LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
LUT School of Engineering Science
Master's Degree Program in Chemical and Process Engineering

HAZAL BURCU AKSOY

Recycling of Deep Eutectic Solvents with Membrane Technology

Examiners: Associate Professor Mari Kallioinen
Professor Mika Mänttäri

Supervisors: M.Sc. (Tech.) Jussi Lahti
D. Sc. (Tech.) Ikenna Anugwom

ABSTRACT

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Penetration towards biomass utilization as an energy source instead of fossil fuels due to its environmental friendliness, leads towards ionic liquid (IL) usage to break lignocellulosic biomass bonds. Deep eutectic solvents (DES) as one kind of ILs are preferred to be used in the place of ILs by reason of mostly environmental advantages. Economic and environmental aspect of the process in terms of amount of utilized solvent, bring about recyclability of DES.

The aim of this study was recycling of deep eutectic solvent (choline chloride: lactic acid, molar ratios 1:9) by membrane filtration to be used again for extraction of lignin from birch wood. Regarding to this, how well is the purification efficiency of the membrane process, as well as lignin extraction efficiency of the purified spent DES are aimed to be answered in consideration of this study. For this purpose, two sets of ultrafiltration, nanofiltration and reverse osmosis membrane utilization in the respective order has been performed as UP005, NF 270, AG and UP005, NFG, AG. In terms of purity, while the membrane process where NF 270 was used as a nanofiltration membrane results in purified spent DES with lignin concentration of 1.30 g/L, membrane process with NFG utilization results in spent DES with higher lignin concentration as 2.63 g/L. This result concludes that higher MWCO membrane utilization as a nanofiltration i.e., NFG, causes higher lignin concentration in the recycled spent DES, thus decreases the purity. In terms of lignin dissolution efficiencies, spent DES from the membrane process where NFG utilization took place, resulted in 32.6% efficiency which is only about 50% of the extraction efficiency of fresh DES.

ACKNOWLEDGEMENTS

“I know it's a mistake, but there are certain things in life where you know it's a mistake, but you don't really know it's a mistake because the only way to really know it's a mistake is to make the mistake and look back and say 'yep, that was a mistake.” Hence this heuristic approach has been implemented to decide on the best approach towards the experimental study during this thesis.

This Master of Science thesis has been performed between 1st of January and 30th of June in the Laboratory of Membrane Technology at Lappeenranta University of Technology. In the first place, I owe my deepest gratitude to my supervisors, M.Sc. (Tech) Jussi Lahti and PostDoc Ikenna Anugwom. I appreciate the support, enthusiasm and the feedbacks which I have received from them, as well as inspiring discussions. Without their guidance and persistent help, this thesis would not have materialized.

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Lappeenranta, Finland 22.06.2018

Hazal Burcu Aksoy

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LIST OF SYMBOLS

a	Constant at 205 nm and 280 nm, g/L
A	Proportionality Constant
Ab	Absorbance at specific wavelength
b	Thickness of quartz, cm
C	Concentration of salt ion in the solution, mol/L
C_f	Concentration of solute in the feed, mg/L
C_p	Concentration of solute in the permeate, mg/L
df	Dilution factor
dx	Direction perpendicular to membrane surface
dX	Driving force gradient
J	Flux, kg/m^2h
n	Moles of particulates which shows osmotic pressure, mol
R	Gas constant, J/mol.K
Re	Rejection, %
T	Temperature, ℃, K
V_f	Volume of feed
V_c	Volume of concentrate
π	Osmotic pressure, Pa

LIST OF ABBREVIATIONS

ABS	Aqueous Biphasic System
AC	Activated Carbon
AIL	Acid Insoluble Lignin
ASL	Acid Soluble Lignin
ChCl	Choline Chloride
CL	Cellulose to Lignin Ratio
CP	Concentration Polarization
Da	Dalton

DES	Deep Eutectic Solvent
DI	De-ionized
DIMCARB	Dimethlycarbonate
DMSO	Dimethyl Sulfoxide
ED	Electrodialysis
FCM	Functional Carbonaceous Material
FTIR	Fourier Transform Infrared Spectroscopy
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
HDS	Hydro Desulfurization
HPLC	High Performance Liquid Chromatography
IL	Ionic liquid
MBR	Membrane Bioreactor
MF	Microfiltration
MWCO	Molecular Weight Cut Off
NADES	Natural Deep Eutectic Solvents
NDIR	Non-dispersive Infrared
NF	Nanofiltration
NMR	Nuclear Magnetic Resonance
NOM	Natural Organic Matter
OSN	Organic Solvent Nanofiltration
PAH	Polycyclic Aromatic Hydrocarbon
PEG	Polyethylene Glycol
PES	Polyethylene Sulfone
PI	Pre-treatment Index
PIL	Protic Ionic Liquids
RO	Reverse Osmosis
$ScCO_2$	Supercritical Carbon Dioxide
SEM	Scanning Electron Microscope
SPE	Solid Phase Extraction

SRNF	Solvent Resistant Nanofiltration
TGA	Thermogravimetric Analysis
THEDES	Therapeutic Deep Eutectic Solvent
TOC	Total Organic Carbon
UF	Ultrafiltration
UV-Vis	Ultraviolet Visible Spectroscopy
VRF	Volume Reduction Factor

1. INTRODUCTION

Ascending world population leads to higher energy requirement and environmental problems in terms of carbon dioxide emissions due to increasing consumption of earth’s crude oil resources. Thus, utilization of biomass in the place of fossil fuels for the purpose of sustainable and renewable energy production has recently drawn attention. (Loow et al., 2017, Lynam, Kumar and Wong, 2017) In this direction, lignocellulose-based biomass is considered as a suitable resource due to its high availability in the nature which serves the purpose of sustainability. Therefore, gaining advantage from lignocellulose originated biomass waste by means of recycling or composting is of importance. Abundance of lignocellulose-based biomass which is reasonably cheap makes it to be considered as an affordable source compared with other renewable means such as crops which has a disadvantage due to its edibility. These biomasses which comprised of cellulose, hemicellulose and lignin are obtained mainly in energy crops, residues of forest industry and wastes originated from agriculture. Their interest is increasing due to its potential to provide benefits of biomass usage by biochemical means especially in Europe. For this purpose, utilization of ionic liquids (ILs) to break the bonds of lignocellulosic biomass has gained importance instead of the use of conventional thermochemical processes which are comparably more expensive. The reason behind this decision lies on attractive properties of ILs, i.e., tuneability, non or very low volatility. However, non-biodegradability, toxicity and expensiveness of ILs makes its utilization less attractive and tend towards sustainable options. Just then, utilization of deep eutectic solvents (DESs) come into play due to being environmentally benign, although their usage is still not widespread. (Loow et al., 2017)

Deep eutectic solvents (DESs) are type of mixtures of which melting point is lower than its constituents which are hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs). This system is obtained from two different solid-state components under eutectic temperature conditions until a thermal equilibrium is achieved. Due to wide range availability of possible HBDs and HBAs in different molar ratios, DESs systems are considered as tuneable. Other properties of DESs such as having a low melting point makes them to be a good option for biocatalytic reactions since maintaining the liquid state of matter is of importance during biocatalytic reactions. DESs are famous for their non-flammable and considerably low volatile feature which is an advantage over volatile organic solvents that enables secure process, since their constituents are mostly solids or uninflammable liquids. Most importantly, easy synthesis procedure which does not need any purification step and abundancy of DES constituents at a cheaper price, makes their utilization considerable. (Xu et al., 2017) Biodegradability and biocompatibility of DES are one of the reasons behind popularity of its utilization lately. DESs which are type of ILs have an advantage over ILs while not possessing the drawbacks of it such as non-readily available expensive constituents, hard preparation steps, non-biodegradability and toxicity. (Kroon, Francisco Casal and van den Bruinhorst, 2013) Due to the beforementioned features of DESs, they have been utilizing for lignocellulosic component extraction from biomass (Škulcová et al., 2016). Recovery and recycling of utilized DES is of importance after extraction of desired components, in terms of environmental and economic aspects of the processes by reducing the cost and required amount of chemicals within the process (Kim et al., 2018).

Due to beforementioned economic and environmental reasons, recycling and recovery of DES or ionic liquids is a matter of importance in which studies have been worked on. Although there are several possible recovery technologies of ILs such as distillation, extraction, adsorption, and induced phase separation, studies are on the side of utilization of membrane technology due to lower energy consumption and solvent requirement. (Mai, Ahn and Koo, 2014) While certain studies focus on recycling of DES from pre-treated biomass, some specific studies consider DES recycling from wastewaters by membrane technologies. According to a study done by Haerens et al. (2010), recovery of DES which comprised of choline chloride and ethylene glycol in a molar ratio of 1 to 2 respectively from wastewaters by using membrane processes where pressure is the driving force (Nanofiltration, Reverse Osmosis and Pervaporation) have been performed. However, it has been concluded that for nanofiltration and reverse osmosis membranes, osmotic pressure has a remarkable adverse effect on the process which causes very low flux and permeability which results maximum DES recovery of 30% of the volume. Additionally, it was concluded that pervaporation which has been used as an alternative requires a large surface area that can lead a costly process. (Haerens et al., 2010) Based on another study performed by Abels et al. (2011), utilization of nanofiltration membranes (Desal DK, Desal DL and Starmem 240) for purification of ionic liquids from saccharide products has been researched. Results were proving that for Desal membranes at lower IL concentration purification of ionic liquids is possible. At higher IL concentrations, membrane processes are not effective in terms of both purification and permeate flux due to created osmotic pressure. However, with Starmem 240 it has been stated that reasonable purification of IL from saccharides was achieved. As another experiment studied by Ho et al. (2017), DES recovery (choline chloride: p-Coumaric Acid (PCA)) from lignin derived phenols were reported as a successful study where switchgrass was used as a DES treated biomass. For this purpose, an ultrafiltration membrane and evaporation were used consecutively where membrane usage was aimed to purify DES solution from lignin and evaporation was used to separate volatile species from DES. It has been also stated that with this recovery method, purified DES can be reused up to three cycles. However, type of ultrafiltration membrane used in this study and concentration of recycled DES solution was not mentioned within the article that it cannot stated whether sufficient flux and purification was obtained.

Based on before mentioned first two studies, having a very low flux, thereupon observing very low purification efficiency due to existence of high osmotic pressure of the solution were considered as the main insufficiencies of the DES recycling process which should be overcame.

This thesis aims to answer the following questions: 1) How well the spent DES can be purified for reuse with membranes; 2) How well does the purified spent DES dissolve lignin from birch compared to the virgin one. Thus, main purpose of this study is to discover a proper type of membrane or membranes which will show sufficient purification efficiency for the spent DES solution at a satisfactory concentration enough to be purified to enable recycling and reuse of purified DES during the process. For this study, DES prepared from choline chloride and lactic acid with the molar ratios of 1 to 9 respectively has been preferred to be used because of its high efficiency towards lignin dissolution during treatment of birch wood.

LITERATURE REVIEW

2. Deep Eutectic Solvents (DES)

Deep eutectic solvents are formed by the self-association of at least two components as hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) which results the formation of an eutectic mixture with a melting point which is lower than the both of its constituents. Representation of a binary mixture which employs a eutectic point which is observed at the intersection of eutectic temperature and eutectic composition is depicted in Figure 1. (Fischer, 2015) DES constituents can also be classified as Lewis acid or Bronsted acid for HBD and Lewis base or Bronsted base for HBA. Despite that Van der Waals forces takes place as an intermolecular interaction between HBA and HBD, dominant interactions are determined as hydrogen bonds as an intramolecular force. This dominant interaction has a key role to determine the properties of the synthesized DES. For instance, strong hydrogen bonds which can be resulted from HBD's ability to be acidified, its structure and interactions within, indicates higher melting point and viscosity for the prepared DES. The reason of that why DES shows a lower melting point than its individual constituents is due to a decrease in hydrogen bonds and energy between the interacted species. (Tomé et al., 2018, Fischer, 2015)

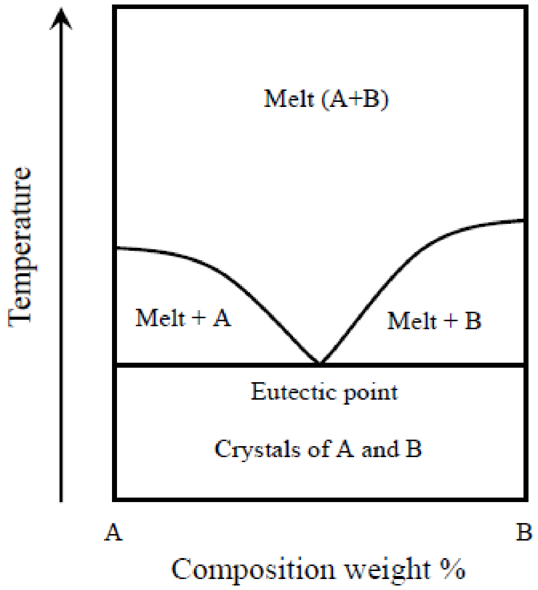


Figure 1: Binary mixture's phase diagram (Fischer, 2015)

Choline chloride (ChCl) is used as the most common HBA in DES preparation. Many studies have been performed for the DES composed of choline chloride and urea as the main components in a ratio of 1:2 (Abbott et al., 2002, C. Gutierrez et al., 2009, Stefanovic et al., 2017, Tomé et al., 2018, Zhekenov et al., 2017). However, focus of this study is in the utilization of DES composed of choline chloride and lactic acid in the molar ratios of 1 to 9 respectively, due to its remarkable lignin extraction efficiency at 60℃ as 59 wt% (van Osch et al., 2017). General representation of DES formation where Choline chloride acts as a HBA and alcohol acts as a HBD is displayed in Figure 2 (Tomé et al., 2018).

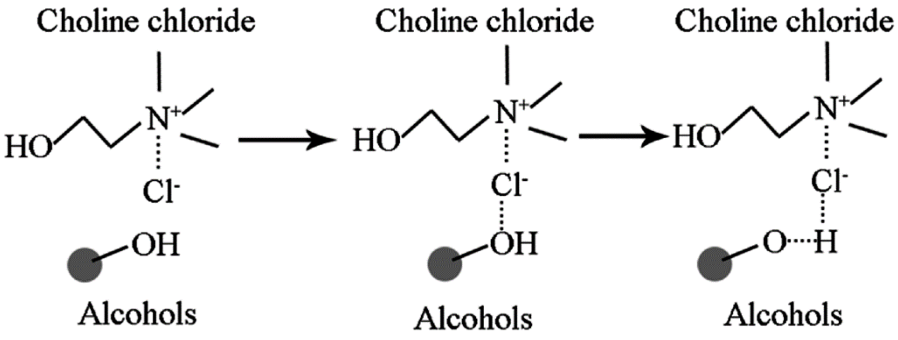


Figure 2: DES formation representation (Wu et al., 2017)

Widely utilized HBAs and HBDs for the purpose of eutectic solvent formation are represented in Figure 3 (Tomé et al., 2018).

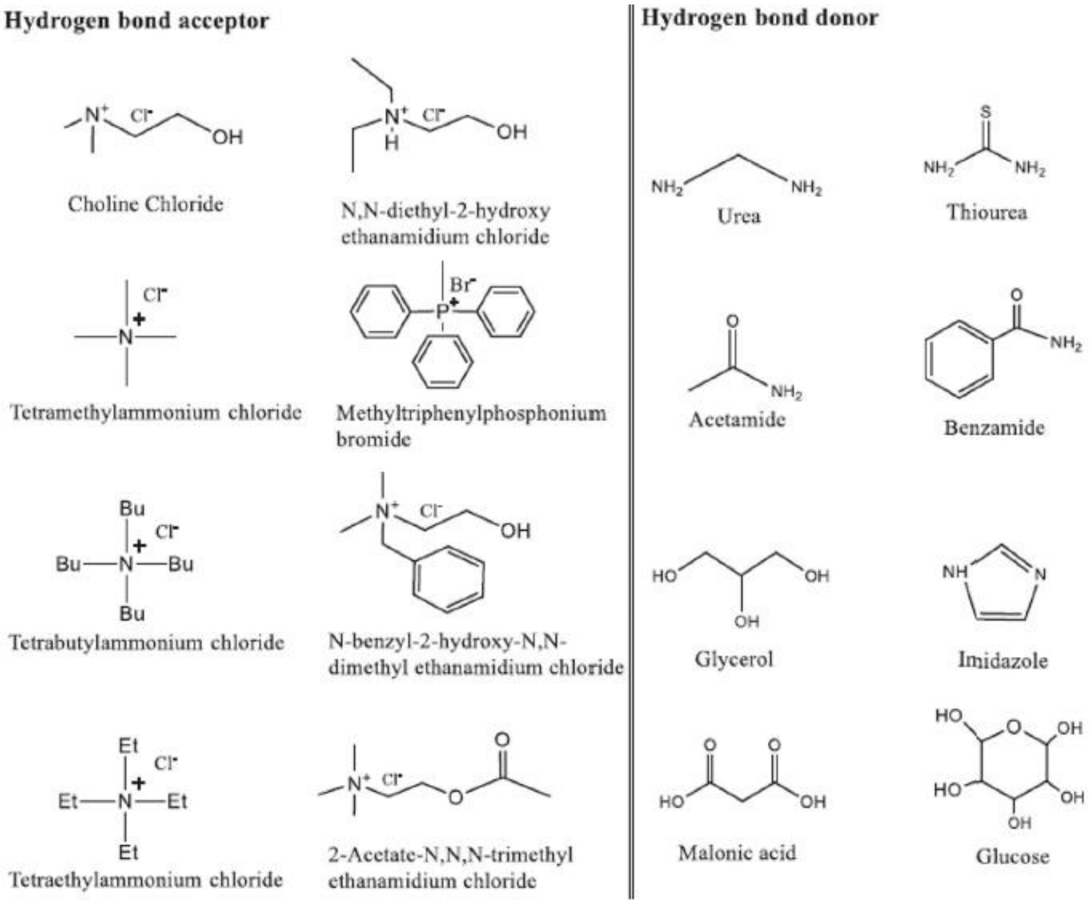


Figure 3: Commonly used HBDs and HBAs in formation of DES (Tomé et al., 2018).

