Batch chromatography was found competitive for SSR especially when the separation factor was high and the feed solution contained higher concentration of the first eluting compound than the last eluting compound. However, the comparison between the productivities provided by the different process modes is no straight-forwards because higher purity was obtained using SSR process than using batch process.

In this work, dynamic simulation is applied for assessing the performance of SSR and batch processes with fixed product purity constraints. To determine whether or not recycling is beneficial, the productivities provided by the two process modes are compared.

2 SIMULATION WORK

Three binary systems with multicomponent Langmuir isotherms but different separation factors were studied. The isotherm parameter values shown in Table A1 were taken from Schlinge et al. [3]. The effect of column efficiency was studied by varying the bead size between 60 and 260 μm. The injection volumes in batch and SSR were optimised for each column efficiency. In order to reduce the calculation load, only one fixed flow rate (4.9 BV/h) and one column size (H_{col} = 25 cm, D_{col} = 2.5 cm) was considered.

Different feed compositions (1:1, 1:4, and 4:1) were compared similarly as in the study of Schlinge et al [3]. Total feed concentration of 50 g/L was assumed similarly as in [3]. The molar mass of both components was assumed 235 g/mol [4]. Total bed porosity of 0.77 was

used in calculations. Intraparticle diffusion coefficient of $1 \cdot 10^{-10}$ m/s was assumed for both components. Axial dispersion coefficient was calculated using the equation of Chung and Wen [5].

Table A1 Parameters of the competitive Langmuir isotherms [3].

α	$q_{m,1}$, mol/L	$q_{m,2}$, mol/L	b_1, L/mol	b_2, L/mol
1.29	1.516	2.553	5.993	4.583
1.47	1.516	2.270	5.993	5.875
1.82	1.516	2.752	5.993	8.343

3 RESULTS AND DISCUSSION

The results of the simulation work are presented in Tables A2–A4. It is observed in the tables that SSR always provides better or equal performance as the batch mode, but the magnitude of improvement depends strongly on the separation factor and column efficiency.

3.1 Effects of separation factor

The effect of the separation factor can be clearly seen when comparing Tables A2–A4. As can be expected, the productivities provided by both SSR and batch processes are higher when the separation factor is larger.

In the case of a difficult separation (α = 1.29, Table A2), the productivity can be doubled or at least significantly increased using an SSR process instead of a batch process. In addition, the eluent consumption in SSR chromatography is over 50% lower than in batch chromatography.

Only a moderate improvement of 4 to 8% was achieved using SSR instead of batch when α was 1.47 (Table A3). The corresponding decrease in eluent consumption was approximately 10%.

In an easy separation case (α = 1.82, Table A4), the productivity was typically not improved at all when recycling was used. Indeed, the advantage of SSR over batch was noticeable only at the very low column efficiency (NTP 72, i.e. when the particle size was increased to 260 μm). On the other hand, SSR was not inferior to batch process in any case studied.

3.2 Effects of column efficiency

Different column efficiencies were realized by changing the particle size. Larger particle size leads to high dispersion in the column and thus reduced the column efficiency. In the studied case, the system with a particle size of 60 µm corresponds to an NTP value of 509. For the system with 120 µm particles, NTP value is 213.

When the column efficiency is decreased, the maximum productivities achievable using any chromatographic separation mode are obviously lower. It is under such conditions when the advantage of SSR over batch chromatography is more pronounced. This is clearly shown in Table A3 for the separation factor α = 1.47. The productivity can be even doubled when SSR chromatography is used instead of batch chromatography at NTP 213, whereas only a minor improvement in the process performance was obtained at NTP 509. This result is in agreement with the conclusions of Kaspereit and Sainio [2].

When the column efficiency is decreased to NTP = 271 (d_p = 100 µm), and the separation factor is low (α = 1.29, Table 3), the desired 98% purity is no longer achieved in batch mode due to dispersion effects. If PU_B is fixed to 98%, the purity of the other fraction is at best only 86%. Nevertheless, the recycling mode enables successful separation with desired purities, although the productivity is low and the eluent consumption high. With a lower NTP value of 213 (d_p = 120 µm), neither batch nor SSR can provide the desired purity for the lowest separation factor (α = 1.29). However, the highest obtainable purity of SSR, approximately 96%, is significantly higher than the maximum purity of a batch process, approximately 78%. These results demonstrate that recycling chromatography not only gives higher productivity but also can often be applied when batch separation is not feasible.

Since the target purity was not obtained using a batch process when the separation factor was low, the whole range of particle sizes was studied only for the highest separation factor. Even at the lowest column efficiency studied (particle size 260 µm, NTP 72) the productivity of batch process was quite high; only 30 % lower than obtained using the smallest particle size studied (60 µm). If the column efficiency would be further decreased, the advantage of SSR over batch would probably increase.

3.3 Effects of feed composition

According to Tables A2 and A3, the combined productivity of components 1 and 2 is highest for the 1:4 feed composition and lowest for the 4:1 feed composition. However, this does not apply to the case of a high separation factor (α = 1.82, Table A4). Schlinge et al. [3] made a similar observation and explained it by the combined effect of two phenomena: tag-along effect and fronting caused by finite mass transfer. The latter phenomenon is emphasized when the separation factor is high, and therefore the productivity of 1:4 feed composition is not as good as could be expected based on the results obtained with lower separation factors. In their study, the best productivity was obtained for 1:1 feed composition in the case of separation factor being 1.82. In the present study, however, the feed composition of 4:1 was found to be the most favourable with respect to productivity. The difference with the results of Schlinge et al. is probably due to the different mass transfer model applied, which makes the fronting even stronger.

Since tag-along effect and fronting result in changes in the composition of the recycle fraction, the benefit of using SSR mode depends on the fresh feed composition [3, 4]. In the case of a low separation factor, the highest improvement is obtained for the 1:1 composition, otherwise the improvement is largest for the 1:4 composition. In the latter case, recycling successfully reduces the effect of fronting.

4 CONCLUSION

Neglecting the small variation caused by the limited number of calculation points and computation precision, the productivity of an optimised SSR process was at minimum the same as the productivity of the optimised batch process in all the cases studied. This result can be expected since a batch process can be actually considered an SSR process in which the recycle width is zero.

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Table A2 Comparison of the maximum productivities and the corresponding eluent consumption of SSR and batch chromatography, α = 1.29. $PU_A = PU_B$ = 0.98. Flow rate: 10 mL/min. H_{col} = 25 cm, D_{col} = 2.5 cm.

	Batch			**SSR**		
c_1:c_2	V_{inj}, % of BV	PR_{tot}, mol/L_{bed}/h	EC_{tot}, L/mol	V_{inj}, % of BV	PR_{tot}, mol/L_{bed}/h	EC_{tot}, L/mol
			d_p 60 µm (NTP = 509)			
1:1	2.9	0.0240	198.9	31	0.0477 (+99%)	81.5 (-59%)
1:4	5.5	0.0381	122.8	29	0.0716 (+88%)	56.0 (-54%)
4:1	2.8	0.0200	240.1	36	0.0336 (+68%)	114.7 (-52%)
			d_p 100 µm (NTP = 271)			
1:1	n.a.	n.a.	n.a.	57	0.0121	283.5
1:4	n.a.	n.a.	n.a.	65	0.0280	117.8
4:1	n.a.	n.a.	n.a.	65	0.0098	338.2

Table A3 Comparison of the maximum productivities and the corresponding eluent consumption of SSR and batch chromatography, α = 1.47. $PU_A = PU_B = 0.98$. Flow rate: 10 mL/min. H_{col} = 25 cm, D_{col} = 2.5 cm.

	Batch			**SSR**		
c_1:c_2	V_{inj}, % of BV	PR_{tot}, mol/L_{bed}/h	EC_{tot}, L/mol	V_{inj}, % of BV	PR_{tot}, mol/L_{bed}/h	EC_{tot}, L/mol
			d_p 60 µm (NTP = 509)			
1:1	21	0.0936	47.4	34	0.0973 (+4%)	42.8 (-10%)
1:4	27	0.1103	38.9	39	0.1190 (+8%)	34.2 (-12%)
4:1	17	0.0818	55.2	46	0.0849 (+4%)	46.0 (-17%)
			d_p 120 µm (NTP = 213)			
1:1	6.3	0.0323	146.4	49	0.0622 (+92%)	62.3 (-57%)
1:4	9.2	0.0410	113.6	43	0.0847 (+106%)	47.4 (-58%)
4:1	6.8	0.0299	159.0	53	0.0456 (+53%)	86.0 (-46%)

Table A4 Comparison of the maximum productivities and the corresponding eluent consumption of SSR and batch chromatography, α = 1.82. $PU_A = PU_B$ = 0.98. Flow rate: 10 mL/min. H_{col} = 25 cm, D_{col} = 2.5 cm.

	Batch			**SSR**		
c_1:c_2	V_{inj}, % of BV	PR_{tot}, mol/L_{bed}/h	EC_{tot}, L/mol	V_{inj}, % of BV	PR_{tot}, mol/L_{bed}/h	EC_{tot}, L/mol
			d_p 60 µm (NTP = 509)			
1:1	111	0.2058	19.0	112	0.2059 (+0%)	18.9 (-0%)
1:4	124	0.2049	18.4	126	0.2055 (+0%)	18.3 (-1%)
4:1	113	0.2107	18.6	113	0.2109 (+0%)	18.5 (-0%)
			d_p 120 µm (NTP = 213)			
1:1	107	0.1924	20.6	110	0.1919 (+0%)	20.5 (-0%)
1:4	120	0.1914	20.1	126	0.1932 (+1%)	19.7 (-2%)
4:1	107	0.1963	20.3	108	0.1960 (+0%)	20.3 (-0%)
			d_p 260 µm (NTP = 72)			
1:1	86	0.1449	28.9	114	0.1494 (+3%)	26.7 (-8%)
1:4	96	0.1442	28.4	129	0.1556 (+8%)	24.9 (-12%)
4:1	85	0.1493	28.1	99	0.1508 (+1%)	27.1 (-4%)

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Steady state recycling chromatography with an integrated solvent removal unit – Separation of glucose and galactose

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ABSTRACT

A process concept where a solvent removal unit is integrated to a steady-state recycling chromatography process (SSR–SR) offers a possibility to significantly increase the performance of single column chromatographic separation. The advantages of solvent removal for a difficult separation task at conditions typical for industrial scale chromatography were demonstrated by investigating the performance of SSR–SR in separation of glucose and galactose. Two limits for the extent of solvent removal were imposed: maximum total concentration of the solution fed into the column (viscosity limit) and the maximum total concentration achievable in the solvent removal unit (solubility or osmotic pressure limit). The process was optimized using numerical simulation. Three SSR–SR configurations with different positions of the solvent removal unit were compared with (1) the conventional batch process, (2) SSR without solvent removal, and (3) batch process with solvent removal. SSR–SR was found to always improve the productivity. In addition, solvent removal reduced eluent consumption in most cases. The concentration limits and the concentration of the fresh feed were shown to determine which SSR–SR configuration yields the best performance.

1. Introduction

Maximization of productivity in industrial or preparative scale chromatographic separation usually leads to such large injection volumes that the components are not completely separated, especially when the separation selectivity is low. Therefore, in binary separations, an unresolved part between the two product fractions may have to be disposed of, if high product purity is required. Different recycling schemes are known to improve productivity, yield and product purity in preparative chromatography [1]. In steady state recycling (SSR) chromatography, the unresolved fraction is recycled back to the column [2]. In the mixed-recycle SSR scheme, the recycle fraction is mixed with the fresh feed before being re-injected to the column. Another approach is to feed the recycled part of the profile as such, adding fresh feed either before or after it [3]. This closed-loop SSR chromatography takes advantage of the partial separation already achieved. In comparison to a batch process, SSR allows operations with higher flow rates and larger injection volumes without any waste fractions [4]. However, the large injection volume and the high flow rate result in a large dilute recycle fraction, which limits the amount of fresh feed processed. Thus the productivity is limited [5] although often substantially higher than in a conventional batch process.

A novel process concept where mixed-recycle SSR is coupled with a solvent removal unit has recently been presented [6]. A similar approach for concentrating internal process streams was earlier introduced for simulated moving bed (SMB) chromatography [7,8]. Theoretical analysis shows that in ideal conditions solvent removal may increase productivity and reduce eluent consumption [6]. This is because the integration of solvent removal with SSR increases the amount of fresh feed that can be processed per cycle. There are several possible positions where the solvent removal unit can be placed in an SSR–SR process. Solvent can be removed from the fresh feed, from the recycle stream, or from the column feed (the mixture of the fresh feed and recycle streams).

In practice, solvent can be removed, for example, in a membrane filtration unit or in an evaporation unit. Chromatographic separation and membrane filtration are well suited to integrated operations as the temperature can be kept constant during the whole process. Unlike evaporation, membrane filtration is suitable also for volatile or heat sensitive compounds, *e.g.* proteins. The drawbacks of membrane filtration may be a limited retention of the target compounds and membrane fouling, which may affect the stability of the process. A recent study has, however, demonstrated the robustness of an integrated process where a bioreactor is coupled with SMB chromatography and solvent removal by nanofiltration [9].

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As the previous theoretical work [6] assumed ideal conditions only, the performance of SSR–SR under actual process conditions, *i.e.* in the presence of dispersion, has not been investigated. The objective of the present work is thus to provide an overview of the performance of SSR–SR under strongly non-ideal process conditions characteristic of industrial scale preparative chromatography.

In addition to dispersion, other practical issues have to be considered when evaluating the effect of solvent removal on the performance of SSR. In the SSR–SR process, the more solvent that is removed, the more fresh feed can be processed per cycle [6]. However, the concentration cannot be limitlessly raised because operating with highly concentrated solutions may not be feasible in practice. Viscous fingering and pressure drop in the column may set a limit for the concentration of the feed solution. The solubility of the compounds may limit the concentration even more, since crystallization in the column or in the solvent removal unit is unacceptable. On the other hand, if the solubility is high, osmotic pressure in membrane separation or vapour pressure in evaporation may become a limit of operation at high concentrations. This work studies the effects of the fresh feed concentration and concentration limits set for the process units on the performance of SSR–SR, which has not been investigated before. In addition, the feasible range of operating parameters for different SSR–SR configurations is discussed.

Previous study has shown that the advantage of SSR over batch chromatography is pronounced in processes with a low separation factor or low column efficiency [5]. Integration of a solvent removal unit would presumably further improve the process performance especially in that kind of difficult separation tasks. Therefore, a difficult separation case, the recovery and purification of galactose and glucose from lactose hydrolysate, was chosen for investigation. An industrial scale chromatographic separation process for this purpose was recently investigated by Saari et al. [10]. In their study, conventional batch chromatography was used. Due to the low separation factor between the two monosaccharides ($\alpha = 1.15$), the product purities remain low (approximately 70%). A higher purity would be preferable, since it would facilitate downstream processing (crystallization of the products). In this paper, the performance of different SSR–SR process configurations in the case of high purity requirements (90%) is investigated using numerical simulation.

2. Principle of SSR–SR

The principle of the SSR–SR process, introduced in [6], is shown in Fig. 1. Solvent can be removed from the fresh feed (I), the recycle stream (II), or the column feed (III), *i.e.* the mixture of the fresh feed and recycle streams. In all three options, the system approaches a cyclic steady state if the amount of solvent removed and the amount of fresh feed introduced remain constant on every cycle. As with the conventional SSR, a method for predicting the steady state of Langmuir isotherm systems under ideal conditions is also available for SSR–SR [6].

All the SSR–SR process configurations are based on mixed-recycle SSR, *i.e.* the recycle fraction is mixed with fresh feed prior to injection to the column. Closed-loop mode of SSR may not be feasible for SSR–SR processes as mixing is difficult to avoid during solvent removal. In addition, mixed-recycle mode is useful in theoretical studies because methods are available for prediction of the steady state and the cut times for recovering the recycle fraction and product fractions that meet the set purity targets [5,11]. In addition, numerical studies of mixed-recycle SSR are more straightforward than of closed-loop SSR because optimization of the extra-column volume and distribution of the recycle fraction during the feed step is not needed.

3. Calculations

The separation of glucose and galactose from lactose hydrolysate was investigated using dynamic simulation. In addition to glucose and galactose, a lactose hydrolysate may also contain salts, some residual lactose, and minor amounts of oligosaccharides. Salts, in particular, can affect solvent removal by increasing the osmotic pressure and changing the permeability of compounds in membrane filtration [12]. However, salt can be separated using ion exclusion chromatography prior to the fractionation of the monosaccharides, which also decreases the cycle time of the chromatographic separation significantly. A binary separation of glucose and galactose is thus investigated in this work.

Sorption of monosaccharides on elastic ion exchange resins is often reported to be weakly nonlinear (anti-Langmuir) [13,14]. However, Saari et al. [15] reported linear isotherms up to concentration 350 g/L for the particular system used here. As reported in [15], the parameters of the linear isotherms on a SAC resin (Finex CS11GC Na^+ form, 5.5% DVB cross-linking) are: for galactose, $K = 1.027\ \mathrm{L/kg_{dryresin}}$ and for glucose, $K = 0.893\ \mathrm{L/kg_{dryresin}}$. These values lead to the following linear isotherm equations:

$$q^*_{glu} = 0.4279 \cdot c_{glu} \quad (1)$$

$$q^*_{gal} = 0.4921 \cdot c_{gal} \quad (2)$$

where q^*_{glu} and q^*_{gal} are the solid phase equilibrium concentrations (mol/L) of glucose and galactose, respectively, and c_{glu} and c_{gal} are the corresponding liquid phase concentrations (mol/L). As seen from the isotherm parameter values, the separation factor for this pair of monosaccharides is very low, $\alpha = 1.15$. For that reason, the purity achieved experimentally in batch operation was as low as 71% for glucose and 65% for galactose [10].

The operation of a pilot scale column described in [10] (column i.d. $D_{col} = 23$ cm, bed height $H = 5.3$ m, resin bead size $d_p = 0.33$ mm, bed porosity $\varepsilon = 0.31$) was simulated. Three different total concentration levels of the fresh feed were investigated: 1.35 mol/L, 0.68 mol/L, and 0.34 mol/L. The ratio of glucose and galactose in the fresh feed was assumed to be 1:0.92 as reported in [10]. The concentration of galactose in lactose hydrolysate is typically lower than that of glucose due to transgalactolytic activity [16]. Diffusion coefficients of $1.50 \times 10^{-10}\ \mathrm{m^2/s}$ and $1.48 \times 10^{-10}\ \mathrm{m^2/s}$ were used for glucose and galactose, respectively.

In the simulations performed here, the purity constraints were fixed to 0.90 (± 0.001) for both glucose and galactose. A threshold concentration of 0.001 mol/L was applied for determining the beginning of the first product fraction (t_{1A}) and the end of the second product fraction (t_{2B}). Together these cut times determine the duration of a cycle. Besides these, only one cut time between the product fractions is used in the conventional batch operation when no waste fraction is allowed. There is only a single injection volume for a specific flow rate that provides the desired purities for both product fractions. This injection volume was found by using dynamic simulations and a least-squares optimization algorithm. In SSR and SSR–SR operation, two additional cut times (t_{2A} and t_{1B}) are applied to collect the recycle fraction. These cut times were first estimated using a short-cut method [5], which uses numerical integration of a simulated chromatogram for the determination of t_{2A} and volume and mass balances for calculating t_{1B}, and then refined by an iteration scheme to meet the purity constraints within the required accuracy.