DES preparation is a simple procedure which requires only mixing of HBA and HBD with each other without having any purification steps (Provides, n.d.). Purity of the formed DES depends on purity of the DES constituents (Fischer, 2015).

HBA and HBD groups can form the eutectic mixtures with different combinations. DESs can be classified into four main categories based on properties and behaviour of eutectic solvents as follows; Type I (quaternary salt and metal halide), Type II (quaternary salt and hydrated metal halide), Type III (quaternary salt and hydrogen bond donor) and Type IV(metal halide and hydrogen bond donor) (Tomé et al., 2018). The DES formed from choline chloride and lactic acid in a ratio of 1:9 can be classified as the Type III. The DESs in this group gain attention because of their ability to dissolve variety of transition metals, chlorides and oxides. Utilized HBDs for Type 3 are usually amides, carboxylic acids and alcohols. (Smith, Abbott and Ryder, 2014)

Eutectic solvents can be classified as Natural deep eutectic solvents (NADES) and therapeutic deep eutectic solvents (THEDES) due to their special properties and high applicability possibilities (Tomé et al., 2018). NADES are eutectic mixtures which consist of large amount of metabolites in cells that have a crucial importance in terms of biological activities. One of the most important specialty of NADES is their potential to form a third liquid phase in living cells apart from water and lipids. (Choi et al., 2011) In fact, it has been studied that NADES can be considered as an alternative to water to dissolve water insoluble matters in living cells, due to better dissolution properties of NADES (Dai et al., 2013). As the other classification, THESES are eutectic mixtures which form bioactive systems where one of the eutectic components is an active pharmaceutical ingredient (API). Advantage of THESES especially in pharmaceutical industry is due to their potential to enhance solubility and permeability of drugs. (Aroso et al., 2015)

3. Properties of DES

Although DES properties can be tailored depending on each specific DES types based on their utilization purpose, it is possible to mention general properties of deep eutectic solvents (DES). These properties can be tuned by altering ratio and nature of DES components, water content and the temperature. These properties are given in Table 1. (J.G.P. van Osch et al., 2017, Tomé et al., 2018)

Table 1: Physicochemical properties of DES.

General DES Properties		
Easy and simple preparation	Low vapor pressure	Low toxicity
Good dissolution properties	Low volatility	Biodegradability
Rich component range	Non-flammability	Environmentally friendly
Cheap and available raw material	Dipolar nature	Biocompatibility
No requirement for purification	Chem & thermal stability	Low melting point
Water compatibility	High solubility	Tuneability

4. DES Preparation

Deep eutectic solvent (DES) is prepared as a result of different HBD and HBA molecules chemical combination where different molar ratios are applied. DESs which are considered as a sub-class of ionic liquids (ILs) are much easier to prepare compared to conventional ILs, since they do not require any excessive purification steps. Preparation method can be either heating, vacuum evaporating, freeze drying or grinding. However, the most preferred method is heating when continuous mixing takes place during preparation. (Lynam, Kumar and Wong, 2017, van Osch et al., 2017)

4.1 Heating

In preparation of DES with mixing under heating no solvent addition is required. By this way, purification steps could be avoided which leads to an economic and an eco-friendly process compared with conventional organic solvents. (Lynam, Kumar and Wong, 2017, van Osch et al., 2017)

4.2 Vacuum Evaporation

As another preparation method for DES, vacuum evaporation includes the step where components which are dissolved in the water are evaporated at around 50℃ under vacuum conditions. Resulting mixture is exposed to drying within a desiccator with silica gel. This process continues until to be sure about no alteration in the sample mass is observed. (van Osch et al., 2017, Jeong et al., 2015)

4.3 Grinding

In this method, grinding of two solid components in a mortar until they reach a homogeneous apparent is performed. This formation of a homogeneous liquid actualizes in the atmosphere of a nitrogen. (van Osch et al., 2017, Jeong et al., 2015)

4.4 Freeze-drying

The freeze-drying method consists of dissolution of HBD and HBA separately in water to get a solution with a solid content of 5%. After that, the prepared solutions are mixed, frozen and freeze-dried respectively until homogeneous solution is formed. Freeze drying method can be considered as advantageous DES preparation method since it enables preparation of several different DES types at once, as well as employing of low process temperatures which prevents degradation of thermally sensitive components. (van Osch et al., 2017, Jeong et al., 2015)

5. Comparison of DES with Ionic Liquids (ILs)

Although deep eutectic solvents (DESs) and ionic liquids (ILs) have similar properties, DESs have an advantage over ILs in several aspects. For instance, one of the most important benefit which can be obtained by DESs utilization over ILs is the scale up possibility. The reason behind this is due to high cost, toxicity, poor biodegradability and limited biocompatibility of ILs which would lead to issues with its sustainability. As another disadvantage of ILs in terms of big scale applications, being not so environmentally friendly can be given. Contrary to ILs, cheap raw material availability, being environmentally friendly due to having good biodegradability, biocompatibility and sustainability, are the main reasons which makes DESs suitable for large scale utilizations. (Jeong et al., 2015)

In terms of preparation, DESs have an advantage over conventional IL, because of simple preparation step mostly by heating and mixing, in addition purification steps are not often required, while ILs require complicated preparation steps in terms of synthesis and purification which makes ILs costly. (Jeong et al., 2015, Rodriguez, Molina and Kroon, 2015)

According to intermolecular forces which dominates within the compounds, ILs have stronger interaction by employing ionic bonds compared to DESs where hydrogen bonding is observed as the major force. It can be concluded that since stronger interaction between molecules leads to higher melting point, DESs have an advantage over ILs in terms of also this aspect. Because due to weaker molecular interactions of DESs compared with ILs, DESs have lower melting points which results in mixtures that are liquid in room temperature which are easy to handle, although individual melting points of the components are much higher. Choline chloride and urea mixture in a ratio of 1:2 can be given as an example where individual melting points of choline chloride and urea are 302 °C and 133°C respectively, while the melting point of the eutectic mixture is 12°C. (Jeong et al., 2015, Abbott et al., 2002)

6. Application Areas of DES

Deep eutectic solvents can be used in several different applications for different purposes as described in Table 2.

Table 2: Application areas of DESs

Application Areas	Advantages and Roles of DESs
Organic Synthesis, as a catalyst and reactant[a]	Non-toxicity of DESs
Electrochemistry[a]	As a solvent for metal deposition due to their high capability to dissolve metals
Biocatalysis[a]	Increased catalytic activity and mass transfer in biotransformation
Chromatography[b]	For separation of target compounds from natural products, as a novel phase additive to increase resolution and decrease peak tailing
Aromatic Removal from Chemical Products[b]	Enhanced aromatic removal by extraction or micro-extraction to decrease aromatic's adverse health effects on humans
Extraction of Bioactive Compounds[b]	As a replacement of organic solvents in extraction to lead more environmentally friendly process
Aromatic Nitrogen Compound Removal[b]	In order to improve fuel quality

[a](Fischer, 2015), [b](Li and Row, 2016)

7. Importance of DES Recycling

Attenuation of climate change is a matter of issue which come into prominence recently due to incremental carbon dioxide and methane emissions. Therefore, it is aimed to reduce or replace the major sources of the emissions which is defined as fossil fuel utilization. In this sense, requirement of a new sustainable and renewable mean of biomass utilization where lignin is the main focus due to its ability to be purified followed with a conversion into a biofuel has gained a significant importance. Thus, an eco-friendly separation method is required for lignocellulosic compounds to enable their conversion into desired fuels and chemicals. In this regard, deep eutectic solvents (DES) which does not have the disadvantages of ILs while keeping the advantages of higher lignin extraction efficiency and cellulose dissolution, have gained importance for cellulosic biomass compounds extraction from their sources as a green alternative. (Lynam, Kumar and Wong, 2017)

As a green alternative point of view, both for ILs and DES, recycling has a significant importance. For ILs reducing the cost of ILs preparation is the main reason while for DES the reason is potential of their recycling to further reduce the synthesis cost, regardless of the low-cost preparation. Besides, DES recycling is important in terms of green and sustainable chemistry ideology by preventing utilization of the same amount of solvent each time for starting up. Additionally, environmental concerns lead consideration of ILs recycling due to their non-biodegradable and highly toxic feature which can cause serious problems especially during their disposal to environment. (Mai, Ahn and Koo, 2014)

8. Comparison of Lignin Isolation Efficiency of Different DES Types

Lignin extraction efficiencies of DES, which consists of different chemical components, during the process where hemicellulose degradation and removal also takes place, has been a research subject. This mentioned research subject has been gained importance recently due to special properties of DESs and their ability to break ether bonds. Three different DES types as choline chloride: lactic acid (ChCl:Lac), choline chloride: urea (ChCl:U) and choline chloride: glycerol (ChCl:Gly) has been studied where raw material of lignin extraction is willow which has high density, fast growing rates. They studied the effect of molar ratios of the components, temperature and residence time on the isolation efficiency. In terms of extraction efficiency, ChCl:Lac in a molar ratio of 1:2 has considerably higher yield in an experiment which is performed at temperatures from 90℃ to 120℃ during 6 hours compared with ChCl:U and ChCl:Gly at the same molar ratios. As it is represented in Figure 4 (Li et al., 2017), while yields are observed around 52%, 9% and 4% respectively for ChCl:Lac, ChCl:U and ChCl:Gly, positive effect of temperature increase on extraction efficiency can also be observed. This results can be due to high hydrogen accepting ability and polarity of ChCl:Lac which results in enhanced lignin dissolution. (Li et al., 2017)

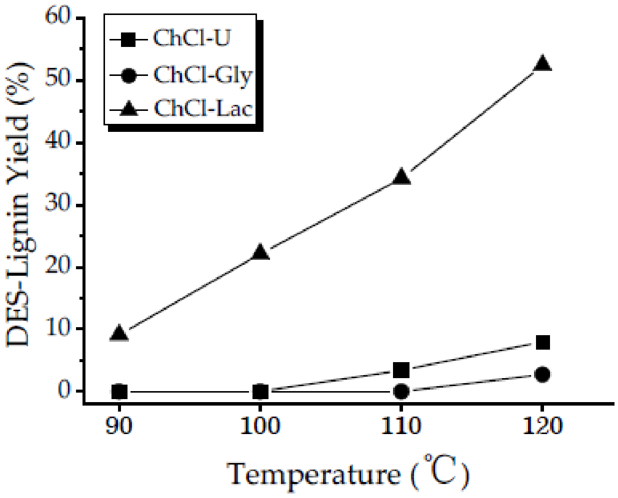


Figure 4: Lignin yield of different DES types *(Li et al., 2017)*

Rather than having various yield values of different DES types, molar ratio alterations has also considerable effect on the extraction yield depending on the utilized DES components. For instance, for ChCl:Lac, as lactic acid concentration increases better results have been observed. The best result as 55% has been obtained at the ratio of 1:10. In addition to the effect of molar ratios, influence of residence time has also been observed, as a result, highest yield was observed as 91.8% at the experiment which lasted 12 hours. Li et al. (2017) concluded that 91.8% lignin extraction efficiency can be obtained by utilizing ChCl:Lac in a molar ratio of 1:10 as solvent for the treatment of willow for 12 hours at 120°C. By considering sufficient efficiency results compared with other DESs, ChCl:Lac has been decided as the research subject of this study.

9. Possible DES Recycling Methods

Only few studies have been published related to purification and recycling of DES (Jeong et al., 2015, Abels et al., 2012, Haerens et al., 2010). Therefore, also the studies concerning recycling of ionic liquids are reviewed below. However, it should be kept in mind that recovery of DESs and ILs can be different, due to difference in their preparation methods which leads to dissimilar properties of these solvents. Beforementioned IL recovery methods i.e., lyophilization, adsorption, distillation, liquid-liquid extraction, induced phase separation, crystallization and membrane technology, are categorized in Table 3 according to their purpose in terms of water removal, lignin removal and IL recovery from aqueous solutions. Most important selection criteria of recovery methods have been decided as water and lignin removal, since the feed solution which needs to be purified which is diluted DES treated birch solution i.e., spent DES, contains water and lignin. By considering all the ILs recovery methods, it can be concluded that more than one recovery techniques can be utilized in order to achieve better recovery efficiency. For instance, after membrane utilization which can remove remarkable amount of water and lignin, adsorption can take place for further purification of spent DES solution from lignin.

Table 3: Summary of ILs recovery techniques reported in literature.

Recovery Methods	Water Removal	Lignin Removal	ILs Removal from Aqueous Solutions
Lyophilization	+		
Adsorption		+	+
Distillation	+		
Liquid-liquid Extraction		+	
Induced Phase Separation		+	
Crystallization			+
Membranes	+	+	

9.1 Lyophilization

Lyophilization or freeze drying is a process where frozen solvent or ice removal takes place during sublimation or desorption process together with the bounded water molecules removal. During the process, since very low temperature values are used, no alterations in the properties and the appearance of the dry product is observed. Especially the materials which are sensitive to heat applied processes are protected by this mean. Since lyophilization occurs during sublimation it is important to understand sublimation process. As it is well known, it is a process where direct phase transition from solid state to gas state takes place without conversion of the compound into the liquid form. This change of state requires energy utilization and very low-pressure conditions. Lyophilization process which is represented in Figure 5 (Barley, n.d.) and actualizes during sublimation can be summarized under following steps as freezing, vacuuming (until reaching a value below the water triple point) and drying which causes sublimation respectively. (Barley, n.d.)

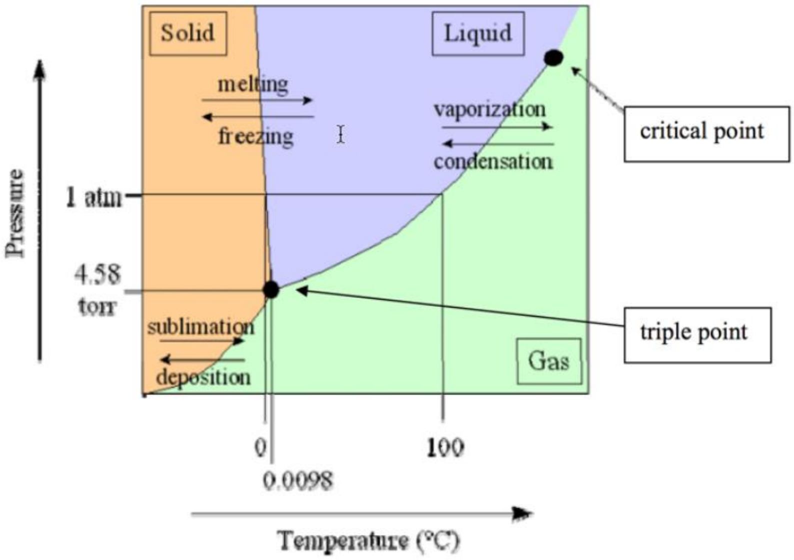


Figure 5: Phase transition graph (Barley, n.d.)

In DES recycling, for specific compound i.e., ginsenosides, recovery lyophilization takes place during the solid phase extraction (SPE) process after washing step under vacuum conditions. Lyophilization process is ceased and DES regeneration is completed when any alterations in mixture weight is not observed. This regeneration process can keep repeated as long as remarkable DES efficiencies are obtained during the process. For instance, in ginsenosides extraction process where DES is used as an extraction medium, it has been observed that DES can be utilized three times after its recycling with extraction efficiencies of 91.1%, 85.4% and 82.6% respectively for after first, second and third recycling. It has been stated that, this experiment is the first in its area which enables DES recycling by a simple method i.e. lyophilization from its solution. (Jeong et al., 2015)

9.2 Adsorption

Adsorption of ionic liquids (ILs) from aqueous solutions is a developing research area. In this sense utilization of activated carbon (AC) during adsorption has been performed by several researchers, although AC is mainly utilized for purification of water from its organic constituents. However, results were not in the favour of AC usage due to their low efficiency. Due to the nature of AC, it is more effective for small, non-polar compounds removal compared with the ones which has ionic and polar nature like ILs. Parameters which affect adsorption efficiency are examined based on ILs which consists of imidazolium. According to Palomar et al., 2009, sizes, hydrophobicity, and nature of ions in ILs and surface properties of AC are the main factors which influence the adsorption efficiency. Hydrophobic ILs adsorption on AC performs well as such 1g of IL adsorption for one gram of adsorbent actualizes, when low concentration polar groups occupied microporous AC on its surface is utilized (Lemus et al., 2012). While adsorption of hydrophobic ILs is affordable in terms of environmental aspect and sufficiently efficient, hydrophilic ILs' adsorption efficiency has a potential for improvement with a modification on AC surface in terms of amount and properties of oxygen groups. As an example, high amount of hydroxyl group present on the AC surface, will enhance interaction between hydrophilic ILs and the membrane surface and will increase the adsorption. (Palomar et al., 2009)

Although AC utilization is not in favour of hydrophilic ILs adsorption as it was mentioned previously, it is crucial in terms of environmental aspect, since hydrophilic nature enables easy release into environment by means of water. In order to prevent this situation, salting out by inorganic salt addition is performed such as Na_2SO_4 to improve hydrophilic ILs adsorption onto AC. (Neves et al., 2014)

There are also reports about the use of carbonaceous material other than AC. They are utilization of functional carbonaceous material (FCM) which is more advantageous than AC. The fact that being as effective as AC with a smaller surface area, and their ability to be regenerated and recycled at least three times, makes FCM utilizations attractive. Cation exchange resin utilization for ILs recycling by using liquid chromatography is another method. This method uses ion change resin as a stationary medium for liquid chromatography where glucose, xylose and ILs recycling efficiencies are observed as 94%, 86% and 92% in the given order based on ILs purification from a biomass hydrolyzate mixture which is acid catalysed. (Qi et al., 2013)

Expensiveness of ILs leads to put more focus on their regeneration to have an economically feasible process. In concern with this, it has been reported that AC can be regenerated with acetone to be sure about consistently sufficient adsorption efficiency. (Torres, 2012)

All in all, adsorption method can be considered as relatively easy to perform, however, requirement of desorption solvents makes other recovery methods mentioned in this section 9 more attractive. (Mai, Ahn and Koo, 2014)

9.3 Distillation

Despite of the discussions which state that ILs cannot be usually distilled due to their non-volatile nature, it has been proved that several ILs can undergo a distillation process under low pressure without causing any decomposition in IL structure (Earle et al., 2006). For compound which has low boiling point and high thermal stability, distillation is considered as the simplest method to recover ILs from them. There are many different applications of distillation for volatile compound removal such as vacuum evaporation, column and molecular distillation. Distillation which requires high energy consumption is usually preferred to be used after processes like decantation, filtration, extraction etc. to remove remained contaminants or compounds which could not be extracted. (Wasserscheid and Welton, 2008, Reinert et al., 2012) For instance, distillation of volatile impurities from cellulose acetylation solution which is homogeneous, enables utilization of IL up to 5 times while preserving the properties of the aqueous system. Additionally, processing time and energy efficiency of the process can be improved with the usage of microwave heating. (Huang et al., 2013)

It has been stated that while distillation at high temperature without causing any decomposition on the aprotic ILs is possible under vacuum conditions, for protic ILs, at the same conditions distillation causes decomposition. While mentioned aprotic ILs refers conventional ILs which usually contains cations like imidazolium or pyridinium and anions like Cl^-, Br^-, BF_4^- and PF_6^-, beforementioned protic ILs refers ILs which are usually formed as a results of neutralization reactions where a transfer of proton between Bronsted acid and base actualize. (Peric et al., 2013, Greaves et al., 2006) However, studies proved that one of the commonly distillable ionic liquids is given as protic ionic liquids (PILs) which has an easy synthesis during the proton transfer from Bronsted acid to Bronsted base that results in formation of hydrogen bonded network (Kirchner, 2013). As a specific example methylpyrrolidinium acetate can be shown for protic ILs. Second IL which can undergo a distillation process easily is dialkylammonium carbamate salts. Dimethylammonium dimethlycarbonate (DIMCARB) can be given as an example. For instance, DIMCARB which is used as a reaction medium for monoarylidene and macrocyclic compound production is removed from the product by utilizing distillation method. (Kirchner, 2013, Greaves et al., 2006)

9.4 Liquid-liquid Extraction

Extraction is a suitable method to purify ionic liquids (ILs) which contains non-volatile and thermally sensitive products that cannot be separated by distillation. Variety of solvents including ILs can be purified from their hydrophilic content by water addition due to their hydrophobic nature. However, non-volatile and thermally sensitive components within the ILs are separated by utilizing an organic solvent. Mostly used solvents are diethyl ether and hexane. (Zhao, Xia and Ma, 2005)

A study has been performed to purify a biomass which is pre-treated with IL from its components such as oleophilic solutes, short carbohydrate chains and lignin by using liquid-liquid extraction in a two-stage process. Utilized mixture as an organic solvent in this experiment consist of acetone, 2-propanol and small quantity of water. Recovery efficiency of the IL has been observed as 89% at the end of the process. (Dibble et al., 2011)

ILs are utilized as an extraction media for metal ion extraction due to their consideration as a green solvent for heavy metal separation and pre-concentration. Thus, this method has gain interest in recent years. (Zhao, Xia and Ma, 2005, Wei, Yang and Chen, 2003) Due to contamination of the IL during the process mostly by acidic compounds, purification of IL for its recycling is required. It can be performed by stripping or extraction by organic solvent. (Wei, Yang and Chen, 2003) As its advantages, simplicity, no requirement for any complex process equipment, selectivity and flexibility can be given for the extraction process. On the other hand, utilization of organic solvents may not be considered as environmentally friendly, when we consider their release into environment, especially the toxic ones. (Mai, Ahn and Koo, 2014)

As it has been mentioned before, utilization of organic solvents such as diethyl ether, hexane and ethyl acetate prohibit assumed green aspect of ILs due to involved organic solvent usage within the method. Thus, another solution which does not include any organic solvent usage such as supercritical CO_2 ($ScCO_2$) which is in the liquid state is considered as a more environmentally friendly option. (Zhao, Xia and Ma, 2005) Usage of $ScCO_2$ as an extraction solvent has many advantages such as its non-toxicity, non-flammability, eco-friendliness and non-expensiveness (Blanchard and Brennecke, 2001). During its utilization, two phase system formation is observed due to exact opposite feature of $ScCO_2$ which is non-polar and volatile and ILs which is polar and non-volatile. Purification of ILs by $ScCO_2$ usage takes place during the transformation of $ScCO_2$ soluble organic compounds from ILs to

$ScCO_2$, since only the organic compounds can dissolve in $ScCO_2$ not ILs. (Zhao, Xia and Ma, 2005) Special properties of $ScCO_2$ avoids any cross-contamination both in the gas phase and in the ILs (Blanchard et al., 1999). Thus, ILs recovery is accomplished as an effective process which displays purification results higher than 95% (Blanchard and Brennecke, 2001).

9.5 Induced Phase Separation

As another approach to purification of ILs from aqueous solutions is to add salt to form aqueous biphasic system (ABS). Addition of salt leads to formations of two phases where the fluid as top phase is rich in IL and bottom phase is rich in salt. Recovery of hydrophilic IL from its aqueous solution is performed with an addition of water-structuring salt K_3PO_4 where the higher salt concentration results in higher efficiency and thus purer IL in the top phase. (Gutowski et al., 2003) Recovery efficiencies of IL i.e., 1-Allyl-3-methylimidazolium chloride, by different potassium salts of same concentrations from the aqueous solution of the IL with salt and water have been compared, and results are represented in the descending order for K_3PO_4, K_2HPO_4, K_2CO_3 (Deng et al., 2009). Among these salts, highest recovery efficiency of 96.8% is obtained for K_2HPO_4 of 46.48 wt% (Deng et al., 2009). As another salt kind, sodium salts such as Na_3PO_4, Na_2CO_3, Na_2SO_4, NaH_2PO_4 and NaCl are investigated. Resultingly, 16.94 wt% of Na_2CO_3 displays the highest extraction efficiency as 98.77%. (Li et al., 2010) As one of the conclusions, an increase in the salt concentration enhances recovery efficiency of the process and results in lignin removal efficiency (delignification) (Deng et al., 2009).

Besides salt addition, carbohydrate addition has also been studied, however results were not as satisfying as before. For instance, 74%, 72%, 64% and 61% recovery efficiencies are observed with sucrose, xylose, fructose and glucose addition respectively. Additionally, it should be kept in mind that in terms of large scale applications, organic matter utilization will increase its presence in the aqueous solutions. (Wu, Zhang and Wang, 2008)

Aluminium salt utilization such as $Al_2(SO_4)_3$ and $AlK(SO_4)_2$) is another performed study which shows significantly sufficient recovery and removal efficiencies of ILs from aqueous solutions which contains cations consists of imidazolium, pyridinium and phosphonium. Effectiveness of this salts can be easily understood from their minimum IL purification efficiency of 96%. In fact, in bigger scale applications, 100% efficiency can be obtained. (Neves, Freire and Coutinho, 2012).

In brief, simplicity, effectiveness and being economic are the advantages of the ABS formation process, while large amount of inorganic content in the salt rich bottom phase which can create an environmental risk is the major concern of the process. (Mai, Ahn and Koo, 2014)

CO_2 addition into ILs which forms ABS is another studied approach. Due to nonpolar nature of CO_2 which is not suitable for ion dissolution, solvation ability of mixture decreases while IL rich phase forms. Meanwhile organic rich phase where CO_2 is soluble inside is formed. (Scurto, Aki and Brennecke, 2002) Dissolved non-polar and low-pressure CO_2 causes a decrease in the dielectric constant which results a formation of a new phase which is free of IL, while IL forms another liquid phase separately. Thus, purification of organic phases from ILs and ILs recycling and recovery are enabled. Utilization of CO_2 addition for ILs recovery takes places usually when IL present in the mixture as a minor component. (Scurto, Aki and Brennecke, 2003) CO_2 induced purification method is considered as a green process. However, costly process equipment utilization and skilled operator necessity are the two main factors which inhibits operation easiness. (Mai, Ahn and Koo, 2014)

ILs recovery from aqueous solutions take place by three phase formations as IL rich phase, water rich phase and CO_2 rich vapour phase which is dissolved within small quantity of water are obtained where CO_2 is added into the solution. This approach is utilized for both hydrophilic and hydrophobic ILs isolation from the aqueous solution. (Scurto, Aki and Brennecke, 2003)

9.6 Crystallization

In ILs purification, crystallization is one of the utilized methods which consists of cooling of a mixture under a specific temperature value where crystal formation is possible. Crucial point in this method is the temperature at which the mixture will be cooled to. After crystal formation, separation of crystals from the mixture can be performed by filtration under vacuum conditions. For instance, Troter et al. (2016) indicated that IL can be purified from the organic solvent where temperature to be cooled down is determined as 20℃. Antisolvent addition is another way to perform crystallization of ILs (Hayyan et al., 2010).

9.7 Membranes

A membrane is simply defined as a thin barrier through which the permeation of solute and solvent molecules actualizes due to mass transfer. During the membrane process, rate of rejected components by membrane is determined by mostly component’s shape and size, while rate of transferring permeable components through the membrane is determined by driving force. (Interstate Technology & Regulatory Council, 2010)

Compared with other separation methods membrane technology has advantages in terms of less energy and solvent utilization (SIRKAR, 1997). In terms of ionic liquid (ILs) purification, membrane utilization shows considerably efficient results despite of their low volatile nature unlike some separation techniques such as distillation. (Hinchliffe and Porter, 2000)

Additionally, product purity of the process is crucial since higher purity results in higher operational cost. For instance, while in distillation and infinitely selective molecular sieve membrane process, product purity is commonly determined as 99%, in polymeric membrane separations, purity of the product can be altered and lowered to an acceptable purity level which can decrease the process cost. (Hinchliffe and Porter, 2000)

In compliance with working principle of membrane technology, a proper membrane based on purified liquid properties should be utilized. Thus, by taking the size and nature of the ILs (ionic/neutral or mono/divalent compounds) into consideration, utilization of nanofiltration (NF) membranes found suitable for this purpose. From the point of view for non-volatile species separation by membranes, two possibilities can be considered. These are; penetration of ILs while observation of non-volatile species retention and just the contrary situation while non-volatile species penetrate, ILs will retain. (Kröckel and Kragl, 2003)

Feasibility of the NF process in terms of purification efficiency based on different membrane materials as polyamide and polyimide has been studied. In this study, removal of saccharides from IL as a feed at various concentrations has been aimed. Overall, ILs purification efficiency is obtained around 80% for both membrane materials, while their performance alters depending on the concentration of the ILs in the feed side. At lower IL concentrations, contamination by saccharide products were observed higher in polyimide compared with polyamide, while at higher IL concentrations, polyimide membranes showed lower contaminant concentration. In general, at higher IL concentrations results were obtained in a pattern to show a decrease in permeability of IL, because of IL’s low permeability and created osmotic pressure difference at that concentration. (Abels et al., 2012)

Organic solvent nanofiltration (OSN) also known as solvent resistant nanofiltration (SRNF) have been used for purification of ILs. (Lim et al., 2017, Han, Wong and Livingston, 2005) Separation efficiencies of specific OSN membrane types (STARMEMTM 120 and 122 membranes) for particular component removal (CYPHOS IL 101 and ECOENG500 in methanol and ethyl acetate) has been observed as over 95% at 30℃ and 30 and 50 bars (Han, Wong and Livingston, 2005).

There are studies which have already been performed for DES purification (Choline chloride: ethylene glycol i.e., Ethaline 200) in a molar ratio of 1:2 by using nanofiltration (NF), reverse osmosis (RO) and pervaporation. Encouraging results were obtain by NF in recovery of ILs from non-volatile products. In this process, IL will permeate through the membrane, while retention of non-volatile products can be observed. For NF and RO membranes it has been observed that osmotic pressure is an important criterion for ion retention and flux efficiency at higher ionic liquid concentrations. Importance of osmotic pressure can be explained by its effect on economic feasibility of the processes where higher osmotic pressure usage requires higher energy utilization which leads an increase in operational cost. Pervaporation is another studied method where process efficiency depends on the interaction between components in the feed side and membrane material as well as chemical potential gradient. Efficiency of pervaporation process was studied and it was proved that recovery of low volatile substances like naphthalene is also possible by pervaporation, besides volatile species separation. In fact, previous studies show efficiency results higher than 99.2% for the recovery of species with a high boiling point. (Schäfer et al., 2001) In one of the performed studies, it has been proved that BMIM PF (1-Butyl-3-methylimidazolium hexafluorophosphate), non-water soluble ionic liquid, can be recovered from various organic solvents and water up to 99.2% by pervaporation. Pervaporation is considered as an alternative method not as the first choice, since its performance is hindered under high water concentration. Even under low water content, observed flux values are not sufficient because of ionic liquid presence which reduces water activity. Additionally, requirement of high membrane surface area makes it less desirable compared with NF and RO. (Haerens et al., 2010)

Purification of IL, Ethaline200 (choline chloride and ethylene glycol with molar ratio of 1:2), from its aqueous solution by different pressure driven nanofiltration and reverse osmosis membranes as well as pervaporation process was studied. Utilized membrane types can be given as follows; FilmTec NF90 (Dow), FilmTec NF270 (Dow) and DK (Geo Osmonics) for nanofiltration, FilmTec 102326 (Dow) and FilmTec BW30-XLE (Dow) for reverse osmosis membranes, PERVAP 1201 for pervaporation membranes. Ion retention efficiencies were observed for two NF membranes as 20% and 88% respectively for Film Tec NF90 and DK (GE Osmonics). Retention efficiencies for two RO membranes were observed as 91.1% and 90.5% respectively for Film Tec 102326 and Film Tec BW30-XLE. As a matter of study effect of flux, retention and recovery ratio and the relation between them has also been studied. Resultingly, it has been concluded that utilization of pressure driven membrane processes was not enough for complete water retention. Thus, they can be put to good use for pre-concentration purpose. For pervaporation membrane PERVAP 1201, relation between the water concentration, flux and selectivity has been represented as increasing water concentration results in an increase in flux while decreasing the selectivity. Representation of utilized membranes for ILs recovery is performed in Table 4. (Haerens et al., 2010)

Table 4: Utilized membranes for ILs recovery
* indicates, retention of methanol, toluene and ethyl acetate

Membrane Type	Membrane	Experimental Pressure (bar)	Manufacturer Ion Rejection (%)	Ethaline 200 Ion Retention Efficiency (%)
OSN	STARME MTM 120-122	30 and 50	-	>95*
NF	Film Tec NF90	20	99 ($MgSO_4$)	20
NF	DK (Ge Osmonics)	30	96 ($MgSO_4$)	88
RO	Film Tec 102326	30	-	91.1
RO	Film Tec BW30-XLE	30	99.5 (NaCl) for BW30	90.5

Electrodialysis (ED) has gained interest in IL purification in the last years where ionic components are selectively separated as a result of a movement towards ion exchange membranes due to applied electrical force. Based on the experiment results where 20 pairs of homogeneous anion and cation exchange membranes i.e., DFG-201 AEM and PEG-001

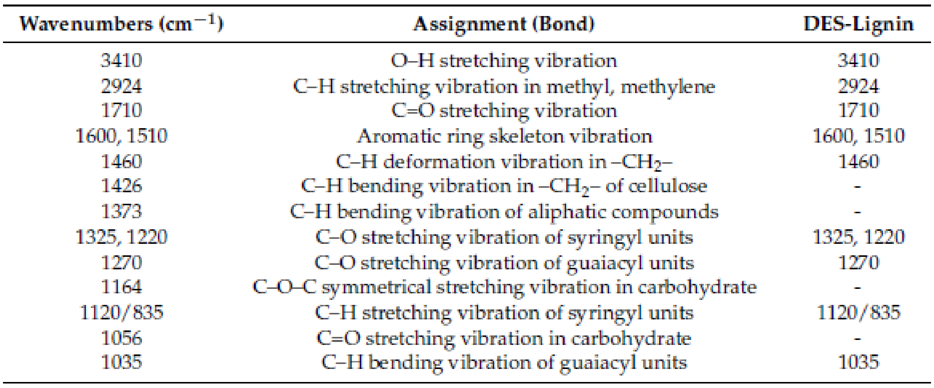
CEM, provided by Zhejiang Qianqiu Group Co., Ltd were utilized, highest recovery efficiency was observed as 85.2% with a current efficiency of 80.9%. Thus, ED can be considered as an effective method for IL purification. Effect of process parameters has been studied to observe the optimal process conditions. For instance, an increase in IL concentration results in a small decrease in current efficiency and recovery ratio. Additionally, an increase in applied electrical force causes a sharp enhancement in efficiency of IL concentration. However, after reaching the maximum value, recovery and current efficiency starts to decrease. As another parameter, effect of volume has been observed as having a linear trend in terms of concentration ratio. (Wang et al., 2012)

Besides all advantages of membrane process, still more understanding such as behaviour of ILs within the aqueous solution or relation between IL and membranes is required. Some studies have been performed in this sense to improve process efficiency by comprehending the chemistry behind the process (Wu et al., 2009). For instance, in order to increase penetration through the membrane, viscosity of the fluid is decreased by addition of ethanol and methanol into ILs (Gan, Xue and Rooney, 2006). Similarly, inorganic salt utilization is performed to reduce agglomerations and retention by membrane (Fernández, Waterkamp and Thöming, 2008). Overall, for better purification results, combination of different membrane processes according to properties of different IL and water mixtures should be performed (Wu et al., 2009).