The retention of solutes in the solvent removal unit was assumed to be complete. Accordingly, the solvent removal causes no loss of monosaccharides. This assumption is probably valid in practice if the solvent is removed using a reverse osmosis membrane, a very dense nanofiltration membrane, or evaporation.

The SSR–SR process was optimized for maximum productivity and minimum eluent consumption by varying injection volume and feed flow rate. The injection volume ranged from 2 to 20% of BV (or up to 40% of BV if a clear optimum was not observed at lower injection volumes) with an interval of 2%-units. Close to the optimum, the injection volumes were scanned with an interval of 0.25%-units. Feed flow rate ranged from 18 to 60 L/h (*i.e.* from 0.08 to 0.27 BV/h) with intervals of 6 L/h, which corresponds to linear velocities of 0.43–1.44 m/h. The number of theoretical plates (NTP) was determined for each flow rate from the moments of a simulated batch elution profile of a narrow galactose pulse (1% of the column volume). The flow rate range corresponds to NTP values from 1650 to 300. The desired purities were not achieved with higher flow rates. The axial dispersion coefficient was calculated using the method presented by Chung and Wen [17].

Solid film linear driving force approximation was employed in the simulation model. The component mass balances in the column were written as follows

$$\frac{\partial c_i}{\partial t} = D_{ax}\frac{\partial^2 c_i}{\partial z^2} - \frac{1-\varepsilon}{\varepsilon}\frac{\partial q_i}{\partial t} - u\frac{\partial c_i}{\partial z} \tag{3}$$

$$\frac{\partial q_i}{\partial t} = \frac{60 D_i}{d_p^2}(q_i^* - q_i) \tag{4}$$

where t time (s), D_{ax} the axial dispersion coefficient (m^2/s), z the axial coordinate (m), ε the bed porosity (–), q_i the solid phase concentration (mol/L), q_i^* the equilibrium solid phase concentration (mol/L), u the interstitial velocity (m/s), d_p the particle diameter (m), and D_i the effective intraparticle diffusion coefficient (m^2/s). The column was assumed to be radially homogeneous and the bed porosity constant.

The following boundary conditions were applied

$$\left.\frac{\partial c_i}{\partial z}\right|_{z=0} = \frac{u(c_i - c_i^0)}{D_{ax}}$$
$$\left.\frac{\partial c_i}{\partial z}\right|_{z=H} = 0 \tag{5}$$

where $c_i^0 = c_i^F$ when $t \le t_{inj}$ and $c_i^0 = 0$ when $t > t_{inj}$. Only one injection at a time was considered in the simulation, and thus $c(z,t=0)=0$, $q(z,t=0)=0$.

The model was validated by simulating the batch separation with the parameters used by Saari et al. [10]. The simulated chromatogram was in agreement with the experimental data presented in [10].

3.1. Constraints for solvent removal

The amount of solvent removed can be limited by a number of factors. Firstly, solubility or osmotic pressure may limit the concentration of the solution treated in the solvent removal unit. Secondly, viscosity or solubility typically limits the concentration of the feed to the chromatography column. In the separation of galactose and glucose, the concentration limits arise from viscous effects or osmotic pressure rather than from solubility issues, since monosaccharides are highly soluble. Based on available multicomponent viscosity data [18], the viscosity of the glucose–galactose solution was assumed to be independent of the composition. Also, the osmotic pressure and vapour pressure of monosaccharide solutions can be assumed linear and independent of the composition of the solution. Therefore, linear concentration limits, $c_{glu} + c_{gal} \le c_{max}$, were used. Since the properties such as viscosity and solubility of multicomponent mixtures are often dependent on the composition, also non-linear concentration limits may occur, but they are beyond the scope of this work. The influence of the concentration limits A–D presented in Table 1 on process performance was of interest in this study. All of the maximum concentrations studied are in the range of linear isotherms according to Saari et al. [15].

Table 1
Concentration limits studied: maximum total concentration of the solution in the solvent removal unit and in the column feed.

Limit	c_{max} in SR unit, mol/L	c_{max} in feed to column, mol/L
A	1.1	–
B	1.4	–
C	1.7	1.4
D	–	1.4

3.2. Evaluation of process performance

The target component in product fraction A is the first eluting component, *i.e.* glucose. The second eluting component, *i.e.* galactose, is the target product of product fraction B. Purities of the product fractions A and B were calculated from the amounts of glucose (component 1) and galactose (component 2) in the product fractions using Eqs. (6) and (7).

$$PU_A = \frac{n_1^A}{n_1^A + n_2^A} \tag{6}$$

$$PU_B = \frac{n_2^B}{n_1^B + n_2^B} \tag{7}$$

Process performance was assessed based on total productivity PR_{tot} and eluent consumption EC_{tot}. PR_{tot} was calculated using the equation

$$PR_{tot} = \frac{V^{FF}\left(Y_1 c_1^{FF} + Y_2 c_2^{FF}\right)}{V_{bed} t_{cycle}} \tag{8}$$

where Y_i is the yield of component i, c_i^{FF} concentration of i in the fresh feed, V^{FF} the volume of the fresh feed per cycle, V_{bed} is the bed volume, and t_{cycle} the duration of a cycle.

The other process performance parameter, specific eluent consumption EC_{tot}, was calculated assuming that the solvent recovered is reused as eluent as shown in Eq. (9)

$$EC_{tot} = \frac{t_{cycle}\dot{V} - V_{inj} - V^{SR}}{V^{FF}\left(Y_1 c_1^{FF} + Y_2 c_2^{FF}\right)} \tag{9}$$

where $\dot{V}$ is the volumetric flow rate and V^{SR} is the volume of solvent removed.

The recovery yields of components 1 and 2 are defined as follows

$$Y_1 = \frac{n_1^A}{n_1^{FF}} \tag{10}$$

$$Y_2 = \frac{n_2^B}{n_2^{FF}} \tag{11}$$

The extent of the solvent removal was represented as the volume reduction factor (*VRF*) defined as follows

$$VRF = \frac{V^{FSR}}{V^{FSR} - V^{SR}} \tag{12}$$

where V^{FSR} the volume fed to the solvent removal unit. Depending on the process configuration, V^{FSR} equals V^{FF} (configuration I), V^R (configuration II), or the sum of these two (configuration III). In addition to *VRF*, the volume of solvent removed per volume of fresh feed treated (V^{SR}/V^{FF}), which characterizes the operational costs of the solvent removal, was also used in assessment of the processes.

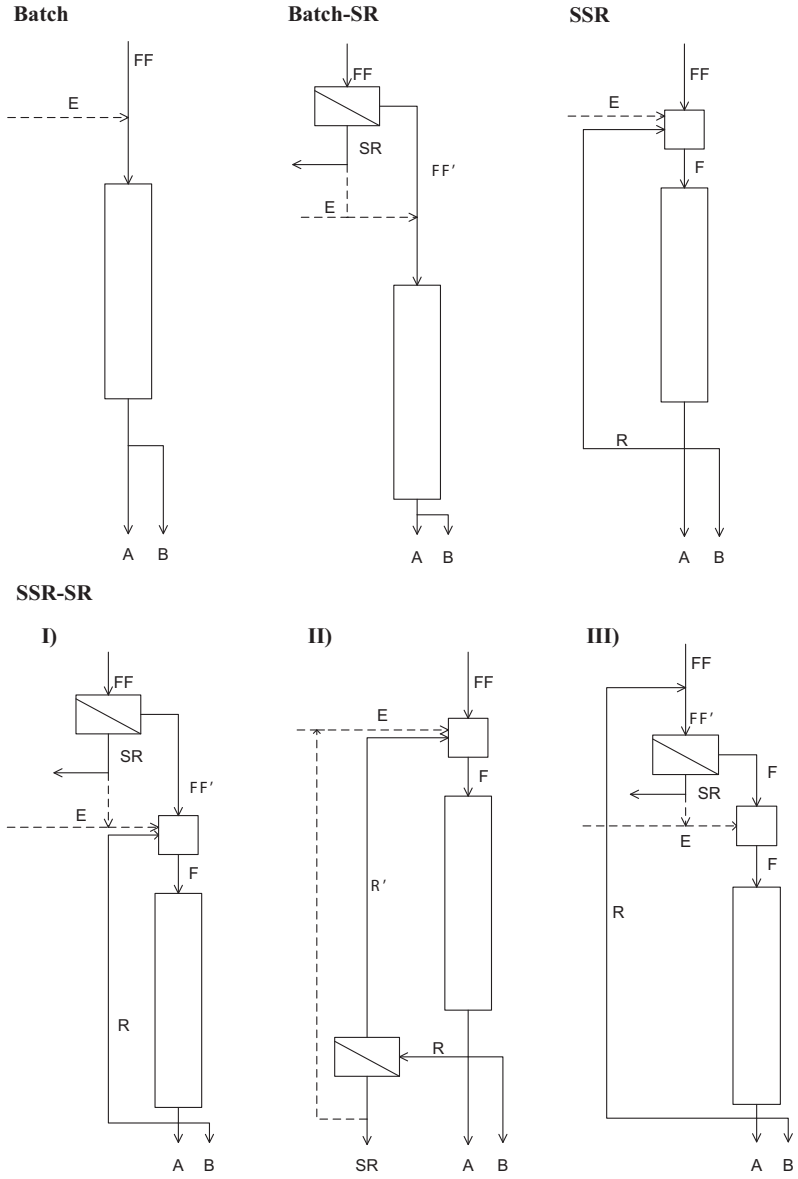

Fig. 1. Chromatographic process configurations investigated. Principles of SSR–SR schemes: (I) Solvent removal from the fresh feed; (II) solvent removal from the recycle stream; (III) solvent removal from the column feed. FF = fresh feed, F = feed to the column, R = recycle fraction, SR = removed solvent, E = eluent. A and B are the product fractions.

4. Results and discussion

4.1. Feasible range of operating parameters

As already mentioned, in conventional batch chromatography there exists only a certain injection volume (for a given flow rate) that fulfils the purity constraints without generating waste fractions. On the contrary, SSR chromatography has one degree of freedom, because any injection volume larger than that in batch chromatography can be used. When solvent removal is applied, one more degree of freedom is added. The SSR–SR process thus has two free operating parameters, namely the injection volume, V_{inj}, and the volume of fresh feed treated per cycle, V^{FF}. Alternatively, the amount of solvent removed, V^{SR}, can be used as an operating parameter instead of V^{FF}.

By removing part of solvent from the injection that enters the column, the volume of fresh feed can be increased. In the interests of productivity, it is favourable to add a maximum amount of fresh

feed to the process on each cycle. On the other hand, an increase in the injection volume leads to prolonged cycle time and thus reduces the production rate.

It has been shown theoretically [6] that the feasible range of applicable operating parameters is not identical for all of the SSR–SR configurations shown in Fig. 1, even when no concentration limits are considered. In this work, the influence of the concentration constraints A–D listed in Table 1 on the feasible range of V^{FF} and V_{inj} is investigated. Fig. 2 illustrates the results for a case where the fresh feed concentration is 0.68 mol/L and the column efficiency is constant (NTP = 1150), *i.e.* the eluent flow rate is constant (24 L/h).

Batch chromatography: The classical batch chromatography process is presented as a filled circle in Fig. 2. In the batch process the volume of fresh feed is equal to the injection volume because no recycling is applied. It can thus be operated only at a single point in the operating parameter space. The amount of fresh feed can be increased by removing solvent from the feed but the injection volume remains constant for linear isotherms. The constant injection volume is contrary to the case of Langmuir isotherms [6] and nonlinear isotherms in general. The feasible operating parameter space of batch chromatography is thus a straight horizontal line limited by the fresh feed concentration and the maximum concentration. This line is shown in orange colour in Fig. 2. The points representing the total concentrations of 1.1 mol/L (limit A in Table 1) and 1.4 mol/L (limits B–D in Table 1) are shown in the figure as open circles.

SSR without solvent removal: The steady state recycling mode allows the use of any injection volume higher than or equal to that of batch mode. The feasible operating parameters for SSR are given by the orange dashed curve in Fig. 2. When the injection volume is increased from that used in batch chromatography, the amount of fresh feed has to be increased in order to prevent the purities of the product fractions becoming higher than required [5]. The curve thus moves up and to the right. However, when the injection volume is increased above a certain level, the amount of fresh feed required to reach the purity constraints becomes constant due to recycling of injection plateau. This phenomenon is clearly seen in Fig. 2: the dashed curve becomes a vertical line after V_{inj} = 6% of BV. This injection volume corresponds to the maximum productivity. With larger V_{inj}, productivity decreases because the cycle time increases while the amount of fresh feed that can be processed per cycle stays constant.

SSR with solvent removal: Applying solvent removal expands the feasible range of operating parameters of SSR chromatography and there is a functional dependency between V^{FF} and V^{SR} [6]. For all three configurations, the curves shown in Fig. 2 correspond to the situation when the maximum amount of solvent is removed, *i.e.* maximum V^{FF} is treated per cycle. It should be noted, however, that SSR–SR can be operated anywhere between these curves and the curve of SSR. For configurations I and III, the lower boundary for V_{inj} is the operating line of batch chromatography with solvent removal.

The dotted lines in Fig. 2 correspond to the SSR–SR configuration where solvent is removed from the fresh feed (SSR–SR I). The maximum V^{FF} is determined by the maximum concentration in the solvent removal unit or, if no such limit exists (constraints of type D), the maximum concentration of the feed to the column. As seen in Fig. 2, the curves of SSR–SR I become vertical after a certain injection volume, in the same way as the curve of SSR. After this point, the amount of fresh feed becomes independent of the injection volume because an injection plateau is being recycled. The maximum productivity is typically obtained with an injection volume corresponding to the inflection point of the curve. The maximum volume of fresh feed that can be treated on each cycle depends on the concentration limits. When the maximum concentration is 1.1 mol/L (limits of type A), maximum V^{FF} is 5.5% of BV. For the limits of 1.4 mol/L (constraints of type B) and of 1.7 mol/L (constraints of type C) the maximum values of V^{FF} are 7.1% of BV and 8.7% of BV, respectively. When no limitation for the solvent removal unit is set, the volume of fresh feed can be increased to 9.1% of BV. A further increase in V^{FF} is not possible due to the constraint of column feed concentration.

The operation range of SSR–SR configuration II, where solvent is removed from the recycle stream, is illustrated as dash-dotted lines in Fig. 2. If no concentration limits are set for the solvent removal unit (limit D, black dash-dotted line), V^{FF} equals V_{inj} at the upper boundary. This is because the injection volume is the sum of fresh feed and recycle volumes, and the latter becomes zero (and concentration infinite) in the solvent removal unit. This behaviour is independent of isotherm type and amount of dispersion, and the same result was obtained earlier for Langmuir systems [6]. When the maximum concentration in the solvent removal unit is limited (limits A–C), the upper boundary of V^{FF} in SSR–SR II is curved. For example, for limit C (green curve in Fig. 2), the column feed concentration limit is met only with V_{inj} > 30% of BV. The corresponding maximum V^{FF} is 9.1% of the bed volume.

The third option is to remove solvent from the column feed (configuration SSR–SR III). The boundaries of this configuration with different constraints are shown as solid lines in Fig. 2. The curves corresponding to limits B–D are overlaid in Fig. 2 because the limiting concentration is 1.4 mol/L in all these cases. In case B the limit is imposed by the solvent removal unit whereas in cases C and D it is the maximum feed concentration to the column. In case A the concentration limit for the solvent removal unit is lower (1.1 mol/L) and the range of operating parameters thus narrower.

It is further observed in Fig. 2, that the boundary of SSR–SR I with limit D coincides with the boundaries of SSR–SR III with limits B–D. This is because the column feed concentration at steady-state is equal in all of these cases. In SSR–SR I, the feed concentration of 1.4 mol/L is obtained by diluting the concentrated fresh feed with the recycle fraction to match the maximum concentration of the column feed. In configuration III, mixing of streams is performed first, and the solution is concentrated to the same level. Also SSR–SR II with limits C and D becomes equal to these configurations at large injection volumes. In those cases, the recycle fraction is concentrated and then diluted with the fresh feed to obtain the concentration of 1.4 mol/L. With small injection volumes, however, this concentration cannot be reached due to the small size of the recycle fraction.

4.1.1. Influence of feed concentration on the feasible range of operating parameters

When the fresh feed concentration is halved from the value in the above discussion, the feasible operating parameters change, as seen in Fig. 3. Since a larger amount of solvent can be removed from more dilute streams before reaching concentration limits, a larger volume of fresh feed can be added in all SSR–SR configurations. In configurations I and III the maximum V^{FF} is doubled when the fresh feed concentration is halved. In configuration II the difference is not as large. The injection volume required to process the largest possible V^{FF} per cycle is substantially increased when the c^{FF} is decreased. For example, the maximum V^{FF} for limit D is reached with V_{inj} = 16% of BV, while V_{inj} = 9% of BV was sufficient for the more concentrated fresh feed in Fig. 2. Nevertheless, it can be concluded by comparing Figs. 2 and 3 that no substantial differences in the shape of any of the concentration limitations is observed if the fresh feed concentration is decreased by 50%.

When c^{FF} is increased to 1.35 mol/L, some interesting phenomena in the feasible operating parameters of SSR–SR are observed (see Fig. 4). Let us first focus on the case of concentration limits A (c_{max} = 1.1 mol/L in the SR unit). Configuration SSR–SR I is not applicable because $c^{FF} > c_{max}$. The same holds for small injection widths

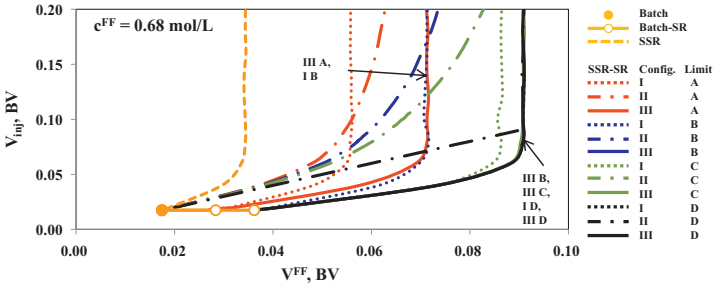

Fig. 2. Bounds of the operating parameter space of SSR–SR for the case c^{FF} = 0.68 mol/L. Position of the solvent removal unit: dotted line = fresh feed (configuration I); dash-dot line = recycle fraction (configuration II); solid line = column feed (configuration III). Concentration limits (see Table 1): red = A, blue = B, green = C, black = D. Dashed line = SSR without solvent removal; filled circle = batch; open circle = batch with solvent removal. Flow rate $\dot{V}$ = 24 L/h. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

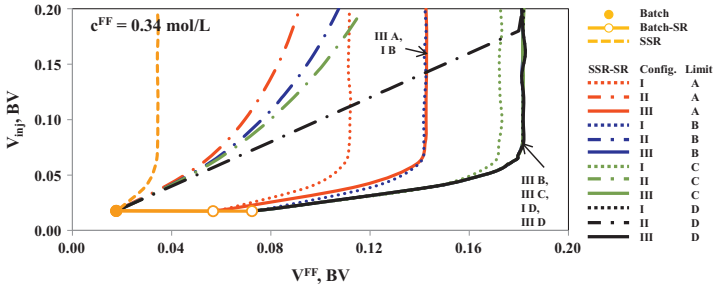

Fig. 3. Bounds of the operating parameters of SSR–SR for the case c^{FF} = 0.34 mol/L. Position of the solvent removal unit: dotted line = fresh feed (configuration I); dash-dot line = recycle fraction (configuration II); solid line = column feed (configuration III). Concentration limits (see Table 1): red = A, blue = B, green = C, black = D. Dashed line = SSR without solvent removal. Filled circle: batch. Open circle: batch with solvent removal. Flow rate $\dot{V}$ = 24 L/h. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

in configuration SSR–SR III. For sufficiently large injections, however, the recycle fraction becomes large enough to dilute the fresh feed, and some solvent can be removed. Consequently, the curve of SSR–SR III A begins from an injection volume of 6% of BV. The range of feasible operating parameters is widest for the configuration in which solvent is removed from the recycle stream (configuration SSR–SR II). However, in this configuration V^{FF} starts to decrease when V_{inj} is increased above a certain level, which can be seen as the peculiar shape of curve SSR–SR II A in Fig. 4. This phenomenon stems from increasing concentration of the recycle stream when larger injection volumes are applied. A smaller amount of solvent can thus be removed before reaching the limit, which restricts the amount of fresh feed processed per cycle. When c^{FF} is sufficiently low compared to the limits, the phenomena discussed above are not observed (Figs. 2 and 3).

As seen by comparing Figs. 2–4, the operating parameters of batch chromatography and SSR without solvent removal are independent of c^{FF} for linear isotherms. Furthermore, the optimal V_{inj} is in most cases the same for each concentration studied. It should, however, be borne in mind that this

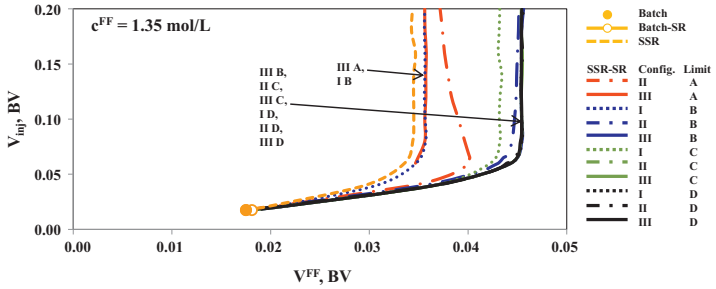

Fig. 4. Bounds of the operating parameters of SSR–SR for the case c^{FF} = 1.35 mol/L. Position of the solvent removal unit: dotted line = fresh feed (configuration I); dash-dot line = recycle fraction (configuration II); solid line = column feed (configuration III). Concentration limits (see Table 1): red = A, blue = B, green = C, black = D. Dashed line = SSR without solvent removal. Filled circle: batch. Open circle: batch with solvent removal. Flow rate $\dot{V}$ = 24 L/h. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

conclusion is only valid for the particular column efficiency used here.

4.1.2. Effects of isotherms, concentration limits, and dispersion

The feasible operating parameters of SSR–SR for Langmuir isotherms under ideal conditions have been investigated by Siitonen et al. [6]. The effect of concentration constraints was not considered in their work. Even if no such limits are set for either solvent removal or column feed, there are limitations for V_{inj} and V^{FF}. These limitations stem, for example, from the fact that V^{SR} cannot exceed the volume of the fraction to which the solvent removal is applied. The results show that under ideal conditions and without concentration limitations configuration III can be operated with the widest range of V_{inj} and V^{FF}.

In the presence of dispersion, the concentration limits set and linear isotherms significantly change the operating parameter boundaries. The main differences between the boundaries presented in [6] and those illustrated in Figs. 2–4 are discussed below.

In batch chromatography, V_{inj} is independent of c^{FF} for linear isotherms and, therefore, the operating line for batch chromatography with solvent removal is a horizontal line in Figs. 2–4. For Langmuir isotherms, the injection volume has to be decreased when the concentration of column feed increases, and the operating line is not horizontal but declining [6]. This would be also the case for anti-Langmuir isotherms which sometimes are observed for monosaccharides.

Under ideal conditions, the operating range of conventional SSR is a straight vertical line, *i.e.* V^{FF} is independent of V_{inj} [6]. In that case, the optimum of SSR is equal to the batch process [11], as recycling is not favourable when no dispersion occurs. In the presence of dispersion, the operating range of SSR becomes curved as seen in Figs. 2–4, and V^{FF} can be increased by increasing V_{inj}.

Similarly to the operating parameter curve of SSR, the upper boundary of V^{FF} for SSR–SR configuration I is curved in the presence of dispersion but straight line under ideal conditions. The lower boundary of configuration I corresponds to batch chromatography with solvent removal, which is different for linear and non-linear isotherms.

The lower boundary of SSR–SR configuration II is a straight line with a slope equal to unity if no limitation for the concentration in the solvent removal unit is set; otherwise the line is curved. For the concentration constraints of type D the shape of the operating area is similar to that presented in [6]. The curved shape of this operating parameter boundary observed in Figs. 2–4 is thus resulted by the concentration limits rather than dispersion or the type of isotherm.

In the ideal case with no concentration limitations, the lower limit for V_{inj} in configuration III is zero. In the presence of dispersion and concentration constraints, the minimum V_{inj} in SSR–SR equals that of batch chromatography and the boundary is strongly curved due to the concentration limit.

It was concluded in [6] that SSR–SR configuration III possesses the widest range of applicable operating parameters and provides the best process performance under ideal conditions and in absence of concentration limits. In the present work, an exception to this common rule was found: when the concentration of the fresh feed exceeds the limit of the solvent removal unit, configuration II outperforms configuration III.

4.2. Process performance

The range of feasible operating parameters discussed in Section 4.1 gives an indication of the performance of the different process configurations. However, the operating parameters give no information on the productivity or eluent consumption of the separation process. Furthermore, the data are shown for a single eluent flow rate only. For better assessment of process performance, the injection volume and eluent flow rate for different SSR–SR configurations were optimized for productivity and eluent consumption. Examples of the optimization results for one fresh feed concentration (c^{FF} = 0.68 mol/L) and one type of concentration constraints (limits C) are shown in Fig. 5.

Fig. 5a illustrates the performance of SSR chromatography without solvent removal. The maximum productivity is obtained using an injection volume of 6% of BV and an eluent flow rate of 30 L/h. If the eluent flow rate is increased above 36 L/h, productivity decreases steeply due to increased dispersion. Eluent consumption decreases with increasing injection volume and decreasing flow rate. Similar results have been reported for separation of sulphuric acid and glucose by SSR chromatography [4].

As seen in Fig. 5b, the productivity of configuration SSR–SR I behaves similarly to that of SSR without solvent removal and has a clear optimum at $\dot{V} = 30$ L/h and V_{inj} = 6% of BV. On the other hand, the maximum productivities of configuration SSR–SR II (Fig. 5c) and SSR–SR III (Fig. 5d) are obtained with the highest applicable flow rate, 60 L/h. The flow rate is limited because the purity constraints cannot be fulfilled with higher flow rates. The configuration giving the highest productivity, 0.038 mol/L_{bed}/h, is SSR–SR III. As seen in all of the subfigures, small injection volumes are not applicable for the highest flow rates.

The differences in the optimum flow rate of SSR–SR I and SSR–SR II (Fig. 5b and c) can be explained by considering the volumes of the recycle fractions. When the flow rate is increased, column efficiency decreases due mass transfer effects. For example, when the flow rate is increased from 30 to 60 L/h, the number of theoretical plates decreases from 1020 to 490. Consequently, a larger recycle fraction has to be collected to reach the desired purities. Furthermore, the recycle fraction is more dilute when the eluent flow rate is higher. If solvent is removed from the recycle fraction or the column feed, more fresh feed can be treated on each cycle and thus the productivity remains high or even increases. If solvent removal is applied to the fresh feed, the productivity is likely to decrease at high flow rates since only a limited amount of solvent can be removed and increased cycle time due to the large recycle fraction cannot be compensated for. Only for concentration constraints of type D, *i.e.* when the concentration of the solvent removal unit is not restricted, are high flow rates preferable also for SSR–SR configuration I.

It thus appears that SSR–SR I is typically not a favourable process configuration. However, the maximum productivity of configuration I in Fig. 5b (0.028 mol/L_{bed}/h) is only slightly lower than that of configuration II in Fig. 5c (0.029 mol/L_{bed}/h). For example, if the eluent flow rate would be limited to 30 L/h due to pressure drop constraints, configuration SSR–SR I would provide a higher productivity than configuration SSR–SR II. Nevertheless, configuration SSR–SR III (Fig. 5d) provides the highest productivity with any flow rate when concentration constraints C are considered.

The contour plots in Fig. 5 correspond to the case of concentration limits C and a fresh feed concentration of 0.68 mol/L only. The optimal operating conditions regarding productivity are summarized in Tables 2–4 for each process mode and configuration investigated. In comparison to batch and SSR, SSR–SR improves productivity in all the studied cases. This improvement is a direct consequence of the possibility to increase the amount of fresh feed treated per cycle.

A large variation in the optimal eluent flow rates can be seen in Tables 2–4. Depending on the process configuration, the eluent flow rate at the productivity maximum may even double when solvent removal is added to SSR, as is also shown in Fig. 5. Less variation is observed among the optimal injection volumes. When c^{FF} is high (Table 2), the optimal injection volume that provides the maximum productivity is practically the same for SSR and for all the SSR–SR configurations. With a more dilute fresh feed (Tables 3 and 4),

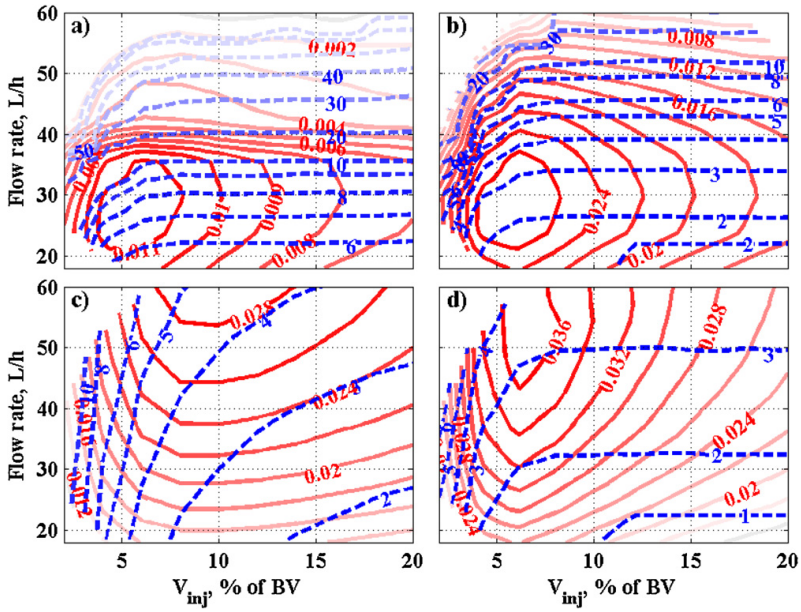

Fig. 5. Process performance of SSR (a), SSR–SR I (b), SSR–SR II (c), and SSR–SR III (d) when concentration limits C (see Table 1) are applied and c^{FF} = 0.68 mol/L. Red solid lines: productivity (mol/L_{bed}/h); blue dashed lines: eluent consumption (L/mol). Removed solvent is re-used as eluent. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

the optimal injection volume is the largest for configuration II, where solvent is removed from the recycle stream. Using SSR–SR configuration I (solvent removal from fresh feed) or configuration III (solvent removal from column feed), the same productivity is achieved independently of the fresh feed concentration. Indeed, the steady-state feed concentration is the same independent of the fresh feed concentration, and the chromatographic separation is, therefore, identical for the fresh feed solutions with different concentrations. The only differences caused by the changes in fresh feed concentration are in the solvent removal process, as a larger amount of solvent has to be removed from a more dilute feed. SSR–SR configuration II (solvent removal from the recycle fraction) differs from the other configurations because the optimal injection width varies as explained above.

Configuration III provides the highest productivity in most cases. SSR–SR configuration II (solvent removal from recycle) is a competitive alternative when the fresh feed concentration is high and the concentration capability of the solvent removal unit is limited.

Table 2
The operation parameters and performance of batch, batch–SR, SSR and SSR–SR processes at productivity maximum. c^{FF} = 1.35 mol/L. Eluent consumption when the removed solvent is not applied as eluent is shown in parentheses.

Process mode	$\dot{V}$, L/h	V_{inj}, % of BV	PR_{tot}, mol/L_{bed}/h	EC_{tot}, L/mol	VRF, –	V^{SR}/V^{FF}, –	c_1^A, mol/L	c_2^B, mol/L
Batch	18	3.1	0.019	3.5	n.a.	n.a.	0.252	0.215
SSR	30	5.5	0.023	4.4	n.a.	n.a.	0.210	0.176
Concentration limits A (column n.a.; SR unit 1.1 mol/L)								
Batch–SR	n.a.	n.a.	n.a	n.a.	n.a.	n.a.	n.a.	n.a.
SSR–SR I	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
SSR–SR II	54	6	0.033	5.1 (5.7)	1.6	0.72	0.187	0.151
SSR–SR III	60	6.3	0.030	6.1 (6.8)	1.3	0.90	0.161	0.131
Concentration limits B (column n.a.; SR unit 1.4 mol/L)								
Batch–SR	18	3.1	0.019	3.4 (3.4)	1.0	0.033	0.264	0.221
SSR–SR I	30	5.8	0.024	4.2 (4.2)	1.0	0.012	0.219	0.184
SSR–SR II	60	6.5	0.037	4.8 (5.5)	1.7	0.91	0.199	0.159
SSR–SR III	60	6	0.038	4.8 (5.5)	1.5	0.93	0.199	0.160
Concentration limits C (column 1.4 mol/L; SR unit 1.7 mol/L)								
Batch–SR	18	3.1	0.019	3.4 (3.4)	1.0	0.033	0.264	0.221
SSR–SR I	30	5.8	0.028	3.5 (3.5)	1.3	0.012	0.264	0.223
SSR–SR II	60	6	0.038	4.8 (5.5)	1.8	0.93	0.199	0.160
SSR–SR III	60	6	0.038	4.8 (5.5)	1.4	0.93	0.198	0.162
Concentration limits D (column 1.4 mol/L; SR unit n.a.)								
Batch–SR	18	3.1	0.019	3.4 (3.4)	1.0	0.033	0.264	0.221
SSR–SR I	60	5.8	0.038	4.8 (5.6)	14	0.93	0.199	0.160
SSR–SR II	60	6	0.038	4.8 (5.5)	1.8	0.93	0.200	0.161
SSR–SR III	60	6	0.038	4.8 (5.5)	1.5	0.93	0.198	0.163

Table 3
The operation parameters and performance of batch, batch–SR, SSR and SSR–SR processes at productivity maximum. c^{FF} = 0.68 mol/L. Eluent consumption when the removed solvent is not applied as eluent is shown in parentheses.

Process mode	$\dot{V}$, L/h	V_{inj}, % of BV	PR_{tot}, mol/L_{bed}/h	EC_{tot}, L/mol	VRF, –	V^{SR}/V^{FF}, –	c_1^A, mol/L	c_2^B, mol/L
Batch	18	3.1	0.010	6.6	n.a.	n.a.	0.132	0.112
SSR	30	5.5	0.012	8.2	n.a.	n.a.	0.109	0.093
Concentration limits A (column n.a.; SR unit 1.1 mol/L)								
Batch–SR	18	3.1	0.015	3.6 (4.3)	1.6	0.39	0.207	0.176
SSR–SR I	30	5.8	0.019	4.6 (5.2)	1.6	0.39	0.175	0.148
SSR–SR II	60	7	0.024	6.7 (8.2)	2.0	0.92	0.134	0.109
SSR–SR III	60	6.3	0.030	5.3 (6.9)	1.7	0.95	0.160	0.131
Concentration limits B (column n.a.; SR unit 1.4 mol/L)								
Batch–SR	18	3.1	0.019	2.6 (3.4)	2.1	0.52	0.261	0.221
SSR–SR I	30	5.5	0.023	4.2 (4.2)	2.1	0.52	0.219	0.184
SSR–SR II	60	7.8	0.027	5.7 (7.2)	2.1	0.92	0.202	0.164
SSR–SR III	60	6.3	0.038	3.9 (5.5)	1.4	0.92	0.200	0.163
Concentration limits C (column 1.4 mol/L; SR unit 1.7 mol/L)								
Batch–SR	18	3.1	0.019	2.6 (3.4)	2.1	0.52	0.261	0.221
SSR–SR I	30	5.8	0.028	2.5 (3.5)	2.5	0.60	0.261	0.221
SSR–SR II	60	10	0.029	4.5 (6.1)	2.0	0.93	0.177	0.145
SSR–SR III	60	6.5	0.038	3.8 (5.4)	1.9	0.96	0.202	0.163
Concentration limits D (column 1.4 mol/L; SR unit n.a.)								
Batch–SR	18	3.1	0.019	2.6 (3.4)	2.1	0.52	0.261	0.221
SSR–SR I	60	6.8	0.038	3.8 (5.4)	17	0.94	0.205	0.162
SSR–SR II	60	6.3	0.038	3.9 (5.5)	13	0.96	0.202	0.164
SSR–SR III	60	6.5	0.038	3.8 (5.4)	1.9	0.96	0.202	0.163

Moreover, when the fresh feed concentration is higher than can be achieved in the solvent removal unit (concentration limits A in Table 2), configuration II is superior to configuration III.

One advantage of solvent removal is increased product concentration, as shown in Tables 2–4. Configurations I and III provide basically the same product concentration for all the fresh feed concentrations. Therefore, the advantage of solvent removal is emphasized with dilute feed solutions. For the lowest fresh feed concentration (c^{FF} = 0.34 mol/L, Table 4), product concentrations substantially higher than the fresh feed concentration were obtained.

It is further observed in Tables 2–4 that batch chromatography with solvent removal is more beneficial than SSR without solvent removal unless the concentration of the fresh feed is so high that only a minor amount of solvent can be removed. Batch chromatography with solvent removal is, therefore, a highly recommended process alternative for the treatment of dilute feed streams.

In Tables 2–4, the process was optimized with respect to the productivity only. The overall process performance consisting of productivity and eluent consumption can be visualized using Pareto frontiers. A Pareto frontier shows the Pareto optimum at which one property can be enhanced only at the expense of the

Table 4
The operation parameters and performance of batch, batch–SR, SSR and SSR–SR processes at productivity maximum. c^{FF} = 0.34 mol/L. Eluent consumption when the removed solvent is not applied as eluent is shown in parentheses.