10. DES Impurity Analysis

10.1 Fourier Transform Infrared Spectroscopy (FTIR)

This analysis is used to determine the presence of hydrogen bonds and any kind of functional groups within the compound (Degam, 2017). Usually, FTIR analysis of DES is performed with a comparison of DES treated biomass i.e., willow, solid residue and pure biomass in order to understand the alteration in the lignin presence within the samples. Observing peaks at specific wavenumbers which indicates presence of specific functional groups as represented in Figure 6 (Li et al., 2017) and specific compounds such as cellulose, lignin, and carbohydrates is one of the most commonly used technique for DES characterization. These peaks are obtained at different wavelengths depending on utilized raw material. For instance, mostly the obtained peaks for solid residue are lack of some peaks which have been previously observed in untreated biomass. This usually, indicates efficient lignin removal from the biomass. Additionally, existence of syringyl units, benzene rings, guaiacyl units, carbohydrates and even small amount of hemicellulose can be determined by FTIR. (Li et al., 2017)



Wavenumbers (cm^{-1})	Assignment (Bond)	DES-Lignin
3410	O–H stretching vibration	3410
2924	C–H stretching vibration in methyl, methylene	2924
1710	C=O stretching vibration	1710
1600, 1510	Aromatic ring skeleton vibration	1600, 1510
1460	C–H deformation vibration in $-CH_2-$	1460
1426	C–H bending vibration in $-CH_2-$ of cellulose	-
1373	C–H bending vibration of aliphatic compounds	-
1325, 1220	C–O stretching vibration of syringyl units	1325, 1220
1270	C–O stretching vibration of guaiacyl units	1270
1164	C–O–C symmetrical stretching vibration in carbohydrate	-
1120/835	C–H stretching vibration of syringyl units	1120/835
1056	C=O stretching vibration in carbohydrate	-
1035	C–H bending vibration of guaiacyl units	1035

Figure 6: FTIR spectroscopy of untreated biomass i.e., willow, sample.

FTIR spectroscopy can be utilized to determine DES pre-treatment efficiency based on cellulose and lignin presence. Calculation of cellulose to lignin ratio (CL) and pre-treatment index (PI), which are represented as CL ratio and PI respectively are two means for this purpose. While CL ratio is calculated of the division of peaks where any cellulose presence observed into the peak where there is lignin, PI is calculated as the ratio of CL ratio of pre-treated sample over CL ratio of raw biomass as it is represented in Eq 1. (Lynam, Kumar and Wong, 2017)

$$PI = \frac{CL\ ratio_{pretreated\ sample}}{CL\ ratio_{raw\ biomass}} \tag{1}$$

Meaning of the pre-treatment index (PI) can be expressed as higher the PI is, higher the cellulose content in the pre-treated sample will be. (Lynam, Kumar and Wong, 2017)

10.2 Thermogravimetric Analysis

As one of the gravimetric analysis methods where alteration of mass during measurements is the key point of the method, thermogravimetric analysis is utilized for characterization of DES (Harvey, 2016). Thermogravimetry is considered under the volatilization gravimetry concept which focuses on decomposition of the sample either in thermal or chemical means, and then measurement of the change in sample’s mass by temperature as represented in Figure 7 (Harvey, 2016, Sivakumar, n.d.). Since, separation of volatile components takes place by this method, it usually is indicated as analysis of volatilization gravimetric methods (Harvey, 2016).

Basis of thermogravimetric analysis is to obtain a thermogram where weight of the sample after its decomposition over temperature is plotted where the process is also called as thermogravimetry. Change in the sample mass is presented as steps in thermogram. By combining thermogravimetry with gas chromatography and mass spectrometry it is even possible to identify specific compounds. (Harvey, 2016)

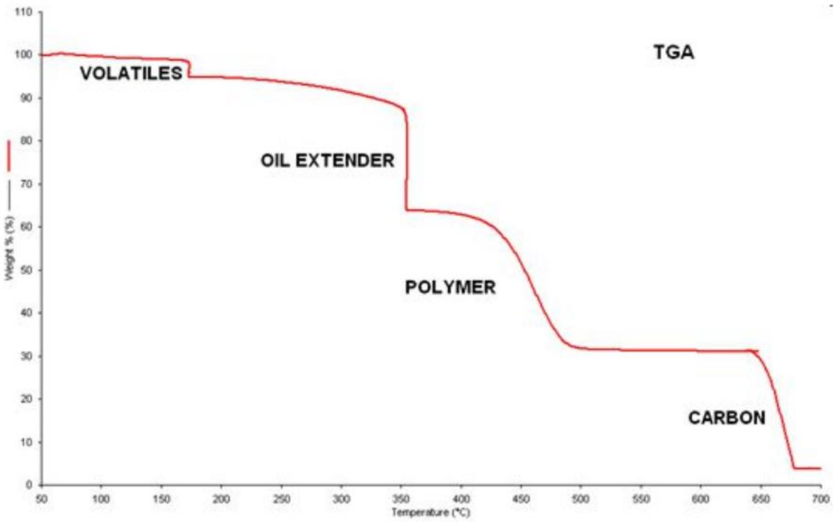


Figure 7: Thermogravimetric analysis graph

Performed thermogravimetric analysis methods (TGA) are aimed to check thermal stabilities of DES and its compounds based on their decomposition temperatures. During the experiments, specific mass loss percentage should be identified at which the decomposition temperatures are measured. Studies carried out by Degam (2017) have proved that thermal behaviour of the DES constituents and DES itself are completely different from each other. (Degam, 2017)

11. MEMBRANE TECHNOLOGY

Membrane technology is defined as a thin barrier in between two sections which controls mass and energy transfer in a special way (Strathmann, 2011).

Depending on the driving force of the process, separation actualizes based on the different criteria such as; pressure difference, concentration difference, differences in electrical potential and temperature difference (Prip Beier, 2007).

11.1 Pressure Driven Membrane Processes

As one of the most common type of membrane separation processes, pressure driven membrane processes such as nanofiltration and reverse osmosis, are mostly based on differences in molecular size. These processes utilize semipermeable membranes. Permeable compounds pass through the membrane and form “permeate”. The concentrated retained molecules in the feed side are called as “retentate”. (Interstate Technology & Regulatory Council, 2010) Basic illustration of a membrane process is represented in Figure 8.

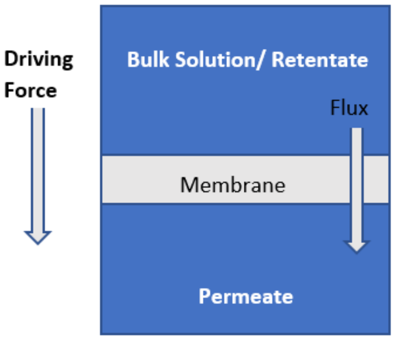


Figure 8: Schematic illustration of a membrane process

Hydrostatic pressure difference between feed and permeate side of the membrane is determined as a driving force in pressure driven membrane processes. As a result of created pressure difference, water permeates through the membrane, while other dissolved components are rejected by the membrane based on their size, shape and charge and form the retentate. Based on retention of the compounds, efficiency of the process in terms of separating rejected and permeated compounds is expressed as in Eq 2. (Van der Bruggen et al., 2004)

$$Re(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

Where C_p is concentration of permeate

C_f is concentration of feed

Re (%) is rejection of the process in percentages between 0 to 100

As an important criterion for pressure drive membrane processes, volume reduction factor (*VRF*) is expressed in Eq 3 (Grandison and Lewis, 2006).

$$VRF = \left(\frac{V_f - V_c}{V_f}\right) \times 100 \tag{3}$$

Where VRF is the volume reduction factor

V_f is volume of the feed

V_c is the volume of the concentrate i.e., retentate

$V_f - V_c$ is the volume of the permeate

Classifications for the pressure driven membrane processes are done based on size, shape and charge of rejected compounds as well as the applied pressure on the membrane. This classification categorizes membranes as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). (Van der Bruggen et al., 2004) Characteristic of all pressure driven membrane processes are represented in Table 5.

Table 5: Characteristics of pressure driven membrane processes

	Microfiltration (MF)	**Ultrafiltration (UF)**	**Nanofiltration (NF)**	**Reverse Osmosis (RO)**
Pore size^b **(μm)**	0.02-4	0.02-0.2	< 0.002	< 0.002
Operating Pressure^b **(bar)**	< 2	1-10	5-35	15-150
Rejected Compounds$^{b, c}$	Particles, clay, bacteria	Particles, bacteria, virus, macromolecules, proteins, polysaccharides	Particles, multivalent ions, macromolecules,	Particles, macromolecules, multivalent ions, monovalent ions (NaCl), small organic compounds,
Separation Mechanism^c	Sieving	Sieving	Sieving, charge of compounds and membrane	Diffusion, charge of compounds and membrane
Configurations^b	Tubular, hollow fibre, spiral	Tubular, hollow fibre, spiral wound, plate and frame	Tubular, spiral wound, plate and frame	Tubular, spiral wound, plate and frame
Commonly used materials^b	Ceramic, Polysulfone (PS),	Ceramic, (PS), Polyvinylidene fluoride (PVDF), Cellulose acetate (CA), polyamide thin film	CA, Polyamide (PA) thin film	CA thin film
Application Areas $^{a, c}$	Removal of colloids, particles, bacteria, for clarification and treatment of waste waters	Removal of macromolecules, bacteria, viruses	Removal of multivalent ions and low molecular weight solutes	Removal of low molecular weight solutes, desalination, production of ultra-pure water

^{a} Prip Beier (2007). ^{b}Interstate Technology & Regulatory Council (2010). ^{c}Van der Bruggen et al. (2004)

As it is expressed in Table 5, nanofiltration and reverse osmosis membranes are much denser compared with microfiltration and ultrafiltration membranes by having comparably smaller pore size (Prip Beier, 2007).

According to Table 5, pore size and applied pressure i.e., driving force, are inversely proportional to each other, since as pore size decreases, flux through membrane also decreases which requires higher pressures to retain the same permeate flux. This phenomenon is expressed in Eq 4 (Prip Beier, 2007).

$$J = -A\frac{dX}{dx} \tag{4}$$

Where J is flux (kg/m^2.h)

A is proportionality constant

X is the gradient of driving force (pressure in this case)

x is direction perpendicular to membrane surface

Minus sign in Eq 4 refers negativity of the driving force gradient in the flux direction which is perpendicular to membrane surface (Prip Beier, 2007).

General information about beforementioned pressure driven membrane processes i.e., microfiltration, ultrafiltration, nanofiltration and reverse osmosis, are summarized in sections 11.1.1 to 11.1.4.

11.1.1 Microfiltration

Microfiltration (MF) is a pressure driven membrane process where sieving works as a physical separation mechanism. Microfiltration performs purification of feed solution from dissolved solids, as well as removal of turbidity and microorganisms depending on the membrane pore size. In sieving mechanism, compounds which are bigger than pore size of the membrane are completely retained by the membrane, while compounds which are smaller than the membrane pore size usually permeates through the membrane, however partial rejection of particles with a diameter smaller than membrane pores such as viral impurities is still possible based on material of the membrane. (Membrane Filtration Technologies, n.d.)

Pore size in microfiltration is in between 0.02-4 μm as it is expressed in Table 5. Suspended particles and bacteria can be completely removed under microfiltration utilization, while for virus removal, partial rejection is observed due to possible virus attachment on bacterial biofilm, although viruses have smaller size compared with MF pore size (Membrane Filtration Technologies, n.d.). Due to large pore size nature of the MF membrane process which results in lower pressure utilization, smaller size compounds cannot be removed by MF membranes. Thus, this membrane type can be used for water resources in which any microbial activity is likely to happen. As a commonly used construction material, polymeric thin films which has uniform pore size distribution where typical porosity is observed around 80% can be stated. (Interstate Technology & Regulatory Council, 2010)

11.1.2 Ultrafiltration

Likewise microfiltration, ultrafiltration is a pressure driven membrane process where separation is mainly based on sieving mechanism. However, interaction of feed solution and the membrane which arises from their contact also has an effect on compound's rejection. As it is given in Table 5, pore size of ultrafiltration membranes alters between 0.02 to 0.2 μm which is smaller than in microfiltration membranes and results in rejection of compounds whose molecular weight differs between 300 and 500,000 Dalton (Da) such as particles, bacteria, virus, macromolecules, proteins and polysaccharides. (Fumatech.com, n.d.) Smaller pore size of ultrafiltration membrane results in higher pressure requirements in a range of 1 to 10 bar compared with microfiltration membranes (Van der Bruggen et al., 2004). Due to having smaller pore size, retention of smaller solutes with less molecular weight which causes an increase in the feed side concentration results in an increase in the osmotic pressure of the solution. Thus, unlike microfiltration, osmotic pressure difference between feed and permeate side of the filtration process affects diffusive flux through the membrane. A representation of ultrafiltration membrane which has an asymmetric structure where there are small pores on the surface of the membrane is displayed in Figure 9. (Strathmann, 2011)

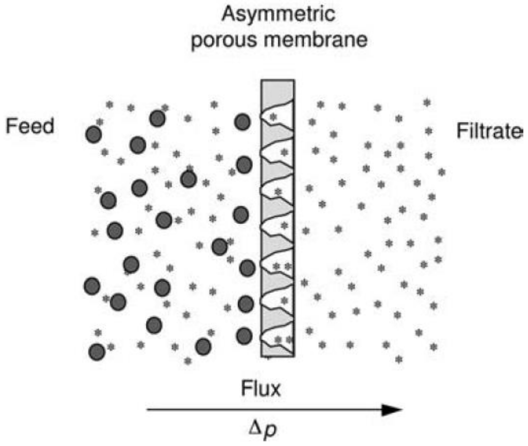


Figure 9: Representation of an ultrafiltration membrane process (Strathmann, 2011)

Classification of ultrafiltration membranes are done according to their molecular weight cut off values (MWCO) which stands for the lowest molecular weight where 90% solute rejection is observed (Fumatech.com, n.d.).

Common application purposes of ultrafiltration membranes are to concentrate or fractionate i.e., purify, dissolved compounds (Fumatech.com, n.d.). One of the typical application areas of ultrafiltration membranes is in water purification to retain particles and macromolecules from water resource to obtain drinking water. Role of ultrafiltration in water treatment plants is to be utilized as secondary or tertiary treatments instead of conventional methods, due to achieving maintenance of sufficient water quality i.e., purification from pathogens up to 90%, without using any chemicals. (Theobald, 2015).

11.1.3 Nanofiltration

Nanofiltration is a pressure driven membrane process considered to be in between ultrafiltration and reverse osmosis processes in terms of separation criteria such as pore size which is smaller than in ultrafiltration and bigger than in reverse osmosis and requirement of hydrostatic pressure which is higher than in ultrafiltration and lower than in reverse osmosis. Usual molecular weight cut off (MWCO) of nanofiltration process is in between 150 and 500 Dalton (Da). (Emis.vito.be, 2010) Separation mechanism of nanofiltration depends on sieving mechanism, diffusion and electrostatic interactions. In sieving mechanism, particle size of the compounds and pore diameter of the membrane is of importance, while, in electrostatic interactions, charge of both compounds and the membrane surface has a significant effect on separation efficiency, due to charged nature of the nanofiltration surfaces which is mostly negative under neutral pH conditions.

(Emis.vito.be, 2010, Sutherland, 2009) As a result of charged membrane surface, molecules with a smaller size than the pore size i.e., chloride and sulphates, can be retained by the membrane because of the presence of repulsion and attraction forces between the compounds and the surface of the membrane which clearly increases the selectivity of the process (Emis.vito.be, 2010). A schematic representation of the nanofiltration membrane is given in Figure 10.