Process mode	$\dot{V}$, L/h	V_{inj}, % of BV	PR_{tot}, mol/L_{bed}/h	EC_{tot}, L/mol	VRF, –	V^{SR}/V^{FF}, –	c_1^A, mol/L	c_2^B, mol/L
Batch	18	3.1	0.005	12.6	n.a.	n.a.	0.068	0.059
SSR	30	5.5	0.006	15.1	n.a.	n.a.	0.057	0.050
Concentration limits A (column n.a.; SR unit 1.1 mol/L)								
Batch–SR	18	3.1	0.015	2.0 (4.3)	3.3	0.69	0.207	0.176
SSR–SR I	30	6	0.019	2.9 (5.2)	3.3	0.69	0.175	0.149
SSR–SR II	60	10	0.017	7.3 (10.4)	2.3	0.91	0.104	0.086
SSR–SR III	60	6.3	0.030	3.6 (6.8)	2.4	0.97	0.161	0.132
Concentration limits B (column n.a.; SR unit 1.4 mol/L)								
Batch–SR	18	3.1	0.019	0.90 (3.4)	4.1	0.76	0.261	0.221
SSR–SR I	30	5.25	0.023	1.8 (4.3)	4.1	0.76	0.211	0.180
SSR–SR II	60	12	0.019	5.6 (8.8)	2.3	0.95	0.124	0.102
SSR–SR III	60	6.5	0.038	2.2 (5.4)	2.8	0.98	0.202	0.163
Concentration limits C (column 1.4 mol/L; SR unit 1.7 mol/L)								
Batch–SR	18	3.1	0.019	0.90 (3.4)	4.1	0.76	0.261	0.221
SSR–SR I	30	5.5	0.028	0.90 (3.5)	5.0	0.80	0.257	0.218
SSR–SR II	60	14	0.020	4.4 (7.6)	2.3	0.96	0.204	0.167
SSR–SR III	60	6.5	0.038	2.2 (5.4)	2.8	0.98	0.202	0.163
Concentration limits D (column 1.4 mol/L; SR unit n.a.)								
Batch–SR	18	3.1	0.019	0.90 (3.4)	4.1	0.76	0.261	0.221
SSR–SR I	60	6.5	0.038	2.2 (5.4)	46	0.98	0.202	0.163
SSR–SR II	60	12.3	0.032	2.1 (5.3)	97	0.97	0.209	0.169
SSR–SR III	60	6.5	0.038	2.2 (5.4)	2.8	0.98	0.202	0.163

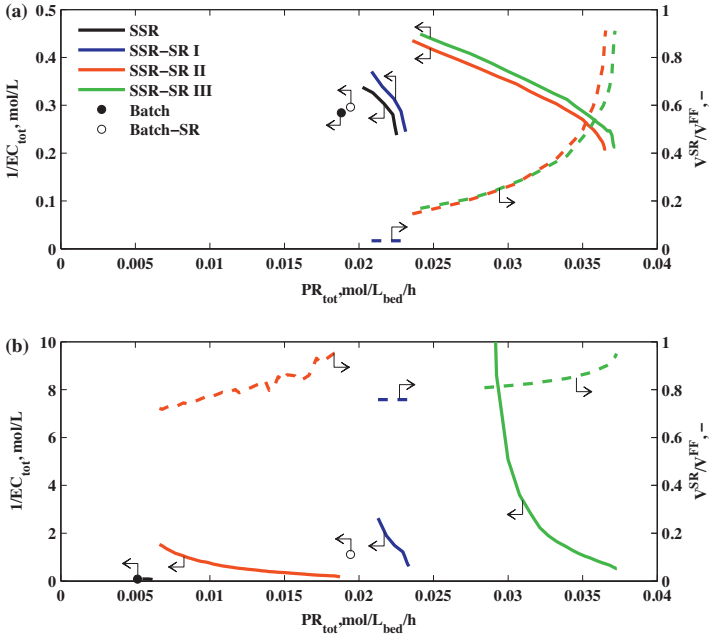

Fig. 6. Pareto frontiers (solid lines) and the relative amount of solvent removed (dashed lines) for different process modes and configurations. Solvent removal unit is the limiting step (concentration limits B). (a) c^{FF} = 1.35 mol/L; (b) c^{FF} = 0.34 mol/L.

other one. In the present case, the Pareto frontiers show the maximum productivity achievable with certain eluent consumption. Since it is favourable to minimize eluent consumption and maximize productivity, the target is in the upper-right corner of the figure. However, only the points at the Pareto frontier are achievable using the process parameters investigated. The maximum productivity, which was presented in Tables 2–4, can be found at the right end of the Pareto frontier.

Examples of Pareto frontier for two different fresh feed concentrations are illustrated in Figs. 6 and 7. The amount of solvent removed is also shown in Figs. 6 and 7. In Fig. 6 the solution is concentrated to 1.4 mol/L in the SR unit (concentration limits B). Fig. 7 illustrates the situation where the column feed concentration of 1.4 mol/L is the only limiting factor (concentration limits D).

It is observed in Fig. 6a that configuration III is slightly more efficient than configuration II when the maximum concentration obtained in the solvent removal unit is 1.4 mol/L. If the concentration limit is decreased to 1.1 mol/L, configuration II is preferable, as can be seen in Table 2. Configuration I is clearly the least favourable of the three SSR–SR configurations.

The Pareto frontier clearly shows that a compromise between productivity and eluent consumption is required in the design of the process. For example, if it is desired to increase the productivity of configuration III from 0.03 mol/L_{bed}/h to 0.035 mol/L_{bed}/h, eluent consumption increases from 2.7 L/mol to 3.5 L/mol, *i.e.* by 29%. Moreover, the amount of solvent that needs to be removed increases rapidly when higher productivity is required. In the example case of Fig. 6a, V^{SR}/V^{FF} increases 76% from 0.27 to 0.47. A moderate ratio V^{SR}/V^{FF} may be favourable for maximum economic efficiency if the costs of solvent removal are high.

When the concentration of fresh feed is low (Fig. 6b), configuration II provides the lowest productivity of the three SSR–SR configurations. Better productivity and lower eluent consumption are provided even by the batch process with solvent removal, for which V^{SR}/V^{FF} equals 0.76. For the dilute feed solution, eluent consumption decreases substantially, since the large amount of solvent removed reduces the amount of fresh eluent required. The reduction in the eluent consumption due to re-use of the removed solvent is emphasized when large injection volumes are applied, which causes the Pareto frontiers of SSR–SR turn concave upward. Since it is even possible to produce more eluent in the solvent removal unit than is consumed in the separation, the Pareto curves may tend towards infinity.

If the removed solvent is not re-used as eluent, the Pareto frontiers of configurations SSR–SR III and SSR–SR I remain unaltered at different feed concentrations. On the other hand, the relative amount of solvent removed (V^{SR}/V^{FF}) changes notably as in Fig. 6. As can be expected, the volume of solvent to be removed is higher when the concentration of fresh feed is lower. On the other hand, the increase in V^{SR}/V^{FF} when pursuing maximum productivity is moderate in Fig. 6b compared to that in Fig. 6a. Configuration I is an exception, as the value of V^{SR}/V^{FF} is constant due to the concentration limitations of type B, in which the fresh feed is always concentrated to 1.4 mol/L. If the concentration limitations are of type D, the V^{SR}/V^{FF} curve of configuration I behaves similarly to the other configurations, as can be seen in Fig. 7.

In Fig. 7a (limits D, c^{FF} = 1.35 mol/L) the Pareto frontiers of different SSR–SR configurations overlap. The same is also observed for the solvent removal curves. The same amount of solvent can be removed in all of the SSR–SR configurations because there are no limits for the concentration achievable in the solvent removal unit. When the concentration is lower (Fig. 7b), the productivity of configuration SSR–SR II is diminished while the productivities of SSR–SR I and SSR–SR III remain the same. Furthermore, the eluent

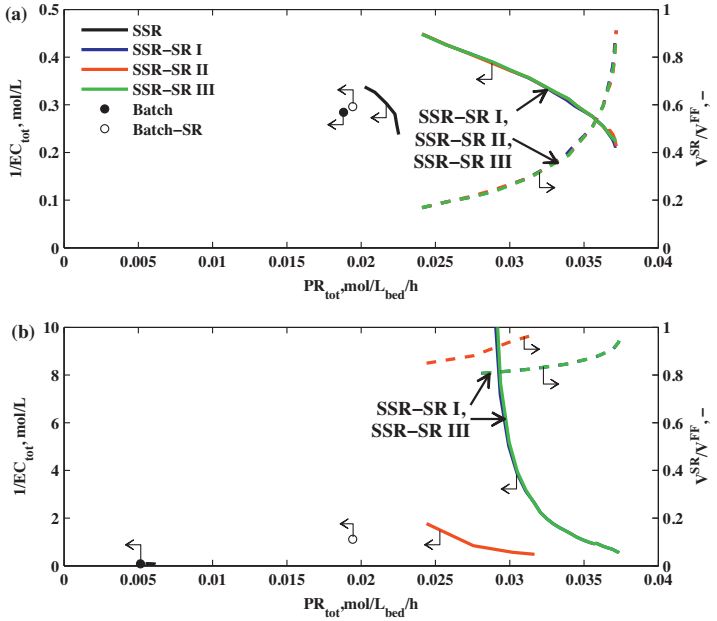

Fig. 7. Pareto frontiers (solid lines) and the relative amount of solvent removed (dashed lines) for different process modes and configurations. Column feed is the limiting step (concentration limits D). (a) c^{FF} = 1.35 mol/L; (b) c^{FF} = 0.34 mol/L.

consumption of both SSR–SR I and SSR–SR III decrease drastically if the removed solvent is re-used as eluent. The reason for the declined productivity of configuration II is the small volume of recycle fraction limiting the amount of solvent that can be removed, as was already observed in Fig. 3.

The Pareto frontiers of SSR–SR configuration III are identical in Figs. 6 and 7. In this configuration, solvent is removed from the feed to the column, and thus the equal concentration limitations of the solvent removal unit concentration and column feed concentration result in the same steady-state column feed concentration and equal Pareto frontiers.

In conclusion, solvent removal from the mixed fraction (SSR–SR III) is in most cases the most favourable configuration with respect to both productivity and eluent consumption. Solvent removal from the recycle fraction (SSR–SR II) is the preferable process mode when c^{FF} is higher than the maximum concentration that can be reached in the solvent removal unit. If the column feed is the limiting factor and there is no limit for the concentration of the solution treated in the solvent removal unit, the result is the same if solvent is removed from fresh feed or from the mixed column feed. In practice, solvent removal from the mixed fraction is favourable also in this case, because the feed to the solvent removal unit is less concentrated and thus the osmotic pressure in membrane separation is lower or the vapour pressure in evaporation is higher, which reduces the energy consumption. Indeed, the energy consumption of solvent removal, even by membrane filtration, can be high when highly concentrated solutions are treated. High pressure has to be applied in membrane filtration in order to overcome the osmotic pressure and to maintain a sufficient flux to ensure that the duration of the solvent removal does not exceed the cycle time. It should also be borne in mind that membrane fouling may decrease the flux during filtration, which means that the pressure needs to be increased to maintain a constant flux. In the light of these facts, it may be attractive to set quite low concentration limits which may also improve the stability of the process.

5. Conclusions

The effect of concentration limits on applicability and performance of different SSR–SR process configurations were investigated by numerical simulation. Recovery and purification of glucose and galactose from lactose hydrolysate was used as a model system. Linear isotherms, which are characteristic of the model system, were used.

From the point of view of maximum productivity, SSR–SR was found to be always preferable over batch or SSR. The results show that a substantial improvement in the process performance of the conventional batch chromatography can also be obtained simply by concentrating the feed in a preceding solvent removal unit. When a solvent removal unit is applied, eluent consumption can be significantly reduced, especially if the removed solvent is re-used as eluent, and the products obtained are more concentrated.

The most advantageous SSR–SR process configuration depends on the feed concentration and on the concentration limits. Usually the best alternative is to remove solvent from the mixture of the fresh feed and recycle stream (configuration III). However, if the maximum concentration that can be reached in the solvent removal unit is lower than that of fresh feed, it is beneficial to remove the solvent from the recycle stream (configuration II).

The effect of possible incomplete retention of solutes in solvent removal by membrane filtration was not taken into account in this study. In practical applications, the solvent recovered is thus not necessarily pure and may decrease the product purity, which needs to be compensated for by applying smaller fresh feed volumes. Decrease in the retention during operation can occur due to concentration polarization or fouling, especially when highly concentrated solutions are treated. Therefore, operating the process

at parameters yielding lower productivities than the theoretical maximum may be favourable to maintain the robustness of the process.

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Size-exclusion chromatographic separation of hydroxy acids and sodium hydroxide in spent pulping liquor

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ABSTRACT

In this work, chromatographic recovery of hydroxy acids and cooking alkali (NaOH) from spent pulping liquor using size-exclusion chromatography (SEC) is investigated. Ultrafiltered black liquors from soda cooking of hardwood and softwood were used as feed and Sephadex G-10 as the stationary phase. Hydroxy acids were successfully separated from sodium hydroxide and the lignin content of the product fraction was reduced significantly. Fouling did not reduce the separation capability of the separation medium in extended runs with more than 40 consecutive injections. High column loadings, up to 25% of the bed volume, were found applicable for separation of authentic solutions without compromising the resolution. This was attributed to size-exclusion of individual ions which leads to co-operative sorption of NaOH in the presence of the sodium salts of hydroxy acids. The proposed mechanism was verified using data from experiments with model solutions.

1. Introduction

Black liquor is the spent cooking liquor of pulping. It contains the inorganic cooking chemicals used in pulping but also alkaline degradation products of lignin and wood carbohydrates. These degradation products include salts of hydroxy carboxylic acids [1–3], which could be widely utilised in the synthesis of various chemicals and polymeric materials [4–6]. However, separation of these hydroxy acids from the inorganics and lignin of black liquor is challenging. Various separation methods for recovering hydroxy acids and other valuable compounds from black liquor have been proposed, including precipitation [7,8], ultrafiltration [9–11], electrodialysis [12], distillation [13], cooling crystallization [9], and chromatography [14]. In this paper, the focus is on chromatographic separation.

Alén et al. utilised ion-exclusion chromatography for separating hydroxy acids from the inorganic compounds of black liquor [14]. This separation technique requires that black liquor is first neutralized [14]. If the feed contains NaOH, several problems are encountered. For example, use of a strong-acid cation exchange resin in Ca^{2+} form under alkaline conditions may lead to precipitation of calcium hydroxide inside the resin which is consequently converted to Na^{+} form. The same precipitation reaction may also occur for resins in other salt forms, as the solubility product of many metal hydroxides is low. As a consequence of hydroxide precipitation, pH of the liquid phase decreases leading to precipitation of lignin, which may cause blockage of the column.

In a recent paper, sodium salts of hydroxy acids were successfully separated from sodium hydroxide (NaOH) of soda black liquor using size-exclusion chromatography (SEC) as a part of a multistep separation process for recovering hydroxy acids from black liquor [15]. A well-established size-exclusion gel, Sephadex G-10 with an exclusion limit of 700 g/mol, was used as the separation medium. The acids were recovered as their sodium salts under alkaline conditions, which enables a straightforward recovery of the cooking chemicals and thus facilitates integration of the process to a pulp mill. However, the separation process based on SEC was not optimised. The target of the present work is to achieve better understanding on the separation mechanisms and on the long-term performance of the separation medium to facilitate the optimisation the process.

The main application area of SEC is protein purification [20]. The separation task in the recovery of hydroxy acids is similar to desalting of proteins, but the difference in molecular sizes of the components to be separated is smaller.

Davankov and coworkers [21–23] have shown that SEC is also applicable for separation of electrolytes with a minor difference in size. They found out that the separation selectivity is determined not only by the size but also by the concentration of ionic species, and observed self-concentration of the separated electrolytes. It is possible that similar phenomena are also present in the case of separating NaOH and sodium salts of hydroxy acids. A better understanding of the separation mechanism is needed for selection of optimal separation material and process parameters. Therefore, the separation mechanism in the separation of sodium salts of hydroxy acids from NaOH on a size-exclusion gel is investigated

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in the present work. In addition, the influence of column loading on process performance is discussed.

In addition to the recovery of hydroxy acids, also other biorefinery applications for SEC have been recently proposed, including fractionation of lignosulphonates [16], and recovery oligosaccharides from biomass hydrolysates [17,18] and from steam-treated wood [19]. However, the feasibility of size-exclusion gels in long-term use at the relatively harsh conditions of biorefinery is not well-established.

Black liquor contains various wood-derived compounds which may cause fouling of the separation medium and thus decrease the separation performance in a long-term use [24]. For example, flux decline due to fouling has been found a major challenge in the design of membrane filtration processes for black liquor [25]. The major foulant in black liquor is decomposed lignin [24]. Considering chromatographic separation, anion exchange resins, which were applied for chromatographic fractionation of hydroxy carboxylic acids already in the 1960s [26], are easily fouled by organic matter [27], which makes their utilisation in processing of raw black liquor challenging. Fouling tendency of size-exclusion gels and its effect on the separation performance is not well known. Palm and Zacchi [19] observed adsorption of lignin on a dextran-polymer-based size-exclusion gel during the recovery of oligosaccharides from a wood extract. Similar behaviour was also found in the processing of black liquor [15]. The effect of this fouling on the separation selectivity is therefore investigated here.

In addition to fouling, the chemical stability of the separation medium is also an important issue when considering its long-term performance in processing of black liquor. NaOH may cause decomposition of the dextran polymer matrix of Sephadex [28]. Therefore, the stability of Sephadex G-10 under alkaline conditions is also studied in this paper.

2. Materials and methods

2.1. Feed black liquor

Softwood (SW) and hardwood (HW) soda black liquors were prepared at VTT (Technical Research Centre of Finland, Espoo, Finland) in laboratory-scale cooking of pine and birch chips at temperature of 170 °C or 165 °C, respectively. The liquor to wood ratio (W/D) was 4:1 and the amount of effective alkali was 5.5 mol/kg. The cooking was continued until H-factor of 1936 for SW or 1324 for HW was reached. The total dry solids content of the SW black liquor was 14.3 wt% and that of HW black liquor 14.0 wt%.

The black liquors were pre-treated by ultrafiltration using DSS LabStak M20 filter unit (Alfa Laval, Nakskov, Denmark) and GR95PP membrane (Alfa Laval, Nakskov, Denmark) with molecular weight cut-off of 2000 Da at temperature of 60 °C and pressure of 10 bar. The dry solids (d.s.) content of the permeate was approximately 10 wt%. To study the effect of feed concentration on the chromatographic separation, part of the solution was concentrated to 25 wt% using a rotary evaporator.

The compositions of the feed solutions to chromatographic separation are presented in Table 1. The amount of NaOH in the feed solutions was determined by measuring the residual effective alkali by titration [29], as in soda black liquor NaOH is the only component responsible for effective alkali. The samples were diluted to ¼ with purified water (Millipore) and titrated with 1 M HCl (Titrisol®, Merck KGaA, Darmstadt, Germany) using an automated titrator (Mettle DL 25, Mettler-Toledo, Greifensee, Switzerland). Hydroxy acids and other carboxylic acids were analysed at VTT (Espoo, Finland) using capillary electrophoresis as described in [9,30]. The following acids were included in the analysis: oxalic acid, formic acid, acetic acid, glycolic acid, lactic acid, 2-hydroxy butanoic acid (2-HBA), 2,5-dihydroxy pentanoic acid (2,5-DHPA), xyloisosaccharinic acid (XISA), and glucoisosaccharinic acid (GISA). The apparent absence of oxalic acid before the concentration of the black liquor (Table 1) is due to the limited sensitivity of the analysis for very small concentrations.

As the experiments were done at alkaline conditions, the ultrafiltered black liquor was used without further pre-treatment. For comparison, in one experiment the pH of the SW black liquor feed was first reduced to 8.5 by adding 95% sulphuric acid (Merck KGaA, Darmstadt, Germany) and the precipitated lignin was separated by centrifugation (3000 rpm, 10 min).

2.2. Chromatographic separation of hydroxy acids

Sephadex G-10 (GE Healthcare Bio-Sciences, Uppsala, Sweden) was rinsed with purified water prior to use. Experiments were done in a laboratory scale glass column (ECO SR 25/200, Kronlab, Sinsheim, Germany, H_{bed} = 20 cm, D_{bed} = 2.5 cm). The bed porosity was determined to be 0.39 by using Blue Dextran 2000 (Amersham Biosciences, Uppsala, Sweden). The total hold-up volume of the column was measured with a 1 mL injection of deuterium oxide (99.9% atom-% D, Sigma Aldrich, Oakville, ON, Canada) to the column using a flow rate of 0.8 mL/min and a value of 0.81 bed volumes (BV) was obtained.