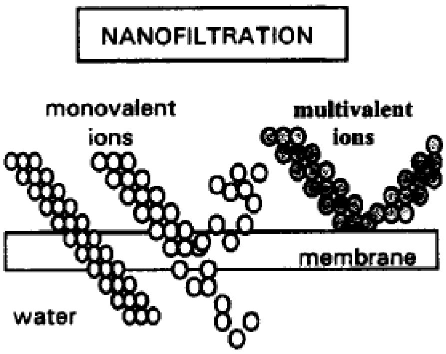


Figure 10: Schematization of nanofiltration membrane process (Van der Bruggen et al., 2004)

One of the most important criteria for nanofiltration membranes is their rejections towards specific molecules. Commonly used molecules to determine rejections are salt solutions such as NaCl, $MgSO_4$ and Na_2SO_4 for charged particles, and polysaccharides such as polyethylene glycols (PEG) which are present at several different molecular weights for uncharged particles. (Emis.vito.be, 2010) Usually, rejection of these molecules i.e., $MgSO_4$, for most of the nanofiltration membranes are above 90% (Sterlitech.com, n.d.).

Nanofiltration membranes are present as various membrane filtration modules such as plate and frame, spiral wound, tubular, hollow fibre and capillary with a production material of synthetic polymers, inorganic materials like ceramics, cellulose derivatives and mixture of organic and inorganic materials (Sutherland, 2009).

Performed progresses in nanofiltration, make the process suitable to be used under very low or high pH conditions. This progress includes NF membrane usage for non-aqueous liquids. Besides improvements in this process, fouling should still be taken care of as a main problem in nanofiltration processes. Therefore, the filtration system should be suitable to prevent fouling as much as possible. For this purpose, appropriate materials with a sufficient cross flow velocity to remove any accumulation from the membrane surface by means of rotation or vibration can be used. (Sutherland, 2009) In brief, pre-treatment is required in cases where high pollutant or suspended solids concentrations are observed, especially for spiral wound membranes (Emis.vito.be, 2010).

As application areas, nanofiltration membranes are usually preferred to be used for water softening and purification of water from pesticides (Emis.vito.be, 2010). They are also used to remove of natural organic matters (NOMs) from water sources as well as unpleasant odours, colours and flavours. In terms of purification of larger water bodies, nanofiltration is utilized to purify them from herbicides. In brief, industries that can benefit from nanofiltration membrane processes can be given as food and dairy industries, pulp and paper mills, chemical processes, textile sector and mainly water processing. (Sutherland, 2009)

11.1.4 Reverse Osmosis

Reverse osmosis is a pressure driven membrane process which works with the opposite principle of osmosis process where a relatively high hydrostatic pressure is required to enable permeation of water from the more concentrated side of the semi permeable membrane through the less concentrated side by preventing diffusion of contaminants in the feed side and concentrating them. Figure 11 represents reverse osmosis process where desalination of concentrated water is achieved which results in ultra-pure water free from dissolved salts, organics bacteria and pyrogens. (Puretec Industrial Water :: Ultrapure Water Solutions, n.d.)

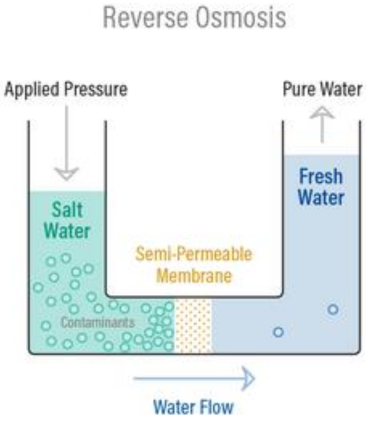


Figure 11: Schematization of reverse osmosis process (Puretec Industrial Water :: Ultrapure Water Solutions, n.d.)

Compared with other pressure driven membrane processes, reverse osmosis, of which working principle is defined as solution-diffusion mechanism has smaller pore sized membrane surface i.e., denser, results in lower permeation flux which needs higher pressures that leads higher energy utilization. (Van der Bruggen et al., 2004)

During reverse osmosis process, higher pressure should be applied on the more concentrated side for the purpose of overcoming water diffusion from less concentrated side to more concentrated side. By this mean, concentration of dissolve salts in the feed side will be increased where rejection of dissolved salts is usually around 95% to 99%. (Puretec Industrial Water :: Ultrapure Water Solutions, n.d.) Therefore, as the concentration of the solution which should be purified increases, the pressure, which must be introduced also increases due to an elevation of the solution's osmotic pressure (Van der Bruggen et al., 2004). During reverse osmosis process which has a cross filtration system, demineralized water i.e., permeate, which penetrates through the membrane is obtained in the permeate side while concentration of contaminants i.e., retentate, is obtained in the filter media. Utilization of cross flow filtration system in all pressure driven membrane processes, prevents any accumulation of contaminants in the filter media by sweeping off which might have an adverse effect on process' separation efficiency. Meanwhile, created turbulence on the membrane surface contributes maintenance of surface cleanness. (Puretec Industrial Water :: Ultrapure Water Solutions, n.d.)

Utilization of reverse osmosis membranes allows rejection of compounds which can already be removed by using microfiltration, ultrafiltration and nanofiltration such as particles, colloids, organics, bacteria and additionally dissolved salts, pyrogens at the ratio of 99%. Removal mechanism of reverse osmosis is based on particle sizes and their charges. In terms of particle size, molecules with higher molecular weight than 200 is likely to be removed by reverse osmosis membrane. In terms of particle charge, higher the molecule's charge is better rejection is likely to be observed. For instance, efficiency of calcium ion's (+2) and sodium ion's (+1) removal can be given where calcium has better rejection. Similarly, sufficient removal of gases like carbon dioxide by reverse osmosis membrane is not possible, due to their non-ionized nature when they dissolve and lower molecular weight. (Puretec Industrial Water :: Ultrapure Water Solutions, n.d.) In brief it can be stated that usually water is the only molecule which can permeate through the membrane. Improvements in reverse osmosis membrane technology make their use more effective due to their prior properties like enabling utilization in large pH range, durability under elevated temperatures and strong chemical environments. This sufficient efficiency and selectivity of the process can be enhanced even more by utilizing hybrid technology which includes concurrency of ultrafiltration, evaporation, distillation and reverse osmosis. (Interstate Technology & Regulatory Council, 2010)

11.2 Filtration Type of Pressure Driven Membrane Processes

11.2.1 Dead-End Filtration

In dead-end membrane filtration systems solution flows through the membrane perpendicularly. Since feed solution moves toward the membrane surface straight, observing a cake formation which leads fouling and increases permeation resistibility of the solvent by decreasing flux is the common problem in dead-end filtration system while undesired particles retained on the feed side and separated. An illustration of dead-end filtration system is given in Figure 12. (Principle of micro-filtration, 2017)

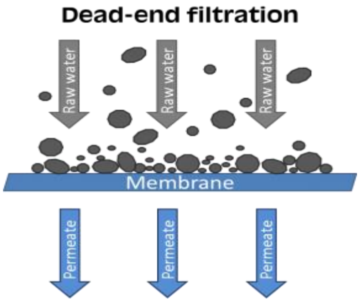


Figure 12: Dead-end filtration system (Atec Neu-Ulm, n.d.)

11.2.2 Cross-flow Filtration

In cross-flow membrane filtration systems solution flows through the membrane tangentially. In cross flow filtration, there are two directions in which feed and permeate of the process. The cross flow over membrane surface can reduce cake layer formation which is the main problem in dead-end filtration system. A cake layer which is formed as a result of a separation of high molecular weight compounds such as suspended or dissolved solids can be controlled and minimized by cross-flow velocity. An illustration of cross-flow filtration system is given Figure 13. (Principle of micro-filtration, 2017)

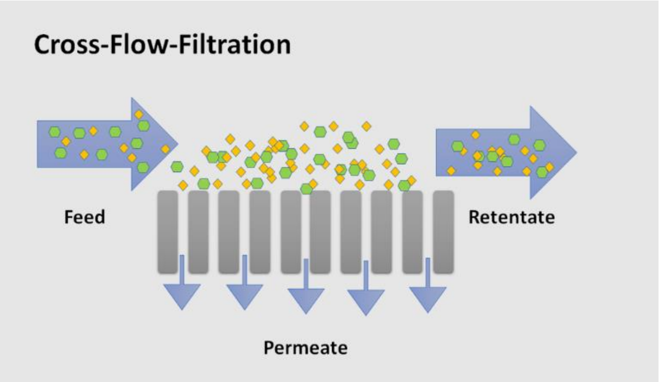


Figure 13: Schematization of cross-flow filtration system (Wesselmann-eng.de, 2016)

11.3 Phenomena in Pressure Driven Membrane Processes

11.3.1 Osmotic Pressure

Osmotic pressure is a phenomenon arises from concentration difference between two sides of the semi permeable membrane. It can be also stated as a propensity to draw more water from low concentration side to more concentrated side for the purpose of dilution. During this process, due water flow through more concentrated side, an elevation will be observed at the liquid level which results in a pressure difference called as "osmotic pressure". Process will continue until an equilibrium level is reached where concentrations of both sides of the membrane are equalized. (Prip Beier, 2007)

Osmotic pressure can be calculated based on Eq 5, for an ideal solution which means that complete dissociation of dissolved salts is observed (Sagle and Freeman, 2004).

$$CRT = \pi \tag{5}$$

Where C is concentration of salt ion in the solution

R is the ideal gas constant

T is the solution temperature

π is the osmotic pressure

11.3.2 Concentration Polarization and Fouling

Fouling during membrane filtration can be seen either an increase in the transmembrane pressure (TMP) to stabilize the flux or a decrease in the flux under constant pressure. In addition it should be kept in mind that in concentration mode filtration also increase of concentration polarisation and osmotic pressure causes the decrease of permeate flux although they do not necessarily lead to fouling of membranes. Membrane fouling is possible in two ways as reversible i.e., can be removed by physical cleaning like backwashing, or irreversible i.e., cannot be removed by physical cleaning. Interactions of fouling components i.e., physically and chemically, in the bulk and on the membrane surface results in fouling, as a result of a mass transfer. Consequently, fouling compounds can accumulate, attached or adsorbed by the surface of the membrane or by the pores of the membrane. (Guo, Ngo and Li, 2012)

Concentration polarization is a situation where more concentrated particles are observed on the membrane surface compared with feed side of the solution which causes a diffusion from high concentrated membrane surface through the less concentrated bulk side i.e., back diffusion, due to existing concentration difference. As a results of concentration polarization, lower quality permeate is obtained since high concentration of particles around membrane surface enables penetration of particles through the membrane. In order to avoid CP, diffusion coefficient and velocity of the particles as well as system temperature can be increased. Quite the contrary, an increase in the applied hydrostatic pressure or flux of permeate will enhance CP which is an undesired situation due to its promotive effect on fouling that results stronger interaction between molecules and membrane surface. A schematization of concentration polarization phenomenon is given in Figure 14. (Guo, Ngo and Li, 2012)

In nanofiltration and reverse osmosis processes, increase in fouling and deterioration of permeate purity can be due to concentration polarization because of an increase of solute compounds on the membrane surface (Guo, Ngo and Li, 2012).

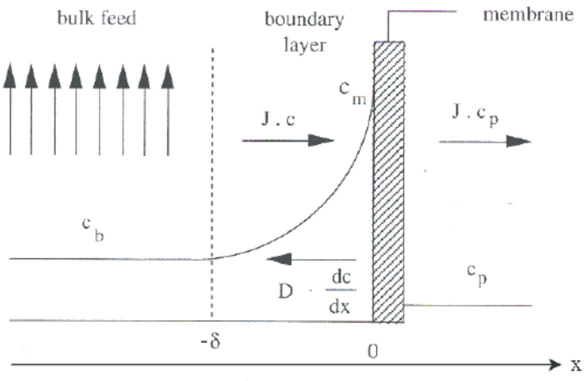


Figure 14: Schematization of concentration polarization (Prip Beier, 2007)

12. MATERIALS AND METHODS

12.1 Materials

Four sets of nanofiltration (NF) and four sets of ultrafiltration (UF) membranes whose properties are presented in Table 6 and Table 7 respectively were utilized in filtration experiments. Permeate flux and retention of different membranes were measured by using model solution and DES.

Table 6: Cross-flow membrane module NF membranes' properties.

NF Membranes	MWCO (Da)	Material	Company
NF 270	200-400	Polyamide	The Dow Chemical Company
AMS 3012	180	Polysulfone acid stable	AMS Technology
Duracid	150-200	Polyamide	GE Osmonics
NFW	300-500	Polyamide	Synder

Table 7: Cross-flow membrane module UF membranes' properties.

UF Membranes	MWCO (kDa)	Material	Company
UH004P	4	Hydrophilic PES	Microdyn-Nadir GmbH
Ultracel	3	Regenerated Cellulose	Millipore
UFX5	5	PES	TriSep
GE/G5	1	Composite poylamide TFC	GE Osmonics

Retentions of different membranes were measured by using different model compounds such as glucose, magnesium sulfate and polyethylene glycol. Glucose (D- (+) Glucose, Mw. 180.2 g/mol, CAS:50-99-7) was supplied by Sigma-Aldrich Chemie, Gmbh, Steinheim (GERMANY) and magnesium sulfate heptahydrate ($MgSO_4$.7H2O, Mw. 246.47 g/mol, CAS: 10034-99-8) with a purity of 49% was supplied by Sigma-Aldrich used as a feed solution for NF membranes by preparing a mixture of both components. Polyethylene glycol (PEG, approx. Mw. 4000 g/mol, CAS: 25322-68-3) was supplied by Fluka AG (Switzerland) utilized as a feed solution when UF membranes were characterised.

Three sets of UF membranes and one NF membrane which are represented in Table 8 with a higher MWCO than the ones used for cross-flow membrane module were utilized to determine flux, permeability and retention of membranes for dead end membrane filtration module.

Table 8: Dead-end membrane module membrane properties

UF and NF Membranes	MWCO (Da)	Material	Company
UP005	5000	PES	Microdyn-Nadir Wiesbaden
UP010	10,000	PES	Microdyn-Nadir GmbH
UP020	20,000	PES	Microdyn-Nadir RM
NFW	300-500	Polyamide	Synder

In the experiments done with the ultrafiltration membranes (Table 8), the 20% spent DES solution (in the DES originally ChCl and Lactic Acid in molar ratios 1:9, DES used in the treatment of birch) was used as feed. Polyethylene glycol (PEG, approx. Mw. 3000 g/mol, CAS: 25322-68-3) used in retention measurements was supplied by Fluka AG (Switzerland). All the experiments were made with ultra-pure deionized water. The filtration with the NFW was done with 100%, pure DES.

Ultrafiltration, nanofiltration and reverse osmosis membranes (Table 9) were used consecutively to observe purification efficiency of process for spent DES.

Table 9: Dead-end membrane module membrane properties

Membranes	MWCO (Da)	Material	Company
UP005	5000	PES	Microdyn-Nadir Wiesbaden
NF 270	200-400	Polyamide	The Dow Chemical Company
NFG	600-800	Polyamide	Synder
AG	-	Polyamide	GE Osmonics

Prepared 5% spent DES solution was used as a feed solution for UP005, while the feed of the NF 270 and the NFG membranes was the permeate of the UP005 membrane and the feed of the AG membrane was the permeate of the consecutive nanofiltration membranes.

Ultra-pure deionized water (conductivity lower than 2 μs/cm) which was provided by CENTRA-R 60/120 system (Elga purification system, Veolia Water, UK) was utilized during all the experiments including pre-treatment of membranes except where the dead-end module filtration system is used. For the dead-end membrane filtration system experiments pure deionized water, of which conductivity is lower than 6 μs/cm was used.

12.1.1 DES Preparation

Among many different preparation techniques, heating under continuous mixing conditions is used to prepare DES (ChCl: Lac, 1:9) with constituents of choline chloride and lactic acid in a specific molar ratio of 1 to 9, is prepared by simply weighting each component based on their molecular weight in relation with their molar ratios in the mixture. Initially, choline chloride is weighted under the created nitrogen environment during DES preparation, in order to avoid any contact with air which can cause water intaking. Since in case of any water content in DES, its removal which require additional processing in the further purification steps should be considered. One mole of choline chloride i.e. 139.64 g, which presents in the crystalline form has been weighted as a first step. Then nine moles of lactic acid i.e. 810.72 g which is in the liquid state has poured onto choline chloride to prepare 1L of DES. Unlike choline chloride, weighting of lactic acid does not require any nitrogen environment creation since it is in the liquid state of matter. Obtained mixture is placed in hot plate magnetic stirrer where temperature was arranged around 100℃ and stirring speed (rpm) was set as 1/250 (1/min).

Homogeneous dissolution of choline chloride within lactic acid is aimed to obtain, in order to ensure that preparation is done. It has been observed that after 30 minutes, complete dissolution of choline chloride was achieved. However, to be sure about prepared DES quality, it has been waited 30 more minutes. In total DES preparation took 1 hour.

12.2 Methods

12.2.1 Cross Flow Filtration for Membrane Characterisation

This filter is used to characterize membrane properties, i.e flux and retention before and after exposure in DES. In order to observe deformation effect of DES on each UF and NF membranes, membrane pieces are totally immersed in pure DES solution for 4 days under

50°C. After immersion period, the flux and retention of membranes were measured with water solution containing model compounds.

Commercial polyamide and polysulfone NF membranes and commercial regenerated cellulose, polyamide and PES UF membranes were used. All membranes were cleaned and utilized based on the mentioned experimental conditions in Table 10. Cleaning of membranes is essential for removal of preservative layer and any possible contamination on the membrane surface.