The column was thermostated at 50 °C with a heating jacket and a water circulation thermostat (Lauda C6C5, Lauda-Königshofen, Germany). Eluent was purified water. Both the eluent and the feed were introduced into the column with a flow rate of 1 mL/min using an HPLC pump (Waters 515, Waters Corporation, Milford, MA, USA), equipped with a degasser (DG-4400, Phenomenex Degassex, Torrance, CA, US). The valves were operated using LabView software (National Instruments, Austin, TX, USA). The column outlet was monitored online using conductivity detector (Conductivity Monitor, Pharmacia Biotech, Uppsala, Sweden), refractivity detector (RI 2000 Schambeck SFD GmbH, Bad Honnef, Germany) and UV-detector (Waters 2487 dual λ Absorbance Detector with 3 mm semiprep flow cell, Waters Corporation, Milford, MA, USA) on wavelengths of 280 and 350 nm. Samples were collected from the column outlet using an automated fraction collector (Frac-100, Pharmacia LKB, Uppsala, Sweden).

HW and SW soda black liquors in concentrations of 10 and 25 wt% d.s. prepared as described in Section 2.1 were used as feed.

Table 1
Composition of black liquors used in the chromatographic fractionation experiments. The concentration of lignin was determined based on UV absorbance at 280 nm, NaOH concentration based on titration, and acid concentrations based on CE analysis.

Black liquor	d.s. (wt%)	Lignin (g/L)	NaOH (g/L)	Oxalic acid (g/L)	Formic acid (g/L)	Acetic acid (g/L)	Glycolic acid (g/L)	Lactic acid (g/L)	2-HBA (g/L)	2,5-DHPA (g/L)	XISA (g/L)	GISA (g/L)
HW	10	18.3	8.00	0.00	3.50	11.50	1.02	1.98	4.08	0.00	3.50	2.97
SW	10	13.9	9.10	0.00	3.85	3.81	1.37	3.45	1.12	0.92	2.72	9.06
HW	25	64.6	9.60	1.41	13.00	39.46	3.26	7.05	16.40	0.00	12.70	10.50
SW	25	42.1	28.4	1.08	10.7	10.77	3.75	9.22	2.89	2.25	7.42	24.56

The feed injection volume was 8% of BV. To optimise the injection volume, the experiments were repeated using HW soda black liquor (d.s. 10 wt%) using larger injection volumes of 12%, 16%, and 24% of BV.

The pH of the fractions was measured off-line. Hydroxy acids and other carboxylic acids were analysed using capillary electrophoresis as described in [9,30]. The amount of alkali lignin was determined by UV at wavelength of 280 nm using absorbance coefficient 19 L g^{-1} cm^{-1} for SW black liquor and 14 L g^{-1} cm^{-1} for HW black liquor. The samples were diluted using 0.1 M NaOH (Titrisol®, Merck KGaA, Darmstadt, Germany) and the spectra were recorded using a UV–Vis spectrophotometer (Agilent 8453, Agilent Technologies, Palo Alto, CA, USA).

2.3. Stability of the separation medium in long-term use

The recommended pH range for Sephadex G-10 by the manufacturer is 2–13 [31]. Therefore, a long term application at highly alkaline conditions at elevated temperature may possibly cause degradation of the polymer.

Thus, the durability of the size-exclusion gel was tested by keeping 2.5 g of the resin for 2–4 weeks at 60 °C in 50 mL of 0.5, 1 and 2 M NaOH solutions and in pure water for comparison. Subsequently, the resin was separated by centrifugation and the liquid phase was analysed for the possible degradation products using a spectrophotometric method applying anthrone reagent and on HPLC (HP 1100, Agilent/HP, Waldbronn, Germany) equipped with UV and RI detectors using a Varian Metacarb 87H (Varian, Palo Alto, CA, USA) column. In the HPLC analysis, 0.005 M sulphuric acid (Titrisol®, Merck KGaA, Darmstadt, Germany) was used as eluent with a flow rate of 0.6 mL/min. The analysis was conducted at 65 °C with injection volumes of 10 μL, and UV absorbance at 210 nm was measured.

In addition, the moisture holding capacity of the resin was measured gravimetrically. If the resin is decomposed, it is likely to swell more easily and to retain more water in its gel structure. The polymer sample exposed to alkaline conditions was immersed in excess of purified water for 3 h and centrifuged (2000 rpm, 10 min). The particles were then kept at 60 °C overnight, cooled in a desiccator, and weighted.

Fouling of the polymer by residual lignin or other minor components of black liquor may impair the separation process. The possible effect of resin fouling for separation performance in long term use was investigated by performing several consecutive separation cycles in a smaller column (H_{bed} = 11.5 cm, D_{bed} = 1.5 cm). A series of 44 injections of 1.63 mL (8% of BV) HW soda black liquor were introduced into the column with a time interval of 90 min. Eluent flow rate was 0.36 mL/min, which equals to 1 BV/h. The superficial flow velocity, 38.4 cm/h, was equal to that used in the larger column. The possible changes in separation performance were assessed based on the online conductivity and RI-signals and by analysing samples from selected fractions on UV–Vis spectrophotometer.

2.4. Separation mechanism

For studying the separation mechanism, sodium tartrate (Na_2Tar) and NaOH were used as model compounds. Sodium tartrate is a disodium salt of tartaric acid, which is a diprotic dihydroxy acid with a molecular weight of 150.1 g mol^{-1}.

Sodium L-tartrate dibasic di-hydrate (BioUltra, ⩾99.0%, Sigma–Aldrich, Steinheim, Germany) and NaOH (GPR Rectapur 99%, VWR International BVBA, Leuven, Belgium) were used without further purification for preparing 0.1 M solutions of pure components and mixtures containing 0.1 M NaOH and either 0.1 M or 0.025 M sodium tartrate.

The experiments with model solutions were performed similarly as the ones with soda black liquor in a glass column packed with Sephadex G-10 (D = 2.5 cm; H_{bed} = 19.8 cm). Injection volumes were 1 mL, 5 mL and 15 mL for pure compounds and injections of 15 mL, 25 mL and 50 mL for the mixtures. Eluent was purified water. To investigate the effect of pH on the elution of sodium tartrate, the experiments with pure sodium tartrate were repeated using 1 mM HCl (Titrisol®, Merck KGaA, Darmstadt, Germany, pH = 3.05) and 0.1 M acetate buffer (pH = 4.76), which was prepared of glacial acetic acid (Merck KGaA, Darmstadt, Germany) and sodium acetate (Riedel-de-Haën GmbH, Seelze, Germany), as eluents.

The column outlet was monitored online using a conductivity detector an RI detector and a UV detector at 195 and 230 nm, and fractions of 2 mL were collected. The pH of the fractions was measured off-line. Sodium tartrate concentration in the fraction samples were analysed on HPLC as described on Section 2.3. NaOH was determined by titration with 0.05 M HCl (Titrisol®, Merck KGaA, Darmstadt, Germany). The samples of 1.5 mL were diluted with 20 mL of purified water prior to titration.

3. Results and discussion

3.1. Recovery of hydroxy acids using SEC

A typical chromatogram of black liquor fractionation using Sephadex G-10 is shown in Fig. 1. A large peak in the conductivity signal at 0.8 BV was verified to be NaOH based on pH and separate Na analyses (data not shown). The smaller conductivity peak represents hydroxy acids, as seen in Figs. 2 and 3, which illustrate the concentrations of acids and NaOH in the column outlet. As can be seen in the figures, hydroxy acids were completely separated from NaOH when injection volume of 8% of BV was applied.

The UV-signals in Fig. 1 are mostly related to the concentration of lignin-derived compounds in the column effluent. The largest lignin fragments are not able to enter the matrix of Sephadex G-10 and elute in the void volume (0.4 BV). This can be observed as a rise in UV-signal at 350 nm in Fig. 1. A large amount of lignin degradation products seems to elute between hydroxy acid and NaOH while smaller amounts occur in hydroxy acid and NaOH fractions.

The profiles of individual acids are shown in Fig. 4. As expected, the separation of individual hydroxy acids was incomplete although some fractionation of the acids based on their molecular sizes does occur. If individual acids are required in high purity, the acid recovered using SEC can be treated chromatographically or using nanofiltration, for example. Considering chromatographic fractionation of carboxylic acid mixtures, ion-exchange chromatography is a well-established technique for that purpose [32] and has been successfully applied for determination of the

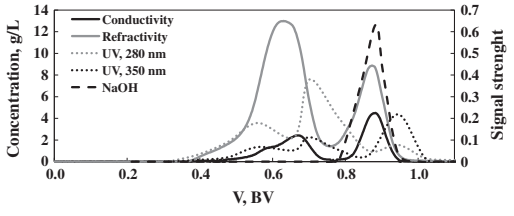

Fig. 1. Chromatograms obtained using the online detectors during fractionation of SW soda black liquor (d.s. 10%) using Sephadex G-10. Concentration of NaOH is estimated base on pH measured off-line. H_{bed} = 20 cm, D_{bed} = 2.5 cm, V_{inj} = 0.08 BV, $\dot{V}$ = 0.61 BV/h.

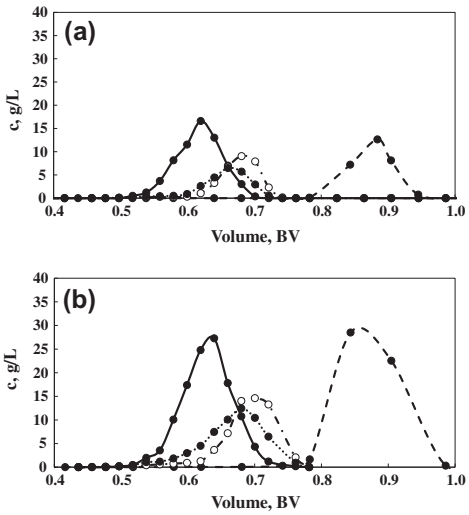

Fig. 2. Outlet profiles in SW soda black liquor fractionation using Sephadex G-10: isosaccharinic acids (solid line); volatile acids (dash-dot line); other acids (dotted line); NaOH (dashed line). (a) Feed concentration 10 wt% d.s. (b) Feed concentration 25 wt% d.s. H_{bed} = 20 cm, D_{bed} = 2.5 cm, V_{inj} = 0.08 BV, $\dot{V}$ = 0.61 BV/h, T = 50 °C. Acid concentrations are determined using CE and NaOH concentrations are estimated based on pH.

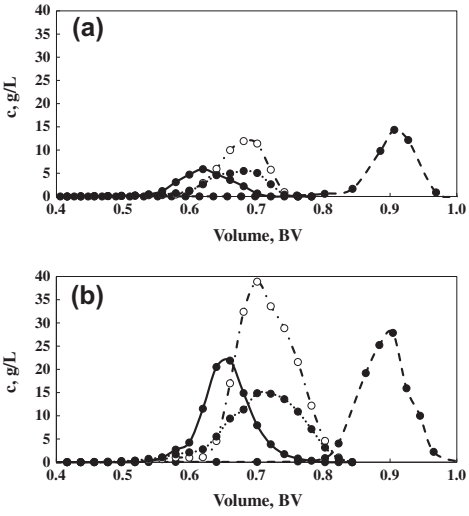

Fig. 3. Outlet profiles in HW soda black liquor fractionation using Sephadex G-10: isosaccharinic acids (solid line); volatile acids (dash-dot line); other acids (dotted line); NaOH (dashed line). (a) Feed concentration 10 wt% d.s. (b) Feed concentration 25 wt% d.s. H_{bed} = 20 cm, D_{bed} = 2.5 cm, V_{inj} = 0.08 BV, $\dot{V}$ = 0.61 BV/h, T = 50 °C. Acid concentrations are determined using CE and NaOH concentrations are estimated based on pH.

carboxylic acids of black liquor [33]. Distillation has also been found feasible in purification of hydroxy acids of black liquor [13].

3.1.1. Effect of feed composition

SW and HW soda black liquors with two different concentrations were tested. In addition, the effect of lignin removal by precipitation using sulphuric acid was studied.

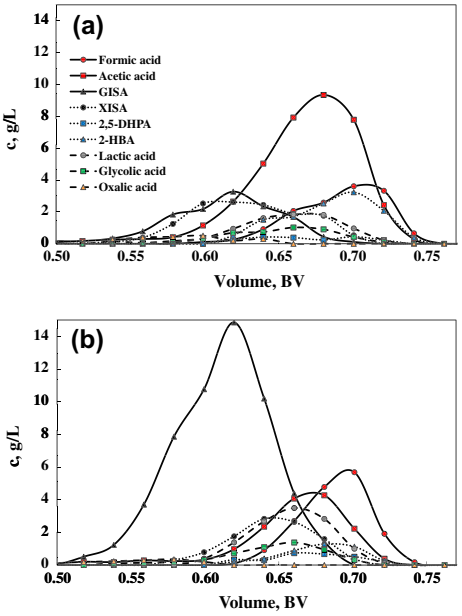

Fig. 4. Concentrations of individual acids in the chromatograms displayed in Figs. 2a and 3a. (a) SW soda black liquor and (b) HW soda black liquor. NaOH is not shown but elutes after the acids (see Figs. 2 and 3). Sephadex G-10 column, feed concentration 10 wt% d.s, H_{bed} = 20 cm, D_{bed} = 2.5 cm, V_{inj} = 0.08 BV, $\dot{V}$ = 0.61 BV/h, T = 50 °C.

The chromatograms of individual acids obtained in fractionation of SW soda black liquor are shown in Fig. 4a. If the target would be to collect a mixture of isosaccharinic acids (GISA and XISA), they can be cut from the beginning of the hydroxy acid fraction. The purity of the isosaccharinic acid with respect to volatile acids and other hydroxy acids in the feed is approximately 53% in the feed (10% d.s.). If the isosaccharinic acid fraction is cut between and 0.5 and 0.68 BV, a purity of 80% is obtained, and the yield of isosaccharinic acids is approximately 70%. For the concentrated feed (25% d.s.), the purity of isosaccharinic acids is slightly lower.

As seen in Fig. 2b, increasing the concentration of the feed solution up to 25 wt% does not significantly deteriorate the separation. The profiles of individual acids were similar to the ones presented for the feed with 10% d.s. in Fig. 4a (data not shown). Carboxylic acids and NaOH are slightly overlapped but the separation remains excellent considering that the productivity has increased by a factor of 2.5 due to using more concentrated feed solution. This is a significant benefit of the size-exclusion method compared to adsorption based chromatographic methods. In the latter, the retention volumes are strongly concentration dependent, and increasing the feed concentration usually leads to lower separation between the product fractions.

The separation of hydroxy acids from HW black liquor was found to be similar to that from SW black liquor despite the differences in the composition and the hydroxy acid content. Typical chromatograms for different feed concentrations are presented in Fig. 3, and the concentrations of individual acids are shown in Fig. 4b. As the feed contains a smaller proportion of isosaccharinic acids (20–25%), a purity of 50% can be obtained with the yield of 70%. Acetic acid, which is the main component in HW soda black liquor, has a broad profile. When the feed is concentrated, the

overlapping of hydroxy acids and NaOH is slightly more severe for HW black liquor (Fig. 3b) than for SW black liquor (Fig. 2b).

Interestingly, for HW soda black liquor, a pink coloured band was observed moving very slowly in the column. The colour was not observed in the case of concentrated HW soda black liquor, which indicated that the compound responsible for the colour was decomposed at the elevated temperature during the concentration by evaporation. The coloured compound was identified as 2,6-dimethoxy hydroquinone, a degradation product of syringyl lignin, in a GC/MS analysis (data not shown). Hydroquinones are undesired impurities in hydroxy acid fractions recovered from black liquor since they may act as inhibitors in polymerisation [34]. If several injections are performed sequentially, the purity of the hydroxy acid fraction may decrease as the hydroquinone passes to the effluent. Therefore, quinone compounds must be removed by washing the resin regularly. Ethanol was found a suitable solvent for washing.

The amount of residual lignin fragments in the feed can be reduced by precipitation using sulphuric acid. However, the reduction of pH by an addition of sulphuric acid impaired the separation of hydroxy acids, because sulphates eluted significantly faster (elution volume of Na_2SO_4 0.52 BV) than hydroxides (elution volume of NaOH 0.80 BV) through the bed of Sephadex G-10. Consequently, sulphate would remain as an impurity in the hydroxy acid fraction.

3.1.2. Effect of injection volume

The injection volume is an important factor for the performance of chromatographic batch separation. In the experiments discussed in previous section, a constant injection volume of 0.08 BV was used. If a larger injection volume can be applied, higher production rate and product concentration may be obtained. Therefore, fractionation of HW soda black liquor was tested using different injection volumes. The outlet profiles obtained are shown in Fig. 5. The estimated purity of a product fraction that provides 100% yield for acids for each injection volume is presented in Table 2.

The optimisation study showed that the injection volume can be increased to 12% of BV and more without largely compromising

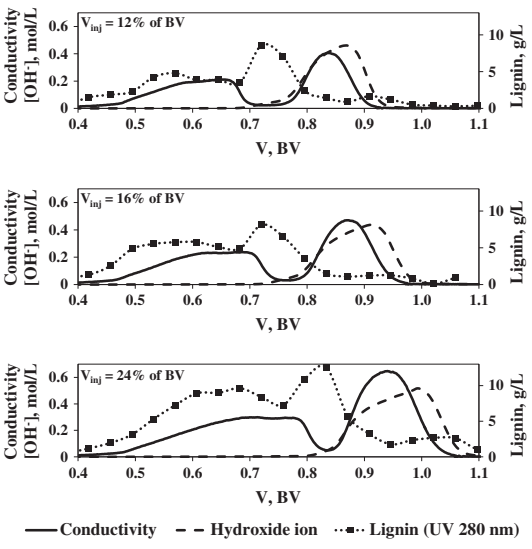

Fig. 5. Chromatograms obtained using different injection volumes of HW soda black liquor (10% d.s.). H_{bed} = 20 cm, D_{bed} = 2.5 cm, $\dot{V}$ = 0.61 BV/h, T = 50 °C.

Table 2
Composition of the feed and acid fractions collected from HW soda black liquor using SEC with different injection volumes. The fraction cut times are chosen so that 100% yield for acids is obtained. Concentrations of lignin and NaOH are determined based on UV absorbance at 280 nm and pH, both measured from samples collected from the column outlet.

V_{inj}, % of BV	OH-acids (g/L)	Other acids (g/L)	Lignin (g/L)	NaOH (g/L)	OH-acids (w-%)
FEED	13.55	15.00	18.30	8.00	0.25
8	3.90	4.32	2.95	0.07	0.35
12	5.43	6.01	4.23	0.10	0.34
16	6.76	7.48	5.80	0.07	0.34
24	8.22	9.10	7.94	0.02	0.33

the yield or product purity (see Table 2). In particular, the first-eluting hydroxy acids of large molecular sizes, GISA and XISA, can be still recovered in high purity while a small amount of NaOH occurs among the smaller hydroxy acids. As seen in Fig. 5, the concentration of lignin is the highest at the rear of the hydroxy acid profile, which further decreases the purity of acids with small molecular size. When the injection volume was raised, the concentration of lignin in the whole hydroxy acid fraction obviously increased. However, the purity of acids with respect to lignin is not substantially changed since the concentration of acids is also increased as seen in Table 2.