Table 10: Cross-flow membrane module experimental conditions

	UFX 5	**UH004P**	**ULTRACEL***	**GE/G5**	**NF 270**	**NFW**	**Duracid**	**AMS 3012**
CLEANING								
Washing	0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min	10 wt% ethanol/ 10 min & 0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min	10 wt% ethanol/ 10 min & 0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min
Pressurizing	8 bar	8 bar	8 bar	8 bar	25 bar	25 bar	25 bar	25 bar
FILTRATION								
Pressure	2.67 bar	9.01 bar	10.7 bar	16.3 bar	9.87 bar	9.22 bar	31.6 bar	13.5 bar
Cross-flow Speed	1.49 m/s	1.49 m/s	1.49 m/s	1.49 m/s	1.49 m/s	1.49 m/s	1.49 m/s	1.49 m/s

For this study 4 parallel rectangular cross-flow flat sheet membrane modules where the construction material is stainless steel (AISI 316) is used. Applicable surface area of the membrane module is calculated as 47.5 cm^2. During all the experiments temperature was set at 25 ± 1°C by the help of a heat exchanger (Lauda Proline RP 855 thermostat, Lauda-Königshofen, Germany) and it was read by use of an in-feed thermometer probe. In the beginning of the experiment, system is rinsed with DI water twice without any pressure in order to be sure that there are not any impurities left in the system. Indication of system purity is verified with water conductivity measurement which should be below 2 $\mu s/cm$ (Knick Konduktometer 703). Thereafter, UF and NF membranes are pressurized under specified conditions in Table 10. Pressurizing is necessary in order to prevent effect of compaction phenomenon and to clean any remained preservative layer on the membrane surface. Pressure within the system is controlled by using a needle valve. After pressurizing, to ensure system purity another water conductivity measurement with the same criteria is done. Afterwards, system is rinsed with 1 litre of feed solutions twice to be sure of inexistence of other components but the feed solution. For all NF and UF membranes, flux and permeability of feed solutions were measured at a constant in line flow meter (Micro flow-captor 4511.30, Weber Sensors) value to keep the flux constant by controlling pressure in order to avoid concentration polarization formation. This constant value is maintained by changing applied pressured by use of a needle valve. Additionally, to determine retention of solute components, feed samples before and after the experiment and permeate samples were taken. After stabilization of cross flow velocity to 1.47 m/s for all NF and UF membranes, for 10 minutes of period permeate samples were taken from each NF and UF membranes. Retention of $MgSO_4$ is determined with a conductivity measurement (Knick Konduktometer 703) using Eq 6, retention of glucose and PEG is measured by total organic carbon (TOC) analyser (Shimadzu TOC-L series, Japan) equipped with a non-dispersive infrared (NDIR) detector using Eq 6.

$$Re\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (6)$$

Where, C_p Corresponds both conductivity and concentration of $MgSO_4$ in downstream

C_f Corresponds both conductivity and concentration of $MgSO_4$ in upstream

12.2.2 Dead End Filtration with DES

A batch mode dead end ultra- and nanofiltration experiments were made to measure of permeate fluxes of pure and spent DES solution and to analyse the retention of dissolved compounds. The spent DES solution also consists of compounds dissolved in wood by DES treatment. The experiments were made by using two different dead end stirred cell filters with the capacities of 300 millilitre and 1000 millilitre and surface area of 38.5 cm^2 and 56.7cm^2 respectively. For handmade dead-end batch membrane module with the effective surface area of 56.7cm^2, NF 270 and UH004P membranes and for the handmade dead-end batch membrane module with the effective surface area of 33.2cm^2, NF 270, NFW, UP005, UP010 and UP020 membranes were prepared and cleaned with the same procedure which has been mentioned in previous section i.e.,12.2.1 Cross Flow Filtration for Membrane Characterization. All the membranes were pressurized with DI water and then pure water and PEG fluxes were measured. After that the DES fluxes i.e. pure and spent DES, were measured under the mentioned conditions (Table 11 and Table 13).

Table 11: Amicon 2 experimental conditions
VRF are very low

	UP005	UP010	UP020	NF 270	NFW
CLEANING					
Washing	0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min
Pressurizing	9.5 bar/ 30 min	5 bar/ 30 min	2 bar/ 30 min	9.5 bar/ 30 min	9.5 bar/ 30 min
FILTRATION					
Pressure at Water Flux	6 bar	1 bar	0.5 bar	9.5 bar	9.5 bar
Pressure at PEG Flux	6 bar	-	-	-	-
Pressure at 20% Spent DES Flux	9.5 bar	4 bar	2 bar	-	-
Pressure at Pure 20% DES Flux	9.5 bar	-	-	9.5 bar	9.5 bar

UP005, UP010 and UP020 UF membranes were utilized with 20% spent DES at 60℃ to see any possible separation of DES and lignin and effect of MWCO on the separation efficiency and flux of 20% spent DES. Separation efficiency is evaluated by performed UV and HPLC analysis which were used to determine lignin and lactic acid concentration in permeate retentate and feed. Another experiment with UP005 where the 20% pure DES at 60℃ was utilized instead of 20% spent DES has been performed to interpret the deformation effect of lignin on the membrane. Again, the UV and HPLC analysis was performed to see lactic acid concentration in collected samples.

In order to see any deformation caused by utilized pure DES or spent DES solutions, water fluxes before and after the DES filtrations were measured in these experiments. Any tightening effect of DES caused on the membranes is studied with another experiment by using UP005 membrane where PEG- water solution is utilized before and after 20% pure DES filtration instead of water. TOC analysis was performed to understand tightening effect based on PEG retentions measured before and after the DES filtration. The retention is calculated according to Eq 6. NF 270 and NFW membranes were utilized to observe effect of temperature on pure DES flux where performed temperature range is between 20℃ to 60℃ with the increments of 10℃.

Table 12: Handmade 1L dead-end batch module experimental conditions

	NF 270 (Spent DES)	UH004P
CLEANING		
Washing	0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min
Pressurizing	25 bar/ 30 mins	8 bar/ 30 mins
FILTRATION		
Pressure at Water Flux	19 bar	6 bar
Pressure at 20% Spent DES Flux	25 bar	10 bar

The wood was treated with 100% DES and when the spent DES was diluted with water to 20% solution some compounds might be precipitated. Therefore, the effect of centrifugation on the flux and retention of the NF 270 membrane was also studied. The same experiment has been repeated with higher MWCO UF membrane i.e. UH004P, to understand whether any improvement can be achieved with an increase in the MWCO. In order to see any deformation caused by utilized spent DES solutions, before and after water fluxes have been measured in these experiments.

As a main experiment consecutive ultrafiltration, nanofiltration and reverse osmosis membranes i.e., UP005, NF 270 and NFG, AG, were used to observe their efficiency in purification of 5% spent DES. Experiments were made by using both handmade dead-end batch membrane modules with the capacity of 300 ml and 1 L. Membranes were prepared and cleaned with the same procedure which has been mentioned in previous section i.e., 12.2.1 Cross Flow Filtration for Membrane Characterization,. All membranes were pressurized with DI water and then 5% spent DES flux have been measured under the mentioned conditions in Table 13.

Table 13: Handmade 1L dead-end batch module experimental conditions

	UP005	NF 270	NFG	AG
CLEANING				
Washing	0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min	0.2 wt% Ultrasil 110/ 15 min
Pressurizing	9.5 bar/ 30 min	25 bar/ 30 min	25 bar/ 30 min	25 bar/ 30 min
FILTRATION				
Pressure at 5% Spent DES Flux	9.5 bar	20 bar	20 bar	25 bar

Filtration of UP005, NF 270, NFG and AG membranes were performed at 60℃, 50℃, 45℃, and 35℃, respectively. Purification of spent DES was determined by UV-Vis analysis and TOC analysis was used in determination of organic carbon content in the samples.

Additionally, in order for better interpretation of low observed flux values, especially during dead-end filtration experiments, osmotic pressure of the 20% pure DES solution is calculated based on Eq 7.

$$\pi = nCRT \tag{7}$$

Where π is osmotic pressures in kPa

n is moles of particles which show osmotic pressure

C is molar concentration in $\frac{mol}{l}$

R is gas constant i.e., 8.314 $\frac{J}{mol.K}$

T is temperature in Kelvin (K)

12.3 DES Characterization

12.3.1 Rheometer Analysis

Tube type pipe rheometer i.e. Anton Paar Modular Compact Rheometer MCR 302 (Austria, PP50/P2 spindle) was used for this rheometer study.

Two rheology analyses are done where one of them is for determination of viscosity behaviour of the solvent and second one is to observe change in viscosity over temperature which will lead to a selection of optimal temperature interval for the membrane process and solvent itself.

Viscosity analysis for DES to understand its behaviour is performed under 20℃, at a shear rate of 50 (1/s) for 30 seconds.

Second rheometer analysis has been performed at a shear rate of 20 (1/s), at a temperature range between 20℃ to 130℃ with a temperature increment of 2℃/min.

Determination of temperature incremental value during the experiment which is 2℃/min has an importance. It has been tried to be careful about using a small temperature increment during the experiment. Since higher increments may results in incorrect measurement due to created temperature difference between the rheometer itself and the solution. Similarly, it has been decided to use a smaller shear rate value in order to avoid causing any turbulence or noise region during the experiment where viscosity was recorded over a change in shear rate.

12.3.2 Filtering Effect of 20% Spent DES on Solid Matter Separation Experiment

In order to see the effect of filtration of the diluted spent DES solution i.e., 20%, on solid matter separation i.e., lignocellulosic compounds, for the purpose of enhancing the membrane filtration flux, this experiment was performed. For this purpose, three consecutive filtrations have been performed on 20% spent DES solution. In order to enable removal of bigger particles as an initial step, and then separate the remained precipitated lignocellulosic materials, filtration paper with a pore size of 2.5 μm was used for the first filtration while for the following filtrations filter paper with the pore size of 0.2 μm was used.

Filtered solution of a previous filtration step was used as a feed solution of following filtration. After each filtration, filter papers where there is removed wood which contains lignin were kept in the oven under 50 ℃ overnight to enable their drying. From the weight difference between filter paper before the filtration and after the filtration, concentration of removed lignocellulosic compounds which can be mostly lignin was calculated.

12.3.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR analysis was performed by using the Perkin Elmer Frontier spectrometer with a universal ATR module of diamond crystal. FTIR analysis of pure choline chloride, pure lactic acid and non-diluted pure DES which consists of 1 to 9 molar ratios of choline chloride and lactic acid and samples from membrane filtration experiments of DES were performed. The FTIR spectra were used to get understanding on possible decomposition of DES during the membrane filtration experiments.

For all analyses, FTIR spectra was measured in the wavelength range of 4000-400 cm^{-1} with the spectra resolution of 4 cm^{-1} in the absorbance mode. For the use of final interpretation of the results, ATR correction, baseline correction and normalization were performed on co-added spectra results.

12.3.4 UV/Vis Analysis

UV analysis was performed for different purposes by using UV/Vis spectrophotometer (Jasco V-670 spectrophotometer, Japan) in the adsorption mode between the wavelengths of 190 nm to 850 nm. 1) UV analysis of pure DES and its 20% water solution were performed as a reference for further analysis for better understanding of any change in the DES solution where DI water was used as a blank. 2) Analysis of 20% pure DES feed, permeate and retentate samples were performed to observe any possible change in the DES peaks to understand bond strength between DES components where DI water was used as a blank. 3) In order to determine amount of lignin in the feed, permeate and retentate samples which can be observed at the wavelength of 280 nm, samples of three different ultrafiltration membranes with an increasing MWCO value respectively as UP005, UP010 and UP020 were analysed. The filtrations were made with 20% spent DES solution. For UV-Vis analysis of these samples, DMSO was preferred to be used as a dilution solvent after freeze drying of the samples, because of its advantage over water to avoid lignin precipitation. Lignin retentions were calculated based on observed lignin peak absorbances at 280 nm, according to Eq 6. 4) UV-Vis analysis of consecutively used ultrafiltration, nanofiltration and reverse osmosis membranes' feed, permeate and retentate samples i.e., UP005, NF 270, NFG and AG, where the feed of initially used UF membrane was 5% spent DES was performed. Based on absorbance peaks around 280 nm where it is possible to locate lignin peaks in alkaline conditions, retentions were calculated according to Eq 6. Besides lignin retentions, lignin concentrations in each sample was calculated in terms of acid soluble lignin content based on Eq 8 (Lin, 1992).

$$ASL = \frac{Ab}{a \times b} \times df \quad (8)$$

Where, ASL is acid soluble lignin concentration (g/L)

Ab is absorbance at that wavelength

a is a constant 14.5 L/g-cm at 280 nm

b is thickness of quartz which is 1 cm

df is dilution factor

12.3.5 Conductivity and pH Measurement

Conductivity and pH measurements were done feed, permeate and retentate samples of 4 sets of nanofiltration membranes i.e., NF 270, NFW, Duracid and AMS 3012, and ultrafiltration membranes i.e., UFX 5, UH004P, Ultracel and GE/G5, together with feed, permeate and retentate samples of three ultrafiltration membranes i.e., UP005, UP010 and UP20, by using pH Meter (744 pH Meter, Metrohm, Switzerland) and conductometer (Konduktometer 703, Knick, Germany).

12.3.6 Total Organic Carbon (TOC) Analysis

Total organic carbon analysis of feed and permeate samples of 4 sets of NF membranes i.e., NF 270, NFW, Duracid, AMS 3012 and 4 sets of UF membranes i.e., UFX 5, UH004P, Ultracel, GE/G5 before and after DES exposure are performed by using total organic carbon analyser (Shimadzu TOC-L, Japan). Moreover, TOC analysis is used to see effect of DES on UF membrane i.e., UP005, by using feed, permeate and retentate samples of PEG solution before and after DES filtration.

Additionally, consecutively used ultrafiltration, nanofiltration and reverse osmosis membranes' feed, permeate and retentate samples i.e. UP005, NF 270, NFG and AG, were analysed in terms of their organic carbon content in order to understand purification efficiency of 5% spent DES throughout the process.

12.3.7 High Performance Liquid Chromatography (HPLC) Analysis

In order to determine lactic acid concentration which indicates concentration of DES in the feed, permeate and retention samples of UF membranes i.e., UP005, UP010, UP020, which were underwent the filtration process with 20% spent DES has been performed by using high performance liquid chromatography (Agilent 1100 Series HPLC Value System, Germany). Lactic acid concentration of the samples was obtained approximately based on area of lactic acid peaks.

12.3.8 Scanning Electron Microscopy (SEM) Analysis

Determination of surface and cross-sectional morphology of ultrafiltration, nanofiltration and reverse osmosis membranes i.e., UP005, NF 270 and AG, before and after exposure to DES in order to see any deformation or detachment on the membrane structure through the filtration process where DES was used as a solvent has been made by using scanning electron microscope (Hitachi SU 3500, Japan) with the acceleration voltage of 10 kV under vacuum condition. Reason behind analysing three different membranes was to observe resistibility of membranes which are made of different construction materials where UP005 membrane is a PES and NF 270 and AG are polyamide membranes. Preparation of surface and cross-sectional morphology analysis of samples were different. For the cross-section analysis, membrane samples were first soaked into liquid nitrogen to enable easy breakage of membranes autochthonously which does not require use of razor blade in order to avoid undesired change in the structure can be caused by any tool usage such as razor blade. For the surface morphology analysis, liquid nitrogen was not required. For both surface and cross-section analyses, samples were prepared before and after DES exposure. While before the exposure membrane pieces were first cleaned with Ultrasil 110 and dried overnight, after the exposure other membrane pieces was soaked into pure DES solution overnight under 50℃ for UP005 and NF 270 membranes and ambient temperature for AG membrane, after cleaning with Ultrasil 110 to be rinsed with water and dried overnight later. As a preliminary step for SEM analysis, membrane pieces were first cooled down with DI water for half an hour, and then a very thin layer of gold is formed on the surface of the samples in order to increase conductivity during the analysis.

12.4. Lignin Analysis

Lignin content in samples are divided into two parts as acid soluble (ASL) and acid insoluble lignin (AIL) concentrations where AIL contains most of the lignin.

12.4.1 Acid Soluble Lignin Analysis

Acid soluble lignin analysis procedure involves initially a lignin dissolution of a biomass by a strong acid which is followed by a quick hydrolysis and a complete dissolution of lignin. Then, vacuum filtration of the solution takes place. For lignin dissolution, 300 mg of treated wood (and if comparison required untreated wood sample) were placed in small glass bottles. Then addition of 3 ml sulfuric acid with a concentration of 72% was followed.