With the large injection volumes of 16% and 24% of BV, the tailing front of NaOH peak clearly overlaps with the end part of the hydroxy acid profile. However, the separation of hydroxy acids and NaOH does not deteriorate much as the retention time of NaOH becomes prolonged with the larger injection volumes. The cycle time increases from 0.95 BV to 1.15 when the injection volume is tripled. This unusual phenomenon was investigated in more detail and is discussed in Section 3.3. As the use of large injection volumes is possible, the dilution of the recovered hydroxy acid can be minimised. The dilution factor reduces approximately by 53% (from 3.5 to 1.6) when the injection volume is increased from 8% to 24%.

The total purity of hydroxy acids was increased by 30–40% during the SEC treatment. As seen in Table 2, the main impurity left in the hydroxy acid fraction is volatile acids, which are present in large amounts in HW black liquor. They can be readily separated by distillation [13]. Residual lignin and sodium can be removed using adsorption and ion-exchange as described in [15].

3.2. Stability of the separation medium

The fouling tendency and chemical resistance of the size-exclusion gel in long term use was studied by performing a series of consecutive injections and by exposing the material to NaOH solutions of different concentration at an elevated temperature.

Example profiles of selected injections during the series of 44 injections of HW black liquor to the column are shown in Fig. 6. No changes in the separation were observed in the conductivity and RI-signals, which indicates that fouling of the stationary phase particles does not affect the separation of hydroxy acids and NaOH. The small differences in the peak heights may be related to minor variations of the feed flow rate.

On the other hand, the purity of hydroxy acid fraction decreased to some extent during the consecutive injections due to accumulation of lignin. Based on UV absorption at 280 nm, the amount of lignin in the hydroxy acid fraction was doubled during the 44 cycles. Therefore, a regular washing of the stationary phase is required to maintain the product purity at a reasonable level. The same observation was made by Palm and Zacchi [19] who applied a similar size-exclusion gel for processing the liquid fraction from steam treatment of spruce wood.

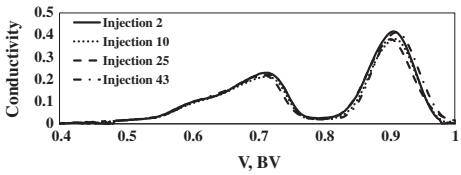

Fig. 6. Conductivity profiles of 4 randomly chosen injections recorded during 44 consecutive pulse injections (V_{inj} 8% of BV) of HW soda black liquor. H_{bed} = 11.5 cm, D_{bed} = 1.5 cm, $\dot{V}$ = 1 BV/h, T = 50 °C.

No significant changes in the moisture retention capacity of the gel were observed during a 4-week-period of exposing the particles to NaOH at an elevated temperature. Nevertheless, emerging of two compounds (retention times 9.8 min and 12.6 min) were observed in the HPLC analysis of liquid phase samples after aging of Sephadex G-10 in 1 M NaOH, and the concentration of these unknown degradation products increased with time (data not shown). However, the quantification of these compounds was not possible with the detectors available. Furthermore, no reliable results were obtained using anthrone method because gelling occurred during the sample pre-treatment. The gelling also made GC/MS analysis impossible, and therefore the degradation components remained unidentified. Therefore, further study is required to assess the alkali resistance of Sephadex G-10.

3.3. Separation mechanism

In fractionation of soda black liquor it was observed that the retention time of NaOH increased with increasing injection volumes (see Fig. 5). This uncommon behaviour is highly advantageous for the separation because it makes the use of large injection volumes possible without compromising the resolution of the compounds. To understand the mechanism leading to increased retention of NaOH, the separation of sodium tartrate and NaOH on Sephadex G-10 was studied.

3.3.1. Effect of injection volume on elution of pure sodium tartrate and pure NaOH

The profiles of 0.1 M sodium tartrate injections of different volumes are shown in Fig. 7. As seen in the figure, sodium tartrate peak is asymmetric with a diffuse front starting at the column void

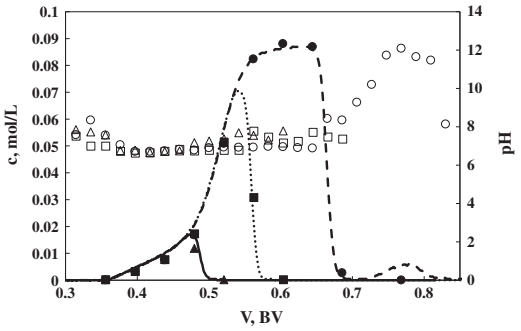

Fig. 7. Effect of injection volume on the elution profile of 0.1 M sodium tartrate in Sephadex G-10. Concentration of sodium tartrate is presented as closed symbols and pH-data as open symbols: V_{inj} = 1 mL (triangles); V_{inj} = 5 mL (squares); V_{inj} = 15 mL (circles). Lines show the scaled online conductivity signal for different injection volumes: V_{inj} = 1 mL (solid line); V_{inj} = 5 mL (dotted line); V_{inj} = 15 mL (dashed line). V_{bed} = 97 mL. Eluent was purified water.

volume (0.38 BV) and a sharp rear. A similar skewed shape can be observed for many of the hydroxy acids in Fig. 4. Such a shape corresponds to an anti-Langmuirian phase equilibrium isotherm caused by electrolyte exclusion due to a small charge of the carboxylic groups on Sephadex medium. This phenomenon was first reported by Neddermeyer and Rogers [35] who measured the ion-exchange capacity of Sephadex G-10 to be 4 μeq/g (dry gel). In their study, strongest peak skewing was observed when low flow rates were applied [36].

The occurrence of ion-exclusion often deteriorates separation in gel filtration but it can be prevented by using an eluent that contains an electrolyte. When the eluent was 1 mM hydrochloric acid (pH 3), a symmetric tartrate peak with an elution volume of 0.56 BV was obtained, and when 0.1 M sodium acetate buffer (pH = 4.76) was used as eluent, a slightly skewed peak with a breakthrough volume of 0.43 BV was observed (data not shown). Similarly, the increased ionic strength resulted in a slightly more symmetrical shape of the hydroxy acid peaks when the feed was concentrated (data not shown). An alternative, albeit less likely, explanation for the fronting of the peak could be dimer formation, which has been found to cause fronting in size-exclusion chromatography of insulin [37].

Interestingly, a second peak in the conductivity signal was observed when the injection volume was 15 mL. The pH data in Fig. 6 reveals that the second eluting compound is alkaline. It is also seen that the pH of the sodium tartrate in the column outlet is approximately 6.8, which is lower than the pH of the feed (8.8). Davankov and Tsyurupa [38] have presented that a salt may resolve into its parent acid and base during size-exclusion chromatography using hyper-crosslinked polymer resins. Their theory is related to cations and anions of the sample and the eluent changing their ion pairs, which was first observed by Okada [36,39]. This ion-exchange reaction has been found to be stronger for Sephadex G-15 than for Sephadex G-25 which has the larger pore size of the two gels [39]. Therefore, it can be expected to be strong also when using Sephadex G-10 that has the densest structure of the Sephadex gels. When water is used as eluent, the only available ions are the protons and hydroxide ions generated through dissociation of water [38]. The partial conversion of sodium tartrate to monosodium tartrate or tartaric acid explains the low pH seen in Fig. 6. pH stayed at a constant level during the elution of sodium tartrate as the acid forms a buffer solution with its salt form. The corresponding base, NaOH, eluted later due to its smaller molecular size, resulting in a rise in pH.

Resolution of sodium tartrate into tartaric acid and NaOH might theoretically increase the yield of NaOH above 100% in its separation from black liquor. Furthermore, the liberation of acids (which is a necessary step if hydroxy acids are used for polymerisation) would be facilitated as part of the sodium could be already substituted by protons during the SEC. However, in the case of small injection volumes NaOH was not observed in the column outlet. In small concentrations it may possibly react with Sephadex G-10 and remain trapped inside the polymer matrix. Another explanation may be that electrolyte exclusion prevents separation of NaOH with the injection volumes smaller than 15 mL and, therefore, no additional peak is observed in the conductivity signal.

When pure 0.1 M NaOH was injected in the column, it eluted later than sodium tartrate, as can be expected because of its smaller molecular size. In the case of a small injection volume, a very broad and highly diluted NaOH band was obtained. With a larger injection volume, the similar anti-Langmuirian profile was obtained as for sodium tartrate, but the elution time was longer (approximately 0.8 BV). The conductivity profile from a 15 mL injection is shown in Fig. 8a.

For the large injections of sodium hydroxide, a rise in the UV absorbance at 195 nm occurred before the peak in the conductivity

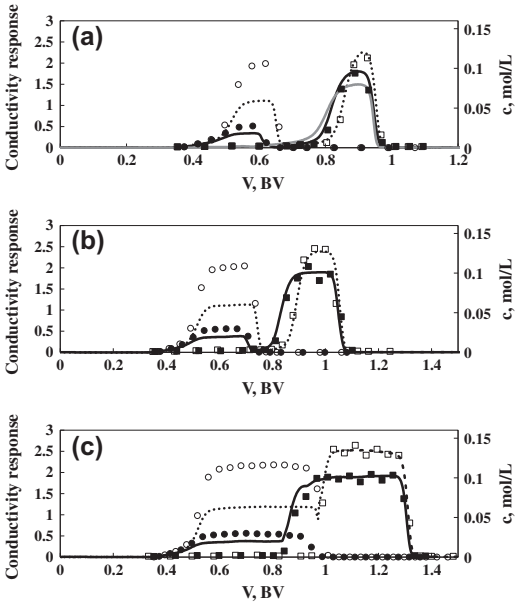

Fig. 8. Effect of injection size and sodium tartrate concentration on the separation of sodium tartrate and NaOH using Sephadex G-10. c_{feed}(Na-tartrate) = 0.1 M (dotted line); c_{feed}(Na-tartrate) = 0.025 M (solid line). c_{feed}(NaOH) = 0.1 M. The grey line in (a) is the signal from a corresponding experiment with pure 0.1 M NaOH. (a) V_{inj} = 15 mL; (b) V_{inj} = 25 mL; (c) V_{inj} = 50 mL. V_{bed} = 97 mL. Eluent was purified water.

signal. In addition, a yellow coloured band was observed moving in the column. As already discussed, it is possible that NaOH causes decomposition of the dextran polymer and the larger degradation products elute before NaOH. Alkaline degradation of dextran polymer changes the swelling behaviour [28] and may thus affect the separation performance of Sephadex gel. This was not observed during the 44 consecutive runs with black liquor, however.

3.3.2. Separation of sodium tartrate and NaOH

The chromatograms of separation of mixtures with different concentration of sodium tartrate with NaOH using different injection volumes are presented in Fig. 8. The figure clearly shows that the elution profile of NaOH is affected by the concentration of sodium tartrate in the solution. While the peak of the pure NaOH is broad and strongly skewed, it becomes sharp and almost symmetric in the presence of sodium tartrate. The change is observed in the beginning of the peak, while the rear of the peak remains the same. The change in the peak shape may be due to the higher ionic strength which prevents the ion-exclusion phenomenon discussed before.

As seen in Fig. 8c, almost complete separation was achieved even with the injection volume larger than 50% of BV when the concentration of sodium tartrate was 0.1 M. In the case of a lower tartrate concentration, sodium tartrate and NaOH overlapped. Based on these results, very high injection volumes are applicable and the separation selectivity is improved by high concentration of sodium tartrate.

It is further observed in Fig. 8 that the retention time of NaOH is dependent on the injection volume. When the injection volume was increased, NaOH eluted later whereas sodium tartrate always eluted in the void volume. The effect is more pronounced when the concentration of sodium tartrate is higher. In the case of a 50 mL injection of a mixture containing 0.1 M sodium tartrate, the retention time of NaOH becomes longer than the time corresponding to the hold-up volume of the column (0.81 BV measured using deuterium oxide). As in the experiments with pure NaOH, an unknown component appeared before NaOH.

The effects of concentration in size-exclusion chromatography of electrolytes have been studied by Davankov and coworkers [21]. They observed a similar improvement in the selectivity of separation with increasing concentration of salts. The phenomenon can be explained by considering simultaneous distribution equilibria of individual ions. To reach equilibrium, sodium ions are distributed between the mobile phase and the stagnant liquid inside the gel. To maintain electrostatic equilibrium, the small hydroxide anions enter the porous structure of the size-exclusion material where the large tartrate anion cannot access because of steric effects. Therefore, NaOH is accumulated inside the pores by size-exclusion.

As seen in Fig. 7, the plateau concentration of NaOH was approximately 30% higher than in the feed when the feed concentration of sodium tartrate was 0.1 M. The maximum pH in the outlet during elution of NaOH fraction (13.55) exceeded, therefore, the pH of the feed (13.46). In the case of the lower concentration of sodium tartrate, the plateau concentration of NaOH was almost equal to its feed concentration. The increase in the concentration of NaOH in the presence of sodium tartrate can be explained by the self-concentration effect, described by Davankov et al. [40] for size-exclusion chromatography of electrolytes using neutral separation media. The self-concentration occurs when the smaller ions accumulate in the small pores of the separation medium as discussed above. In the case of equal concentrations of sodium hydroxide and sodium tartrate in the solution, the bulk solution contains an excess amount of sodium ions, because the divalent tartrate anions cannot fit into the porous volume but the electrostatic equilibrium must be maintained. Therefore, hydroxide ions cannot exit the porous space of Sephadex when sodium tartrate is present in the bulk solution phase. The self-concentration effect is more pronounced for high feed concentrations. Regarding the fractionation of black liquor using SEC, the self-concentration effect is obviously highly beneficial. In addition to the hydroxy acids, the NaOH of black liquor is also a desired product since NaOH is reused in the pulping process. As a concentrated NaOH solution is obtained from SEC process, the efforts required for evaporation are reduced.

The self-concentration effect is significant only for the compound containing the smaller anion, and therefore the concentration of tartrate is not significantly increased during the separation. Furthermore, peak fronting due to electrolyte exclusion discussed before causes dilution of tartrate, but this is a minor factor when high injection volumes are applied. Considering the solution that contains 0.1 M of both sodium tartrate and NaOH, the dilution factors of tartrate for the injections of 15%, 25% and 50% are 2.1, 1.6 and 1.3, respectively. Similarly, the dilution of hydroxy acids in the treatment of black liquor can be further decreased by increasing the injection volume. Considering the further processing of hydroxy acids, high product concentration is highly advantageous, because concentration of the acid mixture by evaporation is energy-consuming.

4. Conclusions

SEC has been found to be suitable for recovering hydroxy acids from black liquor in alkaline conditions. The main advantage of applying SEC is that lignin precipitation by acidification is not required, which reduces chemical consumption, and the cooking chemicals can be readily recovered for re-use. In this paper, the

effects of feed composition, column loading and fouling of the separation medium on the separation of sodium salts of hydroxy acids and sodium hydroxide of soda black liquor was investigated.

Optimisation of the separation process showed that high column loadings can be used without compromising the product purity and yield, and thus high productivity and high product concentration can be obtained. The use of high column loadings is possible because the retention time of NaOH increased with increasing injection volumes. It is apparent that the sodium salts of hydroxy acids force the NaOH to stay inside the Sephadex gel by size-exclusion of individual ions.

Fouling of the separation medium did not affect the separation of NaOH and sodium salts of hydroxy acids. However, the long term alkali resistance of Sephadex G-10 remained unclear and needs to be further investigated.

Black liquors from soda pulping of hardwood and softwood were utilised in this study. As the composition of black liquor depends on the cooking conditions, there may be some differences in separation of hydroxy acids from different sources. In practise, the potential raw material for hydroxy acids is kraft black liquor, which is widely available. The hydroxy acids content of kraft black liquor is very similar to that of soda black liquor [3]. However, kraft black liquor contains sulphur compounds, which are more difficult to separate than NaOH due to their larger molecular sizes. In addition, the possible formation of hydrogen sulphide during the processing of hydroxy acid fraction must be taken into account.

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Purification process for recovering hydroxy acids from soda black liquor

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ABSTRACT

Black liquor, a side product of chemical pulping, contains hydroxy acids that have many potential applications, e.g., as polymer precursors. Currently there are no feasible separation processes available for recovery of hydroxy acids from such solutions. Neutralization is usually though to be a necessary pre-treatment, but it adds into chemical consumption and may impede the integration of the recovery process to a pulp mill. In this work, an experimental investigation of a new process concept for the recovery and purification of hydroxy acids from soda black liquor without neutralization is presented. The process consists of ultrafiltration, size-exclusion chromatography, ion-exchange, adsorption, and evaporation. Mixtures of hydroxy acids in high purity were produced from black liquor of soda pulping using the process. A reduction of 99% in lignin content of the organic acid fraction was achieved. In the chromatographic separation step, the recovery of sodium hydroxide was almost 100%. The average purities of hydroxy acids isolated from softwood and hardwood black liquors were 81% and 63% on mass basis, respectively.

Keywords: Hydroxy acids; Black liquor; Membrane filtration; Chromatography

1. Introduction

Spent pulping liquors represent an untapped source of various valuable chemical compounds. For example, kraft black liquor is traditionally combusted in a recovery furnace. While the inorganic pulping chemicals are recovered for re-use, the organic residue is utilized solely for energy production. Due to an increasing demand for biomass-based substitutes for fossil fuel-derived chemicals, fractionation of black liquor has gained a lot of research interest recently. In particular, the recovery and fractionation of lignin using precipitation, ultrafiltration and extraction has been studied rather intensively (e.g., Toledano et al., 2010b; Gouveia et al., 2012). However, black liquor contains also a major amount of carbohydrate degradation products, mainly carboxylic acids, which possess a low calorific value in comparison to lignin (van Heiningen, 2006). The recovery of these compounds prior to combustion could make the use of the lignocellulosic biomass resource more efficient (FitzPatrick et al., 2010).

The carboxylic acids of black liquor can be divided into volatile acids and non-volatile hydroxy acids, which are formed during the alkaline degradation of polysaccharides according to peeling-off reaction. Hydroxy acids are building block chemicals that can be refined for various purposes. Potential applications of hydroxy acids include biodegradable plastics (e.g., Wang and Huang, 2008), packaging films (Loomis and Ostapchenko, 1991), tissue-engineering (Barralet et al., 2005), and cosmetics (Draelos, 2000). High purity is required especially if the acids are polymerized, since impurities may cause undesired side reactions, catalyst deactivation, or termination of chain length increase. Considering the recovery of hydroxy acids in high purity, black liquor is a very challenging raw material due to its complex matrix that consists of numerous components with unknown properties. From the separation technology point of view, the most challenging impurities are the lignin type compounds. Lignin causes various problems in the processing of black liquor, since its solubility is strongly dependent on pH, and the lignin

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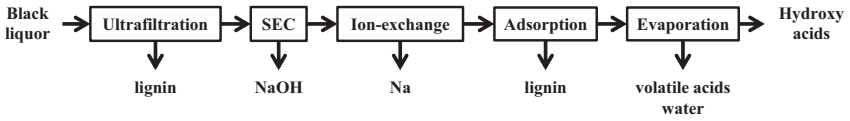

Fig. 1 – Process for fractionation of black liquor.

precipitate formed is difficult to separate due to its colloidal structure (Öhman and Theliander, 2007).

Several separation methods for the recovery of hydroxy acids from black liquor have been studied in the literature. Typically, the processes are relatively complicated because lignin and inorganic compounds are separated from hydroxy acids in separate steps.

Lignin can be removed by precipitation using carbon dioxide or mineral acid (e.g., Merewether, 1961; De and Bhattacharya, 1996; Alén et al., 1986), and precipitated lignin is being commercially produced at several kraft pulp mills (Öhman et al., 2007). The problem with the precipitation of lignin is the colloid formation which impedes the following filtration step (Toledano et al., 2010a). Furthermore, precipitated lignin is readily contaminated with other compounds of black liquor (Toledano et al., 2010b), and thus precipitation may also decrease the yield of hydroxy acids. These issues may cause major problems when aiming to remove a large amount of lignin, which is the case in recovery of hydroxy acids. In addition, lowering the pH increases chemicals consumption significantly and may alter the sulfur-to-sodium ratio of the pulp mill if sulfuric acid is used for neutralization. Therefore, a fractionation process that includes precipitation of lignin by direct neutralization of the alkaline black liquor with mineral acids would be rather expensive to integrate to a pulp mill. On the other hand, the more preferable carbon dioxide precipitation might not be efficient enough for removing lignin.

As an alternative to precipitation, membrane filtration can be applied for reducing the lignin concentration of black liquor (Niemi et al., 2011; Rowe and Gregor, 1986). However, either the lignin concentration or the pH of the ultrafiltration permeate is too high for the next process step, which is the separation of inorganic material by crystallization (Niemi et al., 2011; Alén and Sjöström, 1980), chromatography (Alén et al., 1990), or electrodialysis (Mishra and Bhattacharya, 1987). Therefore, neutralization of black liquor is, nevertheless, required.

In this paper, a new separation process concept for fractionation of black liquor is introduced and used for recovering hydroxy acids from black liquor of soda-cooking of wood. The process scheme is shown in Fig. 1. Membrane filtration is applied as a pre-treatment to separate the most of lignin. Subsequently, the separation of hydroxy acids and sodium hydroxide is carried out with size-exclusion chromatography (SEC) using Sephadex G-10 size-exclusion gel. The reported biorefinery applications of SEC include fractionation of lignosulfonates (Ouyang et al., 2011), and recovery of oligosaccharides from biomass hydrolysates (Moura et al., 2007; Cara et al., 2012) and from steam-treated wood (Palm and Zacchi, 2004), but it has not been applied previously for isolating hydroxy acids from pulp mill black liquor. Chromatographic recovery of hydroxy acids reported by Alén et al. (1990) was based on ion-exclusion using a strong acid cation exchange resin as a separation medium, which requires that the black liquor is acidified. As the neutralization of black liquor is not required using SEC, the chemical consumption of the proposed process is low and the process offers a facile, straight-forward recovery of cooking chemicals. The hydroxy acids, which exist as their sodium salts after being recovered under alkaline conditions, can be liberated using ion-exchange. The residual lignin is then removed by adsorption. Finally, the product fractions are concentrated by evaporation to compensate the dilution that occurs during processing. The advantage of evaporation as a concentration method is that the volatile acids are simultaneously removed. The aim is that the purity of the concentrated product is sufficient for polymerization. Separation and purification of single hydroxy acids is not necessary, because mixtures of hydroxy acids can be copolymerized (Mehtiö et al., 2012).

Since the separation process presented in Fig. 1 is does not involve neutralization of black liquor, chemicals are required only for washing of the separation materials and for the regeneration of the ion-exchange resin. As the chemical consumption is thus determined by the required washing frequency, prevention of fouling is a key issue for process economics.

When treating black liquor, fouling of the separation media is mainly caused by adsorption of lignin. Fouling may occur in the membrane filtration step, but also during chromatographic separation and ion-exchange steps. Considering the resin fouling in the latter process steps, the selection of the membrane for the membrane filtration step is a key issue as it determines the lignin content in the solution used for further processing. The smaller the membrane cut-off, the purer the permeate with respect to lignin. However, a higher pressure is required while using a membrane with low cut-off, and membrane fouling may also be more severe. As the main operating costs in membrane filtration of black liquor are due to pressurization and pumping (Jönsson and Wallberg, 2009), a loose membrane may be preferred to reduce energy consumption. The lignin removal pre-treatment by membrane filtration is thus of major importance when optimizing the overall process. The effect of membrane cut-off on the later process steps is therefore also investigated.

2. Materials and methods

Hardwood (HW) and softwood (SW) soda black liquors were prepared by cooking of birch and pine wood chips, respectively, with sodium hydroxide. SW cooking was carried out at a temperature of 170 °C until an H-factor[1] of 1936 was reached, and HW wood chips were cooked at 165 °C until an H-factor of 1324. The liquor to wood ratio was 4:1 and the amount of effective alkali was 5.5 mol/kg.

2.1. *Lignin removal by membrane filtration*

Black liquor was filtered using a cross-flow flat sheet membrane module and Microdyn-Nadir NP010 ultrafiltration

[1] H-factor indicates the delignification rate. It is calculated as a function of cooking temperature and time: $H = \int_0^t \exp(43.2 - 16113/T)dT$. 1 h at 100 °C is equivalent with H-factor 1.

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membrane, which is a polyethersulfone (PES) membrane with a molecular weight cut-off (MWCO) of 1000 Da. The same membrane type was also used by Niemi et al. (2011) for ultrafiltration of kraft black liquor. PES membranes resist alkaline conditions and are less expensive than ceramic membranes.

The membrane area was 0.01 m^2 and a cross-flow velocity of 2.3 m/s was applied. The permeate was collected continuously and the retentate was recycled back to the feed tank during the filtration. Since the thermal stability of polymeric membranes under alkaline conditions is limited, the filtration was carried out at 60 °C. Pressure was adjusted between 6 and 20 bar aiming to keep the permeate flux constant, 40 kg/(h m^2). Constant flux mode was used because it may provide higher average flux with less membrane fouling than constant pressure filtration if the target flux is properly chosen. The filtration was continued until a volume reduction, calculated as $(V_{feed} - V_{retentate})/V_{feed}$, of approximately 80% was reached, i.e., the total volume of permeate was about 80% of the original volume. This high volume reduction target was set to maximize the yield of hydroxy acids.

To investigate the effect of lignin removal efficiency of the ultrafiltration step on the down-stream processing, a similar filtration was done using a loose membrane, Microdyn-Nadir UP010 ultrafiltration membrane with a MWCO of 10,000 Da. The filtration procedure was the same as with the NP010 membrane. The applied pressure ranged from 2.5 to 10 bar to reach a flux of 70 kg/(h m^2).

The dry solids content of the feed, permeate and retentate solutions were measured using a standard method (SCAN-N 22:96). The ash content was determined by burning the sample at 700 °C (KCL 59:83). The carboxylic acids were analyzed using capillary electrophoresis and lignin concentration was determined on UV–vis spectrophotometer as described in Sections 2.6.1 and 2.6.4, respectively.

2.2. Size-exclusion chromatography

The permeate obtained in the membrane filtration step was further processed using chromatography. Hydroxy acids were separated from NaOH using Sephadex G-10 size-exclusion gel (GE Healthcare), which has an exclusion limit of 700 Da and a dry bead diameter of 40–120 μm. The separation experiments were done in a thermostated glass column (Kronlab, H_{bed} = 40.7 cm, D_{bed} = 5 cm) at 50 °C. The injection volume was 10% of the bed volume (BV), and purified water was applied as an eluent. The feed and eluent were introduced into the column with a flow rate of 8 mL/min using HPLC pumps (Waters 515) equipped with a degasser (Phenomex Degassex model DG-4400). The applied flow velocity equals to 0.6 BV/h. Valves were operated using LabView software (National Instruments). The column outlet was monitored online using conductivity detector (Pharmacia Biotech), refractivity detector (Schambeck SFD GmbH RI 2000) and UV-detector (Waters 2487) on wavelengths of 280 and 350 nm.

2.3. Liberation of acids using ion-exchange

Sodium–proton ion-exchange was done using a strong acid cation exchange resin (Finex CS11GC) in a glass column (Kronlab, H_{bed} = 20 cm, D_{bed} = 2.5 cm). The experiments were done at room temperature to avoid vaporization of volatile acids. To minimize dilution, the fractions were injected to the column as a single large pulse with a flow rate of 0.33 mL/min. The column outlet was monitored using an online conductivity detector and the product was collected based on the signal strength. The most diluted parts in the beginning and at end of the profile were discarded.

The reduction in pH during the ion-exchange may cause precipitation of lignin in the column and consequent blocking of the column. The effect of the amount of lignin in the feed on the performance of the ion-exchange resin was studied using the hydroxy acid fractions recovered by SEC from the permeate of the loose UP010 membrane. The ion-exchange was carried out for the fractions as such and after reducing their lignin concentration by acidification, in which the pH of the fractions was adjusted to 3 using concentrated sulfuric acid and the precipitated lignin was separated by centrifugation.

The resin was regenerated using 1 M HCl. To avoid blocking of the column due to precipitation of lignin during regeneration, adsorbed lignin was removed by washing with 75 wt% ethanol or 1 M NaOH prior to the regeneration.

2.4. Adsorptive purification

Further purification of hydroxy acid fractions was performed using Amberlite XAD-16 (Rohm & Haas Co.), which is a neutral PS-DVB resin. The resin was thoroughly washed with purified water and vacuum filtered prior to use. The adsorption was done in a sealed flask using 5 wt% of dry resin and the mixture was agitated at 50 °C in a thermostated rotary shaker with a rotation speed of 250 rpm. Samples were withdrawn every 30 min and analyzed as described in Section 2.6. After 1.5 h, the amount of adsorbent was doubled and the agitation was continued for 1 h, which was found to be sufficient to reach equilibrium based on UV absorbance measurement of the liquid phase. The resin was separated by centrifugation.

2.5. Evaporation

Hydroxy acid fractions were concentrated in open flasks in a vacuum oven at 50 °C and pressure of 100 mbar until the mass of the samples had decreased to 20% of their initial mass.

2.6. Analysis methods

The concentrations of acids were determined using capillary electrophoresis and GC/MS. The degree of protonation was determined by potentiometric titration. The amount of lignin was estimated based on UV absorption data.

2.6.1. Capillary electrophoresis

The amounts of acetic acid, formic acid, oxalic acid, lactic acid, glycolic acid, xyloisosaccharinic acid (XISA), glucoisosaccharinic acid (GISA), 2-hydroxy butanoic acid, and 2,5-dihydroxyacid (2,5-DHPA) were determined using capillary electrophoresis (CE) as described in (Niemi et al., 2011; Rovio et al., 2010). These are the main carboxylic acids present in black liquor.

2.6.2. GC/MS

To detect the hydroxy acids that are present only in trace amounts and other minor components, gas chromatography combined with mass spectrometry (GC/MS) was applied. The analysis was performed as described by Niemelä (1989).

2.6.3. Titration

The degree of protonation of the acids was determined by potentiometric titration using an automated titrator (Mettler

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DL25). Samples of 5 mL were diluted to 50% with 5 mL of purified water, and 10 mL of 2 M NaOH was added to increase the initial pH and sample volume. 1 M hydrochlorid acid was applied as titrant. The end-point of the titration was set to pH = 1. Gran plot was applied for determination of the inflection points of the titration curve (Harris, 1987) and the degree of protonation was calculated as a function of pH. The degree of protonation in the fractions collected from the ion-exchange step was determined based on their pH and the titration data.

2.6.4. *UV–vis spectrometry*

UV-spectra were recorded using an UV–vis spectrophotometer (Agilent 8453). The wavelength range was from 190 to 400 nm. The samples were diluted with 0.1 M NaOH to eliminate the effect of pH on the UV absorbance. The amount of lignin in the samples was estimated from UV absorbance at 280 nm using an absorbance coefficient of 19 L/(g cm) for SW soda black liquor and 14 L/(g cm) for HW soda black liquor.

3. Results and discussion

3.1. *Membrane filtration of black liquor*

Membrane filtration was applied to separate lignin from the black liquor. Lignin was concentrated in the retentate, and the permeate was further processed. The lignin concentrations, dry solids contents and ash contents of the raw black liquors, the permeates and the retentates are presented in Table 1. The concentration of lignin in the permeate of the NP010 membrane was 80% lower than in the feed. The reduction in lignin concentration was slightly higher than reported by Niemi et al. (2011) for the same membrane in filtration of kraft black liquor at 70 °C.

The flux and pressure profiles during the membrane filtration are shown in Fig. 2. As seen in the figure, the flux was not constant in the end of the filtration but started decreasing rapidly after the volume reduction of 60%. At this point the lignin concentration of retentate had approximately doubled from the initial feed concentration. Such high lignin concentration increases the viscosity and causes fouling of the membrane. The filtration was continued using constant pressure until the flux decreased below 10 kg/(m^2 h) or problems occurred with the pump due to the high viscosity of the solution. The volume reduction at the end of the filtration was 76% for SW soda black liquor and 83% for HW soda black liquor when the NP010 membrane was used, and 82% for SW soda black liquor and 83% for HW soda black liquor in the case of the UP010 membrane. Despite the high volume reduction, up to 75% of the black liquor's lignin was recovered in the ultrafiltration step. The retentate was concentrated with lignin (up to 285 g/L), which can be burned or further processed as a side product. If a lower yield for hydroxy acids is accepted, a higher lignin yield can be obtained.

Table 1 – Concentration of lignin (determined from UV absorbance at 280 nm), dry solids content and the percentage of ash in the feed soda black liquors and in the permeates and retentates of the NP010 and UP010 membranes.

	Lignin (g/L)	Dry solids (wt%)	Ash (wt%)
HW feed	79.5	14.1	5.7
HW NP010 permeate	16.2	9.0	4.9
HW NP010 retentate	285.4	28.7	6.9
HW UP010 permeate	32.6	10.4	5.1
HW UP010 retentate	244.8	25.3	6.3
SW feed	72.0	14.9	5.6
SW NP010 permeate	14.6	10.8	5.0
SW NP010 retentate	238.4	26.7	6.4
SW UP010 permeate	22.5	10.3	5.3
SW UP010 retentate	270.5	28.0	6.6

Some differences in the filtration of cooking liquors of different wood species were observed. When applying the UP010 membrane, the reduction in lignin concentration was higher for SW soda black liquor (69%) than for HW soda black liquor (59%). In addition, lower pressures were needed to obtain the target flux with SW soda cooking liquor than with HW cooking liquor with both NP010 and UP010 membranes (Fig. 2). The difference was higher with the 1 kDa membrane than with the 10 kDa membrane. The difference in the lignin concentration of the feed may not fully explain the filtration behavior of the black liquors of different origin. It should be noted that a lower H-factor of delignification was used in the cooking of HW chips. Therefore, HW soda black liquor is likely to contain more high molar mass compounds which may be related to the higher pressures required in filtration. There are also differences in the structure of lignin as well as in the occurrence of fouling components in different wood species.

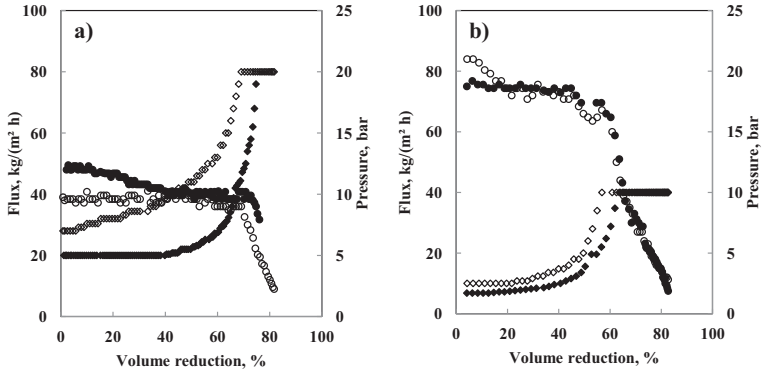

Fig. 2 – Pressure (diamonds) and flux (circles) in the ultrafiltration of HW soda black liquor (open symbols) and SW soda black liquor (filled symbols) using (a) the NP010 (1 kDa) and (b) the UP010 (10 kDa) membranes. Temperature was 60 °C and cross flow velocity about 2.3 m/s.

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Table 2 – Concentrations of carboxylic acids in the feed soda black liquors and in the permeates and retentates of the NP010 and UP010 membranes. Data from CE analyses.

	XISA (g/L)	GISA (g/L)	2,5-DHPA (g/L)	2-OH-butanoic acid (g/L)	Lactic acid (g/L)	Glycolic acid (g/L)	Oxalic acid (g/L)	Acetic acid (g/L)	Formic acid (g/L)	Total (g/L)
HW feed	3.2	7.3	1.1	4.0	2.8	1.2	0.5	13.7	5.4	40.3
HW NP010 permeate	2.8	6.8	0.9	4.4	1.8	1.2	0.3	13.6	4.7	37.2
HW NP010 retentate	4.3	5.5	0.8	2.4	1.1	1.3	0.6	9.0	3.9	29.5
HW UP010 permeate	4.5	6.0	0.8	4.0	2.5	1.4	0.5	16.0	6.0	42.6
HW UP010 retentate	2.2	7.1	1.2	2.6	1.4	1.8	0.5	10.4	5.4	33.3
SW feed	3.7	15.7	1.3	1.3	4.2	2.8	0.5	4.4	5.4	40.0
SW NP010 permeate	4.4	18.3	1.1	1.3	4.9	2.1	0.7	4.7	5.9	44.3
SW NP010 retentate	3.5	13.7	0.9	1.0	3.0	2.8	0.5	3.7	4.9	34.6
SW UP010 permeate	4.9	18.7	1.3	1.4	4.8	2.4	0.7	5.2	5.9	45.9
SW UP010 retentate	1.5	14.5	1.1	1.1	3.4	1.9	0.7	3.5	5.2	33.4

The concentrations of carboxylic acids before and after the membrane filtration are presented in Table 2. The main differences in the acid compositions of HW and SW soda black liquors are the larger amount of GISA in SW black liquor and the higher concentrations of 2-hydroxy butanoic acid and acetic acid in HW black liquor. As seen in the table, the concentration of the acids were in some cases higher in the permeate than in the feed, which means that the acids have a negative retention (Mänttäri and Nyström, 2006). The negative retention is an advantageous phenomenon here since it improves the acid yield. The total yield of hydroxy acids in the permeate varied between 71 and 91%.

3.2. *Separation of sodium hydroxide and hydroxy acids*

A typical chromatogram from chromatographic fractionation of HW soda black liquor on Sephadex G-10 size-exclusion gel is shown in Fig. 3a. The first peak (at $0.45 < BV < 0.8$) in the conductivity signal consists of polyelectrolytes (lignin), hydroxy acids, and volatile acids whereas the second peak (at $V > 0.8$ BV) is sodium hydroxide. Sodium hydroxide is completely dissociated (strong electrolyte) and, since the Sephadex gel is not an ion exchange material, both Na^+ and OH^- can access a large fraction of the pore volume of the gel. It is thus more strongly retained than the hydroxy acids. The separation is based mostly on the size of the hydrated molecules, although some interactions may also occur because the weak and strong electrolytes have the same cation (Na^+).