In order to enable efficient and full dissolution of carbohydrates, samples were mixed every 5 to 10 minutes for 2 hours. Followingly, mixed samples were diluted with 84 ml of pure water. Thereafter, carefully mixed samples were put into an autoclave for 90 min at over 121°C under 1.1 bar. Hydrolysed samples in autoclave were cooled down to room temperature in order to be vacuum filtered. For ASL analysis, UV-Vis analysis of the collected and diluted filtrate was performed at 205 nm, since effect of furan aldehydes are lower compared with wavelength of 280 nm (Lin, 1992). Based on Eq 9, ASL concentration is calculated (Sluiter et al., 2012).

$$ASL = \frac{Ab \times Volume \times df}{a \times b \times sample\ weight} \times 100 \qquad (9)$$

Where, *ASL* is acid soluble lignin concentration (g/L)

Ab is absorbance at that wavelength

*V*olume is taken as 86.7 ml

a is a constant 110 L/g-cm at 205 nm

b is thickness of quartz which is 1 cm

df is dilution factor

12.4.2 Acid Insoluble Lignin Analysis

Acid insoluble lignin is measured from the weight difference before and after the filtration of glass disc crucibles which are used for filtration. After filtration which takes place in ASL analysis, remaining solids in the glass disc crucible were washed properly in order to be dried at the oven under 105 °C and weighted. Based on Eq 10, AIL concentration is calculated (Sluiter et al., 2012).

$$AIL = \frac{Weight\ of\ filtered\ birch}{Initial\ weight\ of\ birch} \times 100 \qquad (10)$$

Where, *AIL* is acid insoluble lignin concentration (g/L)

Weight of filtered birch is the difference of glass crucible weight before and after filtration

13. RESULTS AND DISCUSSION

Results and discussion section is divided into three sections as preliminary experiments, spent DES purification experiments and experiments to determine efficiency of purified spent DES. Membrane resistances to non-diluted pure DES and 20% pure DES (diluted), solvent characterization and study to observe tightening effect of DES on membrane structure have been performed as preliminary experiments. Membrane resistances to non-diluted pure DES has been studied to observe resistances of nanofiltration and ultrafiltration membranes before and after DES exposure based on flux and retention measurements, as well as SEM images of different material membranes i.e., PES and polyamide, ultrafiltration, nanofiltration and reverse osmosis membranes. Besides DES exposure, membrane resistances have also been studied based on membrane retention ability before and after DES filtration where 20% concentrated pure DES has been used with ultrafiltration membrane i.e., UP005. Solvent characterization includes viscosity of pure DES as a function of temperature, any possible improvements in the flux of pure DES as a function of temperature, bond and precipitation of dissolved materials in 20% spent DES solution. Study to observe tightening effect of DES on membrane structure includes a membrane filtration experiment with 20% pure DES where PEG solution filtration with molecular weight of 3000 g/mol before and after the pure DES filtration was performed.

In spent DES purification experiments, two different concentrations of spent DES solutions (20% and 5%), were used as feed solutions in membrane filtration processes. For the filtration process where 20% spent DES was used as a feed solution, NF 270 membrane filtration was performed in order to see the centrifuge effect on solid matter separation. In order to understand whether any improvements in the permeate flux can be achieved, an ultrafiltration membrane process i.e., UH004P, was performed with the same feed solution i.e., 20% spent DES. Additionally, series of ultrafiltration membranes which have the same production material with different MWCO values i.e., UP005, UP010 and UP020, were utilized to understand whether higher MWCO value can enhance the permeate flux. For the filtration process where 5% spent DES was used as a feed solution, two different sets of ultrafiltration, nanofiltration and reverse osmosis membranes were used respectively, in order to compare their purification efficiencies of 5% spent DES solution.

As experiments to determine efficiency of purified spent DES, acid soluble and acid insoluble part of birch lignin were analysed. In this experiment, birch was treated with purified spent

DES from the membrane filtration process where UP005, NFG and AG membranes were used consecutively.

13.1 Membrane Resistances to DES

13.1.1 Effect of DES Exposure on Ultrafiltration and Nanofiltration Membranes

Nanofiltration Membranes

In order to understand resistibility of nanofiltration and ultrafiltration membranes to non-diluted pure DES solution in terms of, permeability and retention, four nanofiltration and four ultrafiltration membranes were used in cross-flow membrane filtration module. For nanofiltration set, utilized membranes were preferred to have different production material, MWCO and operable pH range, in order to understand resistibility of membranes. For these four membranes whose pressurizing was performed under the same conditions, two separate feed solutions i.e., magnesium sulfate ($MgSO_4$) and glucose, with a concentration 0.49 g/L and 1 g/L, respectively, were chosen. The reason behind this decision was to see the effect of size exclusion on glucose solution and effect of particle size and charge on $MgSO_4$ solution done by nanofiltration membrane, since retention of nanofiltration membrane is affected by both criteria. Under a constant flux values for each membrane, permeability and retention of membranes were examined and results are presented in Table 14.

Table 14: Permeability and glucose and magnesium sulphate retention values of cross-flow filtration nanofiltration membranes at constant flux before and after the exposure on pure DES. $MW_{Glucose}$= 180 $\frac{g}{mol}$, MW_{MgSO_4}= 120 $\frac{g}{mol}$, Filtration temperature 25℃, Cross-flow velocity 1.47 $\frac{m}{s}$.

	NF 270	**NFW**	**Duracid**	**AMS 3012**
P_b; Pressure before DES exposure **P_a; Pressure after DES exposure**	**P_b=9.9** **P_a=7.1**	**P_b =9.2** **P_a =4.3**	**P_b =31.6** **P_a =30.0**	**P_b =13.5** **P_a =31.3**
MWCO (Da)	**400**	**300-500**	**150-200**	**180**
Material	**Polyamide**	**Polyamide**	**Polyamide**	**Polysulfone**
pH Range	**2 to 11**	**4 to 10**	**0 to 9**	**0 to 12**
Before the first DES Exposure, Permeability (kg/(m^{2}hbar))	9.1	9.5	2.7	6.4
After the first DES Exposure, Permeability (kg/(m^{2}hbar))	12.3	19.9	2.7	2.8
After the second DES Exposure, Permeability (kg/(m^{2}hbar))	11.5	22.4	2.6	2.2
Before the first DES exposure, Glucose Retention, -	0.77	0.77	0.6	0.24
After the first DES exposure, Glucose Retention, -	0.76	0.67	0.82	0.56
After the second DES exposure, Glucose Retention, -	0.78	0.56	0.81	0.75
Before the first DES exposure, $MgSO_4$ Retention, -	0.74	0.91	0.56	0.16
After the first DES exposure, $MgSO_4$ Retention, -	0.79	0.93	0.83	0.52
After the second $MgSO_4$ Retention, -	0.81	0.82	0.83	0.75

In terms of permeabilities, as a conspicuous result, observed low permeability of Duracid membrane among other membranes’ comparably higher permeability values can be given.

However, this obtained low permeability value i.e. 2.72 kg/m^{2}h.bar, is also observed in another study where flux of pure water before cleaning of Duracid membrane is recorded as 15 L/m^{2}h under 8 bar which refers to permeability of 1.88 kg/m^{2}h.bar (Nir, et al. 2018). In terms of permeability change of membranes before and after the DES exposure, while in the permeabilities of the NF 270 and the Duracid membranes any considerable change was not seen, for the NFW and the AMS 3012 membranes trend was different. The DES exposure caused a significant increase in permeability of the NFW membrane. Moreover, the glucose retention was decreased due to the exposure to DES. Thus, it can be concluded that the exposure to the DES opened the porous structure of the NFW membrane. As an additional reason of why NFW membrane displays a lower glucose retention after DES exposure, following explanation can be given. The used DES was really acidic compared to the pH limits given for the NFW membrane by the manufacturer. Thus, from that point of view it was not surprising that the membrane was clearly changed due to the DES exposure by showing higher flux and followingly lower retention. On the contrary, the exposure to DES caused a decrease in the permeability and increase in the glucose retention of the AMS 3012 membrane. This indicates that the AMS 3012 was tightened due to the DES exposure.

In terms of $MgSO_4$ retentions, they were increasing for all the tested nanofiltration membranes due to the DES exposure. Reason for this might be that the DES exposure changes surface charge of the membranes (Degam, 2017). The increased electrical conductivity of the membrane increases the repulsion between charged molecules and membrane surface. Additionally, observed very low $MgSO_4$ retention of the AMS 3012 membrane before any DES exposure and an increase in the $MgSO_4$ retention after the DES exposure is a conspicuous result. This can be explained with the change in the membrane surface charge.

The second exposure of DES solution have been performed to prove whether there is a trend in permeability and retention results compared with the first DES exposure results. As a result, there wasn’t any considerable change in observed permeabilities and, glucose and $MgSO_4$ retentions weren’t change enough to be taken into an account, except AMS 3012 membrane which still shows an increasing trend.

As another point, observed glucose and $MgSO_4$ retention values are lower compared with the literature values provided by manufacturers where $MgSO_4$ retention values for NF 270, NFW, Duracid and AMS 3012 are 99.2%, 98.0%, 97.0% and 96% respectively (Sterlitech.com, n.d.). The reason can be explained due to difference in experimental conditions such as mixing efficiency, concentration of feed solution and process temperature. For instance, feed solution with a very low concentration which underwent a membrane filtration process under ambient temperature, which are not the process conditions in DES filtration processes, is more likely to display higher retention results.

In brief, it can be concluded that although glucose retention values are lower than expected for NF 270 membrane before its exposure to DES, after the exposure twice, any considerable change in the glucose retention values have been observed. Similarly, in $MgSO_4$ retentions NF 270 does not show a big change after the DES exposure, especially compared with other membranes whose construction material is not only polyamide i.e., Duracid and AMS 3012. Thus, it can be stated that polyamide membranes are quite resistible to DES solution and can be used without a dramatic efficiency loss.

Ultrafiltration Membranes;

For the same purpose of nanofiltration membranes, one set of four ultrafiltration membranes were utilized to understand resistibility of membranes to non-diluted pure DES solution in terms of permeability and retention. For these four membranes whose pressurizing was performed under the same conditions, polyethylene glycol (PEG) with a concentration of 1 g/L and molecular weight of 4000 g/mole, was used as a feed solution. At a constant flux values for each membrane, permeability and retention of membranes were measured and results were represented in Table 15.

Table 15: Permeability and PEG (4000 g/mol) retention values of cross-flow filtration ultrafiltration membranes at constant flux before and after the exposure on pure DES.MW_{PEG} 4000 $\frac{g}{mol}$, Filtration temperature 25℃, Cross-flow velocity 1.47 $\frac{m}{s}$.

*** Indicates different operational conditions**	**UFX 5**	**UH004P**	**ULTRACEL***	**GE/G5**
P_b; Pressure before DES filtration P_a; Pressure after DES filtration	P_b=2.67 P_a=1.02	P_b =9.01 P_a =2.88	P_b =10.74 P_a =0.22	P_b =16.33 P_a =21.83
MWCO (kDa)	5	4	3	1
Membrane material	PES	Hydrophilic PES	Regenerated Cellulose	Composite polyamide TFC
Before the DES Exposure Flux, kg/(m^2h)	86.9	84.3	83.3	-
After the DES Exposure, Flux, kg/(m^2h)	85.4	94	1141	83.8
Before the DES Exposure, Permeability, kg/(m^2hbar))	32.5	9.36	7.75	-
After the DES Exposure, Permeability, kg/(m^2hbar)	86.7	32.6	5188	3.84
Before the DES Exposure, PEG Retention, -	0.25	0.94	0.99	-
After the DES Exposure, PEG Retention, -	0.88	0.85	0.22	0.49

Based on the results presented in Table 15, it can be stated that after the exposure to DES solution, the ULTRACEL membrane was broken: after the DES exposure a huge increase in the flux was measured. Thus, it can be concluded that regenerated cellulose is not resistible to non-diluted pure DES solution used here.

For the UH004P membrane, before the DES exposure, a reasonable PEG retention was observed i.e.,94%, where MWCO of the UH004P membrane and molecular weight of PEG solution is 4000 g/mol. However, after the DES exposure, observed PEG retention got lowered. In relation to this, after the DES exposure a dramatic increase in permeability, while flux was kept constant during the experiment, has been observed. As a result, it is concluded that the membrane got more open due to the DES exposure. Therefore, if PES membranes will be used, DES solution should be diluted. For the UFX5 membrane, before the DES exposure, remarkably low PEG retention i.e., 0.25, was observed which is the same trend in another study where PEG of higher molecular weight i.e., 4000 g/mol, was used with UFX5 membrane and retention around 0.25 is observed under the same pressure conditions i.e., 2 bar (Caesar, 2011). After the DES exposure, the pressure needed to achieve the used constant flux was decreased and nearly halved which enhanced permeability. However, an unexpected pattern is observed. Despite of the increase in permeability, an increase in retention of PEG molecules was obtained.

Even though there is a change in PES membranes' permeability and retention i.e., the UH004P and the UFX5, after the DES exposure, compared with the other membranes tested in this thesis, the PES membranes were the most resistible ones for filtering of the DES used in this thesis. Additionally, since, during the spent DES filtration experiments, diluted spent DES will be used, effect of DES on PES membranes will be lower. However, metallic or ceramic membrane utilization may show better resistibility against DES solution.

13.1.2 SEM Images of PES and Polyamide Membranes

Due to resistibility of PES and polyamide materials against the used DES solution, it was decided to see the effect of DES exposure on membrane structures by using SEM analysis. In Table 16, presented SEM images belong to surface of PES and polyamide membrane. According to Table 16, there is not any change observable in the membrane surfaces after their exposure to DES. However, for more accurate interpretation of the effect of DES solution on membrane structures, cross-sections of membranes were analysed and presented in Table 17. According to cross-section images presented in Table 17, it can be concluded that there is not any decomposition or deformation on the PES and polyamide membrane structures caused by DES, which can have an adverse effect on membrane filtration process efficiency. Therefore, they are suitable for processes where DES usage takes place.

Additionally, thickness of the membranes was observed from the cross-section of membranes before their exposure to DES. In the respective order, thickness values are measured approximately as 240 µm, 140 μm and 160 μm for UP005, NF 270 and AG membranes. In order to understand effect of DES exposure, thickness values after the exposure are measured approximately as 240 μm, 140 μm and 150 μm for UP005, NF 270 and AG membranes respectively. Thus, it can be stated that no significant change has been observed due to DES exposure in the thickness of membranes.

Table 16: Surface images of PES and Polyamide membranes before and after DES exposure