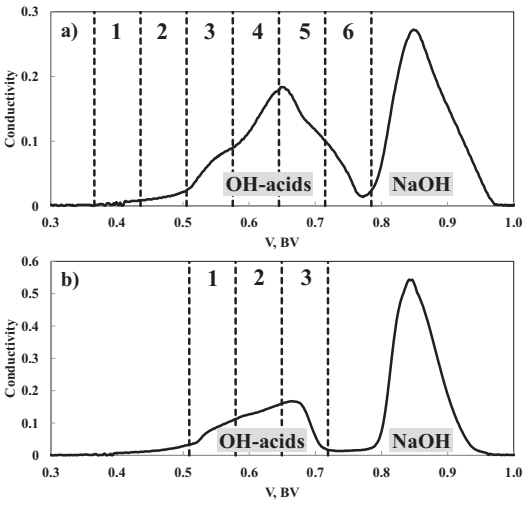

Fig. 3 – Fractionation of hydroxy acids of (a) HW soda black liquor and (b) SW soda black liquor using Sephadex G-10. H_{bed} = 40.7 cm, D_{bed} = 5 cm, V_{inj} = 0.1 BV; eluent flow rate 0.6 BV/h.

Six hydroxy acid fractions were collected as indicated in the figure. Since only trace amounts of hydroxy acids were observed in the first two fractions of HW soda black liquor, only 3 fractions were collected in the experiments carried out with SW soda black liquor. The elution volumes equivalent to the fraction cut times are shown as dashed vertical lines in Fig. 3b. The separation of hydroxy acids and sodium hydroxide is slightly better for SW black liquor than for HW black liquor.

The concentrations of carboxylic acids in the fractions collected from HW and SW soda black liquors after SEC are presented in Table 3. Fractions 1 and 2 recovered from HW soda black liquor contained only minor amounts of formate and oxalate. The low concentration of the salts was also indicated by the low pH of the fractions (7.0 and 7.5) in comparison to fractions 3–6 (pH 10–11). Since hydroxy acids did not occur in fractions 1 and 2 of the HW feed, those fractions were discarded. Therefore, only the concentrations of the acids in fractions 3–6, which were further processed as described below, are presented in Table 3.

The total concentrations of acids were approximately 29% and 40% of the concentrations in HW and SW feed solutions, respectively. These concentrations are slightly lower than could be expected based on the dilution factors calculated from the volumetric ratio of the collected fractions and the feed injection (2.8 for HW feed and 2.1 for SW feed). The total yield of acids in the size-exclusion chromatographic separation was 81% for HW feed and 85% for SW feed. The yield of hydroxy acids was 71% for the HW feed and 78% for the SW feed. Based on the conductivity signal shown in Fig. 3, a higher yield could have been expected. The small acid concentrations may be because the CE analysis was carried out using a different analysis instrument.

Though the main aim of the SEC was not to fractionate the acids but to remove sodium hydroxide, some fractionation of the acids by size-exclusion also occurred. Isosaccharinic acids elute fast due to their large molecular sizes, and therefore the highest concentrations were observed in fractions 3 and 4 obtained from HW soda black liquor. Interestingly, dicarboxylic acids were also enriched in fractions 3 and 4. Smaller

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Table 3 – Concentration of carboxylic acids in the fractions recovered from HW and SW black liquors using Sephadex G-10. Ultrafiltration using the NP010 membrane was applied as pre-treatment.

Fraction	XISA (g/L)	GISA (g/L)	2,5-DHPA (g/L)	2-OH-butanoic acid (g/L)	Lactic acid (g/L)	Glycolic acid (g/L)	Oxalic acid (g/L)	Acetic acid (g/L)	Formic acid (g/L)	Total (g/L)
HW soda black liquor										
3	1.1	1.4	0	0.30	0.34	0.25	0.29	1.80	0.18	5.6
4	2.1	2.3	0	2.0	1.2	0.66	0.23	7.40	1.71	17.6
5	0.98	0.61	0	3.1	1.0	0.57	0	8.36	3.31	17.9
6	0	0	0	0.48	0	0	0	0.65	0.71	1.8
SW soda black liquor										
1	0.63	5.8	0	0	0.44	0.50	0.33	0.75	0	8.5
2	3.1	11.4	0.68	0.93	3.7	1.6	0	4.02	2.07	27.6
3	1.3	0.52	0.54	1.6	2.5	0.82	0	4.21	6.06	17.5

2-hydroxy butanoic acid was accumulated in fractions 5 and 6. However, all the fractions collected were acid mixtures with volatile acids as main components. As seen in Table 3, highest acid concentrations occur in fractions 4 and 5, while the concentration of acids in fraction 6 is very low. GC/MS analysis also revealed the presence of polar aromatic acids, which can be detrimental to polymerization reactions, in fraction 6. Therefore, the sixth fraction might not be applicable for polymerization.

For SW soda black liquor, only three fractions were collected. As seen in Table 3, GISA is the main component in fractions 1 and 2 while smaller hydroxy acids occur in fraction 3. Volatile acids are also enriched in fraction 3. The purity of GISA in the first fraction was as high as 69%. If the aim is to purify single hydroxy acids, the partial fractionation obtained is very useful.

The concentration of lignin in the recovered hydroxy acid fractions was 1.4–4.3 g/L (see Fig. 4). Removal of the residual lignin in discussed in Section 3.4. A minor fraction of lignin also ends up to the NaOH fraction, which would not be expected based on the molecular size. Therefore, adsorption of lignin on the size-exclusion gel seems to affect the separation.

Chromatographic separation experiments were carried out also with black liquors filtrated with the UP010 membrane to see the effect of membrane cut-off on the chromatographic separation. It was observed that the hydroxy acid composition of the fractions collected from size-exclusion column was nearly independent of the membrane used in the preceding step. It can be thus concluded that the fouling of the resin due to a higher lignin concentration in the feed does not affect the separation of hydroxy acids and NaOH. On the other hand, the amount of lignin in the fractions collected from SEC was clearly higher when the feed was permeate of the UP010 membrane than when treating the permeate of the NP010 membrane. However, the ratio of lignin concentrations of the fractions recovered to the feed concentration was approximately the same. Palm and Zacchi (2004) have observed that lignin can be adsorbed on the size-exclusion gel, which becomes saturated at some point and, consequently, lignin start passing to the product fractions in increasing amount. When the concentration of lignin in the feed solution is higher, this saturation is likely to be reached earlier. Therefore, more frequent washing is probably required if the pre-treatment is done using a loose ultrafiltration membrane.

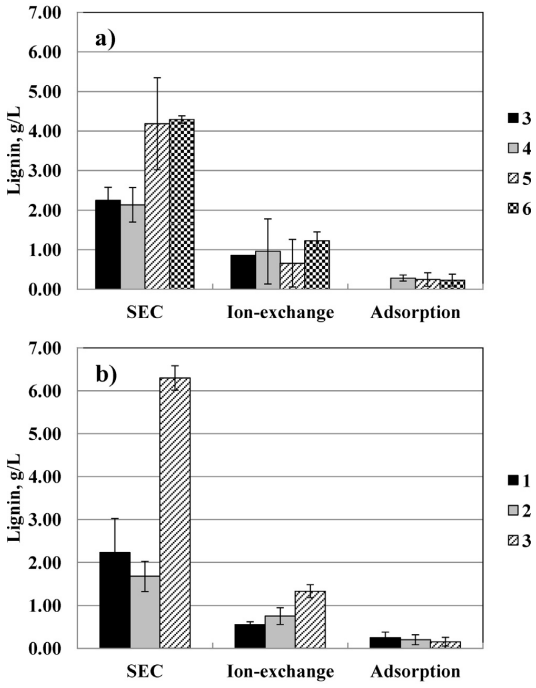

Fig. 4 – Concentration of lignin in the fractions after the different process steps: (a) HW soda black liquor and (b) SW soda black liquor. The NP010 membrane was applied for pre-treatment.

3.3. *Liberation of the acids*

The pH of the fractions recovered using SEC was about 10. At this high pH, carboxylic acids occur as sodium salts. To liberate the acids and to remove the residual sodium, a cation exchange resin in H^+ form was used. The pH of the fractions after the ion-exchange ranged from 1.6 to 2.9. Based on the degree of protonation determined by titration of the feed, the conversion of sodium salts to acid form was 90–100% in the ion exchange step. The ion-exchange was thus successful in liberation of the acids.

The solutions were slightly diluted during the ion-exchange. Consequently, the average total concentration of hydroxy acids and volatile acids in the fractions after ion-exchange was 72% of the feed concentration. Such dilution can be minimized by collecting only the concentration plateau as the product, which slightly reduces the yield. The yield of ion-exchange was 68% when the most dilute parts of the front and tail were left out of the product fraction. It should be noted, however, that no loss of acids due to adsorption onto the

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stationary phase was observed. Overall, the acid composition was unchanged with the exception that GISA was converted to its lactone form according to GC/MS. This conversion occurs due to a decrease in pH (Ekberg et al., 2004).

When the black liquor was pre-treated using the looser UP010 membrane instead of the NP010 membrane, the resin required more frequent washing due to the higher concentration of lignin in the feed. In particular, when HW soda black liquor was treated, it was necessary to wash the resin after each fraction. To efficiently remove the lignin precipitate formed in the column, it sodium hydroxide was used for washing the resin. As a consequence, the resin had to be regenerated every time after washing. Therefore, only a minor part of the ion-exchange capacity could be applied for liberation of the acids.

Using acidification with sulfuric acid as a pre-treatment for ion-exchange, the problems caused by lignin precipitation were diminished. In addition, the degree of protonation was increased when this two-step process for liberation of acids instead of ion-exchange only. The pH of the fractions after acidification and ion-exchange ranged from 0.9 to 1.5, i.e., the conversion of acids was complete. On the other hand, an extra purification step would be needed to remove the sulfate added in the acidification step.

Based on the experiments, ion-exchange was found feasible for liberation of acids only if the concentration of lignin is relatively low. Though treatment of the permeate of a loose membrane in the SEC step was successful, the ion-exchange step was not possible unless acidification was applied. Because the permeate of the NP010 membrane allowed a straight-forward processing without additional process steps, the application of a tight membrane in the pre-treatment is recommended.

The drawback of applying ion-exchange is the production of sodium salts during the regeneration of the resin. For example, if the sulfuric acid is used for regeneration, sodium sulfate waste is generated. To avoid disturbing the sodium–sulfur balance of the pulp mill, this waste stream must be treated separately. For example, electrodialysis can be applied to convert sodium sulfate back into sodium hydroxide and sulfuric acid (Davis et al., 2008; Thompson et al., 1995).

3.4. *Lignin removal*

Though the concentration of lignin was substantially reduced during processing, some residual lignin (or smaller lignin-derived compounds) remained in the product fractions even after the ion-exchange stage. This residual lignin was removed by adsorption on a neutral hydrophobic polymer resin.

The concentration of lignin after the different process steps in the fractions recovered from soda black liquor filtered with the tight membrane is shown in Fig. 4. As seen in the figure, ion-exchange, besides being an efficient method for liberation of the acids, also effectively purifies the fractions with respect to lignin. The most substantial reduction in the lignin content during ion-exchange was observed in the fractions with a high initial concentration of lignin. It has to be borne in mind that part of the reduction in lignin concentration is due to dilution. A reduction of approximately 15% can be expected in the lignin concentration as a consequence of dilution during the multistep process.

The lignin concentrations after the different process steps for the black liquor pre-treated using the loose UP010 membrane are presented in Fig. 5. The amount of lignin in the fractions recovered from HW soda black liquor using SEC was approximately doubled when the UP010 membrane was

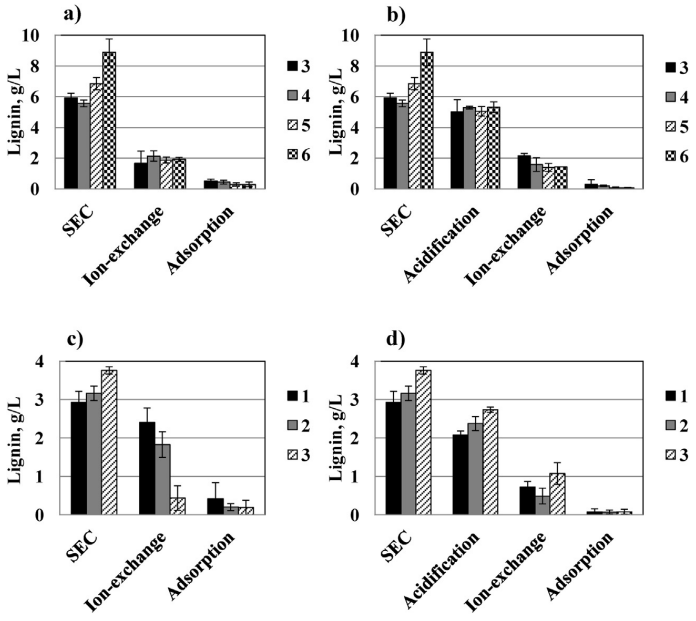

Fig. 5 – Lignin concentration in the fractions after the different process steps: (a) HW soda black liquor without acidification; (b) HW soda black liquor with acidification; (c) SW soda black liquor without acidification; and (d) SW soda black liquor with acidification. The UP010 membrane was applied for pre-treatment.

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Table 4 – Composition of the concentrated final product fractions purified from soda black liquors. Lignin was removed by ultrafiltration using the NP010 membrane. Lignin concentration is based on the UV absorbance measured at 280 nm and acid concentrations are determined using CE.

Fraction	Mass reduction (wt%)	Lignin (g/L)	XISA (g/L)	GISA (g/L)	2,5-DHPA (g/L)	2-OH-butanoic acid (g/L)	Lactic acid (g/L)	Glycolic acid (g/L)	Oxalic acid (g/L)	Acetic acid (g/L)	Formic acid (g/L)
HW black liquor											
3	85	1.21	6.2	7.4	0.0	0.0	0.4	1.0	3.0	2.5	0.0
4	89	1.41	46.2	22.9	0.0	10.2	7.9	9.7	1.5	23.3	3.9
5	85	2.13	5.0	2.2	0.0	16.3	4.9	3.5	0.0	20.9	10.6
6	92	1.92	0.0	0.0	0.0	4.1	0.6	0.3	0.5	2.8	2.8
SW black liquor											
1	92	1.03	5.2	45.8	0.0	0.0	1.7	2.9	3.8	3.6	0.7
2	96	4.00	53.4	148	4.38	7.9	34.1	24.0	0.0	13.0	9.2
3	89	2.49	8.4	2.0	2.20	5.6	8.5	5.0	0.0	7.0	15.2

applied for the ultrafiltration instead of the NP010 membrane. However, the lignin concentration of the final product was approximately same independent of the membrane of pretreatment, mainly because of the lignin removal occurring during ion-exchange. This result is in agreement with the fact that more frequent washing of the resin bed was required while processing these fractions to avoid lignin break-through to the product.

In the case of SW soda black liquor, the amount of lignin after the fractionation using Sephadex G-10 was, interestingly, approximately the same for the permeates of the both membranes applied. Because the relatively low initial lignin concentration and the small molecular size of the lignin, pH adjustment to 3 leads to precipitation of a minor amount of lignin only. However, the process with the acidification step results in a final product with a lower lignin concentration. This is probably because a larger amount of lignin is adsorbed both on the ion-exchange resin and on the neutral adsorbent when the solution is more acidic.

No significant losses of hydroxy acids were observed during adsorptive lignin removal. Accordingly, the XAD-16 resin is quite selective towards lignin. The yield of acids in the lignin removal step was 97%. The lignin adsorbed on the resins is desorbed during cleaning with an organic solvent and can be recovered if necessary.

3.5. *Concentration by evaporation*

After the adsorptive lignin removal, the hydroxy acid fractions were concentrated by evaporation at reduced pressure. Evaporation was found to beneficial also for the purity of the hydroxy acids as the relative amount of volatile acids (formic acid and acetic acid) was reduced by 40–70%. The proportion of volatile acids of all carboxylic acids in the concentrated fractions varied. The smallest concentration of volatile acids was found in fractions 1 and 2 recovered from SW soda black liquor (7 wt%, which corresponds to 16 mol%). This purity appears to be sufficient for polymerization. Furthermore, these fractions could be a useful resource for production of pure individual hydroxy acids. For example, the first fraction recovered from SW soda black liquor contained GISA in a purity of 71 wt%. The largest amount of volatile acids remained in the fractions with highest concentrations after SEC (fractions 5 and 6 recovered from HW soda black liquor and in fraction 3 recovered from SW soda black liquor), which contained up to 50 wt% of volatile acids. These fractions could be further purified by evaporation to obtain concentrated, relatively pure 2-hydroxy butanoic acid. However, the GC/MS analysis revealed that the third fraction from SW soda black liquor contained also a relatively high amount of glycerol (2.6 g/L), which cannot be removed by evaporation. If higher purity is required, the product can be purified, e.g., by crystallization (van Krieken, 2006). The concentrations of the final products are presented in Table 4.

Evaporation is a very energy-intensive unit operation. The concentration could be also performed using membrane filtration, providing that a membrane that resists acidic conditions is used. With a suitable membrane, the volatile acids could also be separated from hydroxy acids in the concentration step (Hausmanns et al., 1996). However, the yield of the hydroxy acids would most probably decrease, as the retention of small organic compounds in nanofiltration is typically incomplete.

The total yield of hydroxy acids in the multistep recovery process was 40–50%. Since black liquor is available in large amounts, high yield is not a necessity. However, the yield in the last separation steps should be as high as possible. By optimizing the process, higher hydroxy acid yield can be obtained. A complete optimization was, however, beyond the scope of this work, and thus conclusions of the process economics cannot be drawn.

In this work, a multistep separation procedure was developed for recovering hydroxy acids from black liquor of soda-cooking of wood. Due to the differences in the composition of the cooking liquors from different pulping processes, the results may not be generalized for the black liquor of kraft pulping, which is the dominating pulping process for wood (Francis et al., 2008). However, the separation process presented here may be applicable also for kraft black liquor with some modifications. Special attention has to be paid to the process safety in the ion-exchange step, in which hydrogen sulfide may be formed.

Five separation steps were required for the recovery and purification of hydroxy acids from soda black liquor, and even a slightly more complicated process may be required for kraft black liquor. Multiple steps are required because of the complex nature of black liquor raw material. Therefore, also direct uses for black liquor have recently been developed. For example, black liquor could be utilized to enhance biomass hydrolysis as suggested by Zhu et al. (2013). In their work, high lactic acid yields were obtained since part of the carbohydrate residue of black liquor was also converted into small acids. The advantage of the multistep fractionation process over this alternative approach to black liquor utilization is that a wide range of products, including 2-hydroxy butanoic acid and isosaccharinic acids which are quite rare compounds with

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a limited availability, can be obtained. In addition, the fractionation process allows easy recovery of cooking chemicals for re-use and lignin for energy production, which may be crucial for the pulp mill.

4. Conclusions

A novel separation and purification process for the recovery of hydroxy acids from black liquor was developed and verified experimentally. The process consists of ultrafiltration to remove most of lignin, size-exclusion chromatography to separate hydroxy acids and NaOH, ion-exchange to convert the sodium salts of acids to protonated form, adsorption to remove residual lignin, and evaporation to concentrate the product fractions and to remove volatile acids. The main advantage of the process is that neutralization of black liquor is not required, and the chemical consumption is thus low.

The total purity of hydroxy acids increased from 19 wt% to 81 wt% for SW soda black liquor and from 13 to 63 wt% for HW soda black liquor. Such hydroxy acids fractions are most probably sufficiently pure for polymerization. The concentration of lignin, which is the most critical impurity, was reduced by approximately 99% during the processing black liquor.

The produced hydroxy acid mixtures can be further fractionated to obtain single hydroxy acids. However, a relatively high purity for some single hydroxy acids can be achieved already with the process described here. For example, GISA in purity >70 wt% was recovered.

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