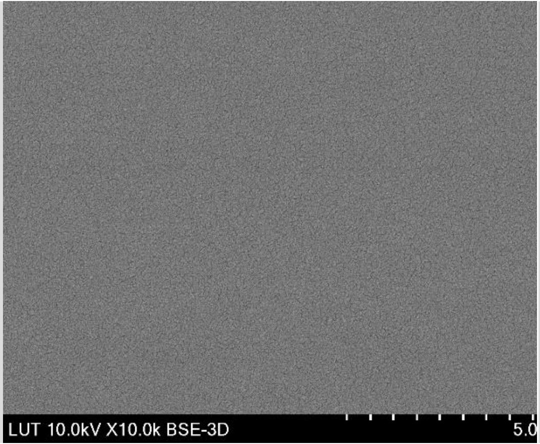
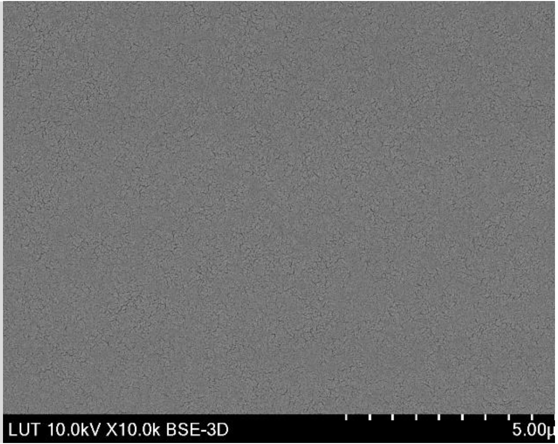
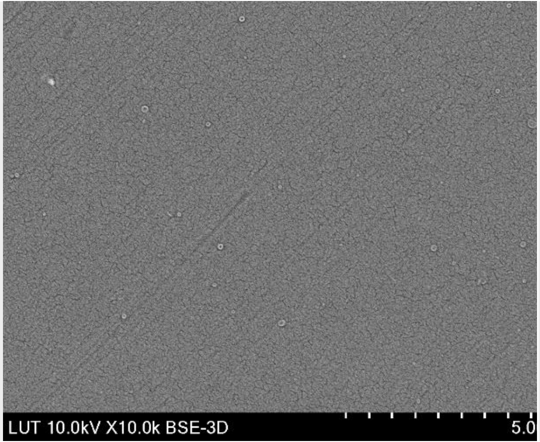
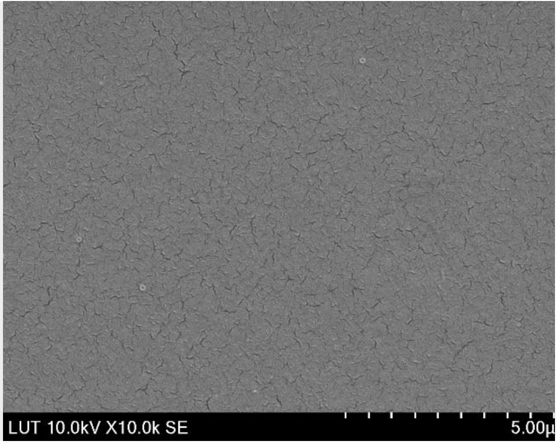
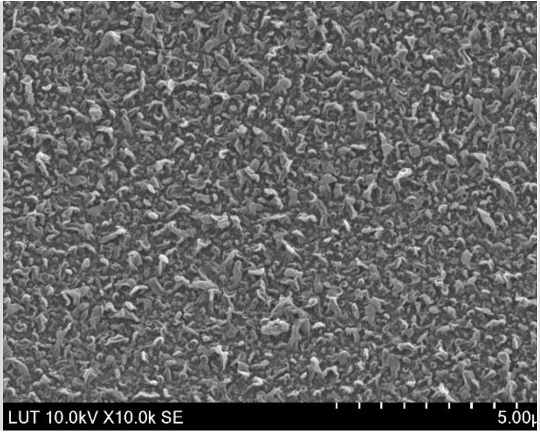
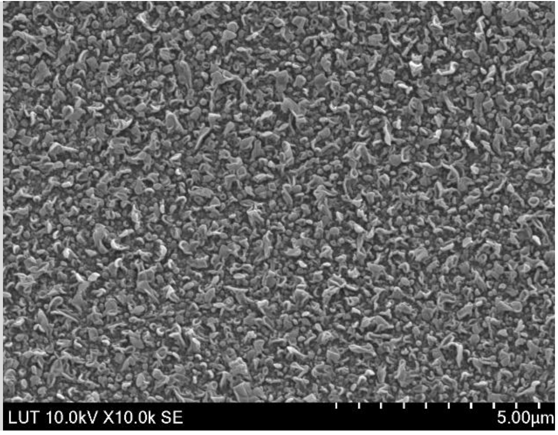
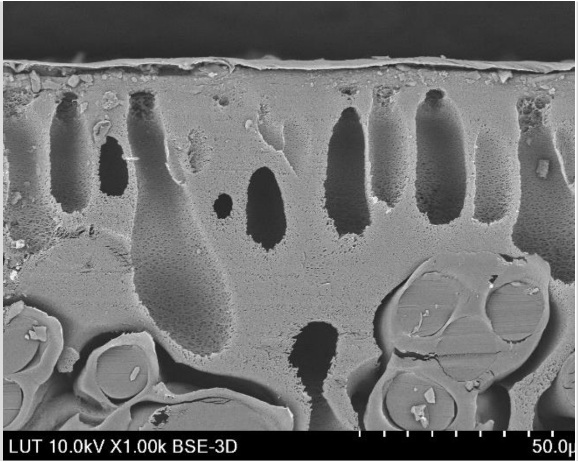
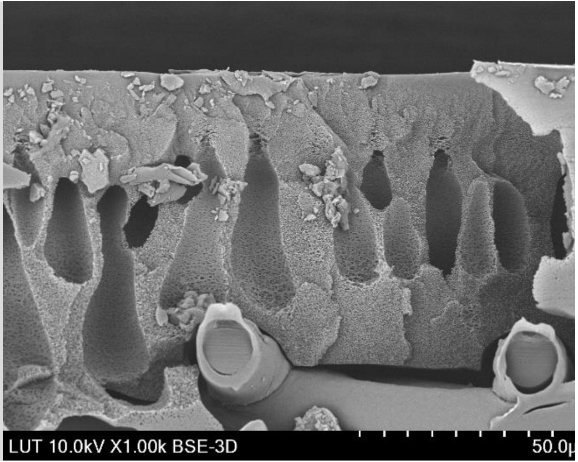
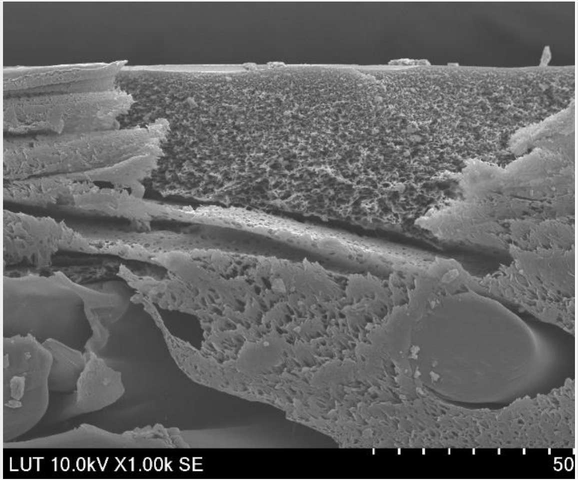
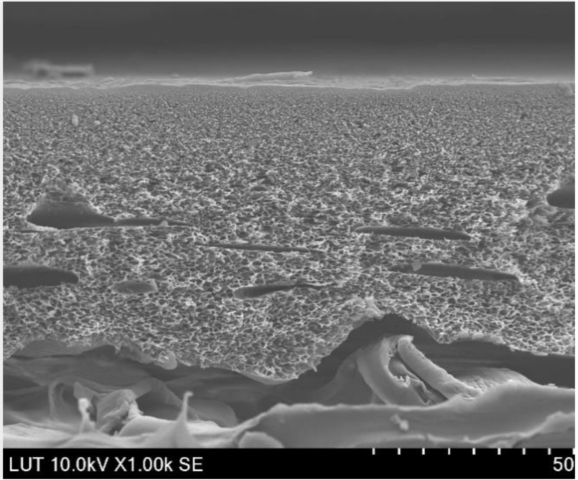
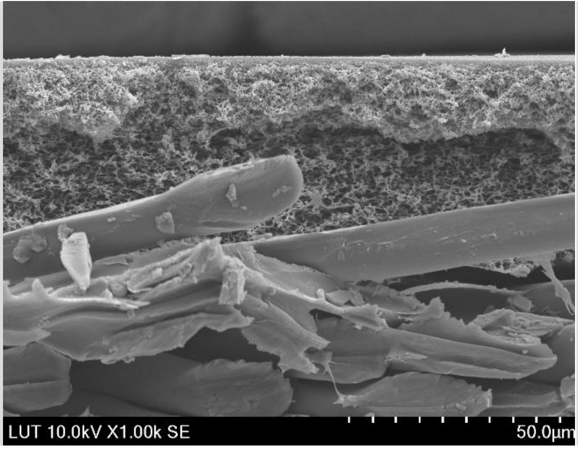
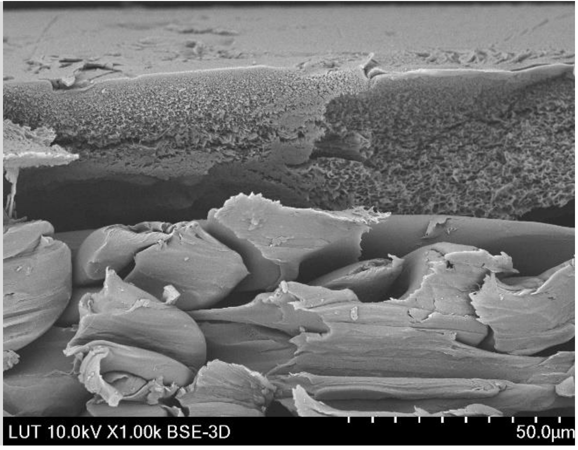
	Before DES Exposure	**After DES Exposure**
UP005 (PES)		
NF 270 (Polyamide)		
AG (Polyamide)		

Table 17: Cross-sectional images of PES and Polyamide membranes before and after DES exposure

	Before DES Exposure	**After DES Exposure**
UP005 (PES)		
NF 270 (Polyamide)		
AG (Polyamide)		

13.2 Solvent Characterization

13.2.1 Rheometer Analysis

Rheometer analysis is crucial in this study in terms of determination of optimum temperature range where decomposition of the membrane structure will not be observed and satisfying flux values of the membrane can be obtained.

Initially DES rheology behaviour with a change in shear rate was analysed in order to better understanding of change in DES viscosity with temperature. It has been expected to observe a Newtonian behaviour based on previously performed experiments on different DES types (Rengstl et al., 2014). According to performed experiments, results were matching with the expected Newtonian fluids phenomenon due to exhibited constant viscosity values along with a change in shear rate (RheoSense, n.d.).

During the performed experiment where viscosity change over temperature was observed, optimal operating temperature range of filtration experiments where pure DES was used as feed solution has been decided until 60℃. The reason behind this is an observed remarkable decrease in the DES viscosity until this temperature value.

Presented viscosity results in Figure 15 have an expected pattern. Since Newtonian fluids show an increase in mobility in other words a decrease in viscosity with elevated temperatures.

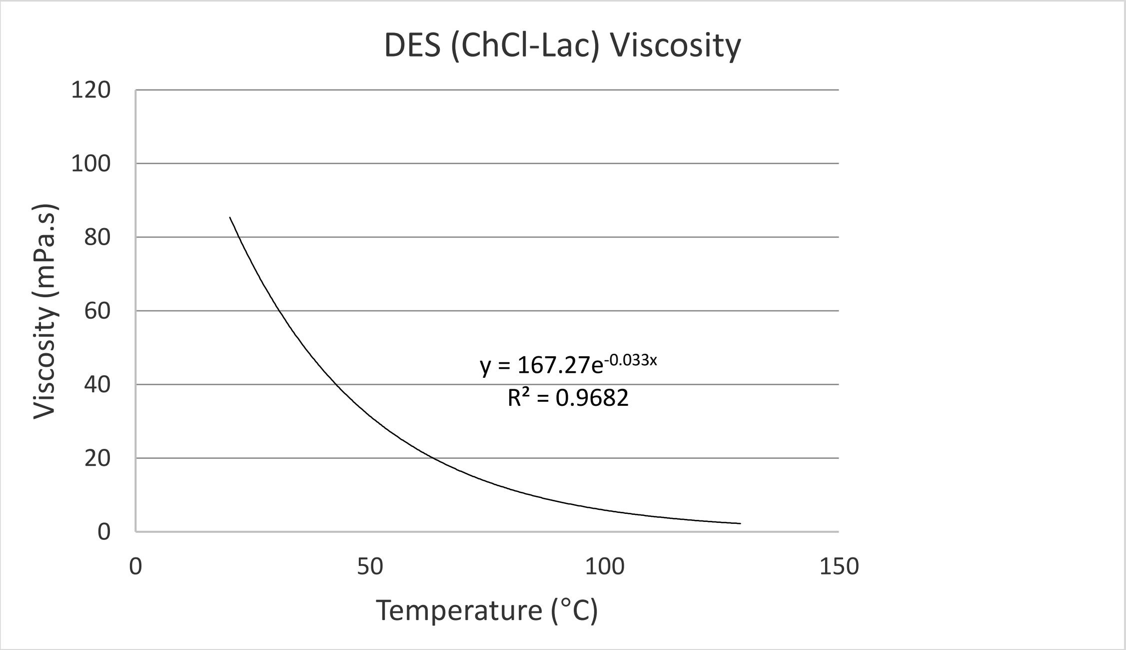


Figure 15: Viscosity of DES (ChCl: Lactic Acid) over temperature

13.2.2 Temperature Effect on Pure DES Flux

Temperature effect of pure DES's flux has been measured for two nanofiltration membranes i.e., NF 270 and NFW. The NFW has a higher MWCO, in order to understand whether there is any positive effect of higher MWCO on pure DES flux. Experimental conditions and measured water and DES fluxes for the NF 270 and NFW membranes are given in Table 18.

Table 18: Experimental conditions of dead-end membrane filtration modules for NF 270 and NFW at 60 °C and 9.5 bar for pure DES membrane filtrations
* represents average flux of Pure DES measured in first 10 minutes

	NF 270	**NFW**
Water Flux Before the DES Filtration, kg/(m^{2}h)	118.9 T= 20°C P=9.5 bar	123.2 T= 20°C P=9.5 bar
Water Flux After the DES Filtration, kg/(m^{2}h)	154.3 T= 20°C P=9.5 bar	210.6 T= 20°C P=9.5 bar
***Flux of Pure DES, kg/(m^{2}h)**	0.57 P=9.5 bar	1.27 P=9.5 bar

Although using the higher MWCO membrane i.e., the NFW membrane results slightly higher DES flux, still a remarkably low flux value is observed which demonstrates the difficulty of non-diluted pure DES filtration through nanofiltration membranes.

Pure DES flux values of NF 270 and NFW membranes together with pure DES viscosities as a function of temperature is presented in Figure 16.

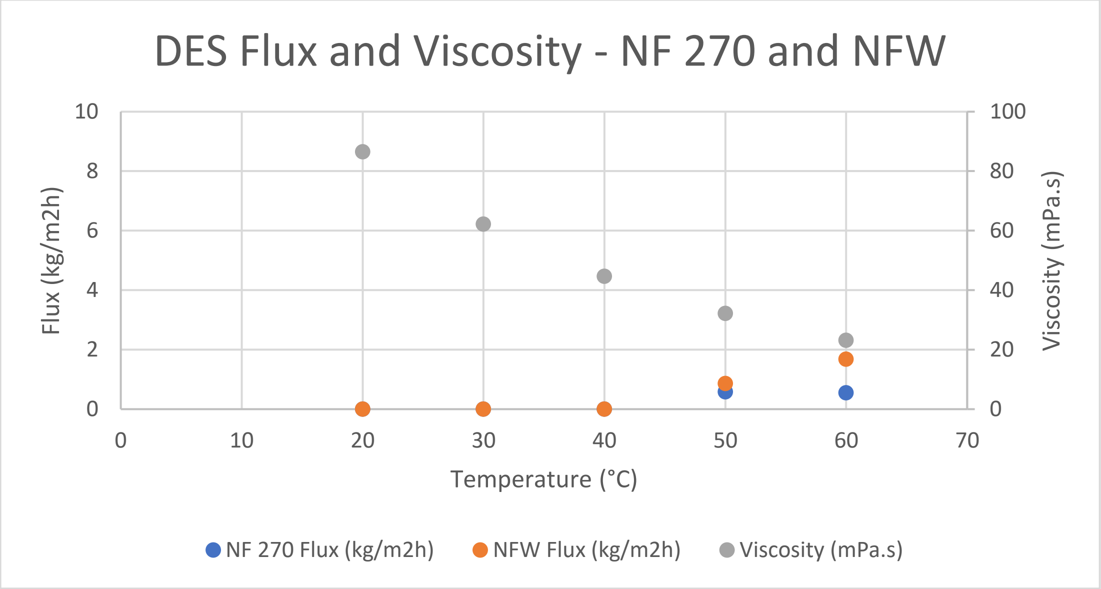


Figure 16: DES flux and viscosities of dead-end membrane filtration modules for NF 270 and NFW at 60 °C and 9.5 bar for pure DES membrane filtrations

As it is seen in Figure 16, at 40°C no flux was observed for both nanofiltration membranes. Although in the Figure 16, it seems like there is an increase in the pure DES flux, it cannot be concluded that whether the flux is slightly increasing just at 50°C or before that, because the flux was measured at 40°C and at 50°C. Additionally, between 50°C and 60°C very low flux was obtained despite of a sharp decrease in pure DES viscosity which was expected to increase the pure DES flux.

In order for better understanding of DES's viscosity behaviour, it has been compared with the viscosity of water based on the literature data of water viscosities at various temperatures (Fig. 17).

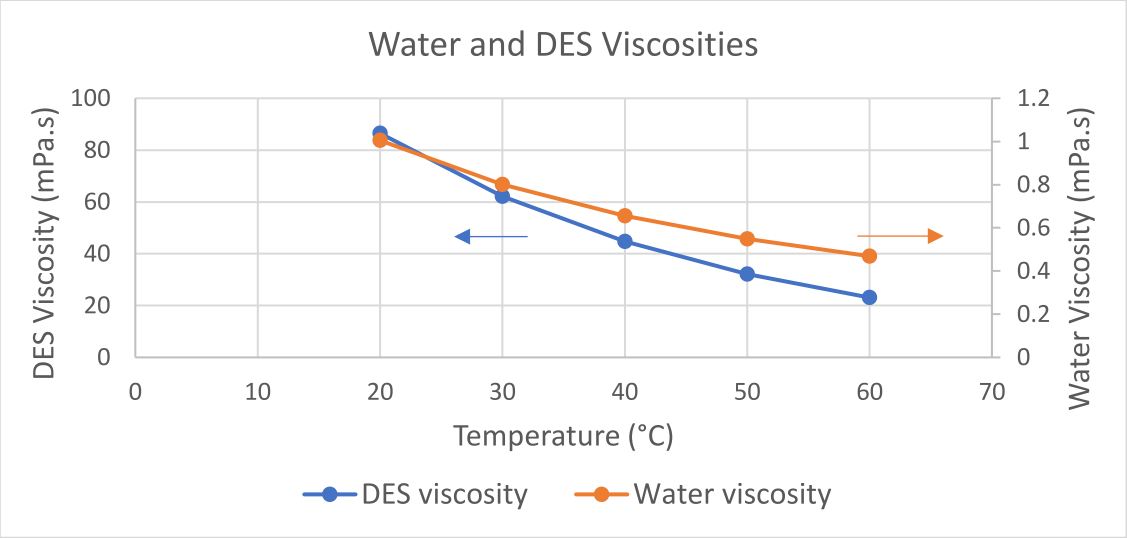


Figure 17: Water and DES viscosities over temperature

13.2.3 Precipitation of Dissolved Materials in 20% Spent DES Solution

After DES (100%) treatment of wood the solution was diluted to 20% DES solution with water in order to enable its filterability. Since precipitation of lignin in the presence of water occurred and it can have a detractive effect on membrane filtration process, it has been decided to observe whether any possible improvements on permeate flux can be achieved or not by using solid-liquid separation (filtration) before the membrane filtration process. Obtained results are represented in Table 19.

Table 19: Lignocellulosic material concentrations after filtration of 20% spent DES followed by a waiting under ambient temperature throughout the night

	Lignocellulosic Compound Concentration (g/L)
After 1st Filtration (2.5 μm)	0.13
After 2nd Filtration (0.2μm)	0.11
After 3rd Filtration (0.2μm)	0.005

According to Table 19, it can be clearly seen that only a small amount of dissolved material was precipitated and removed by filter paper. This result can also be supported with the pictures of 20% spent DES solution which are taken after waiting overnight after each filtration step which are given in Figure 18. As it can be seen, while after 1st filtration, lignin precipitation can still be observed, at the end of the 3rd filtration, lignin precipitation cannot be observed by naked eye.

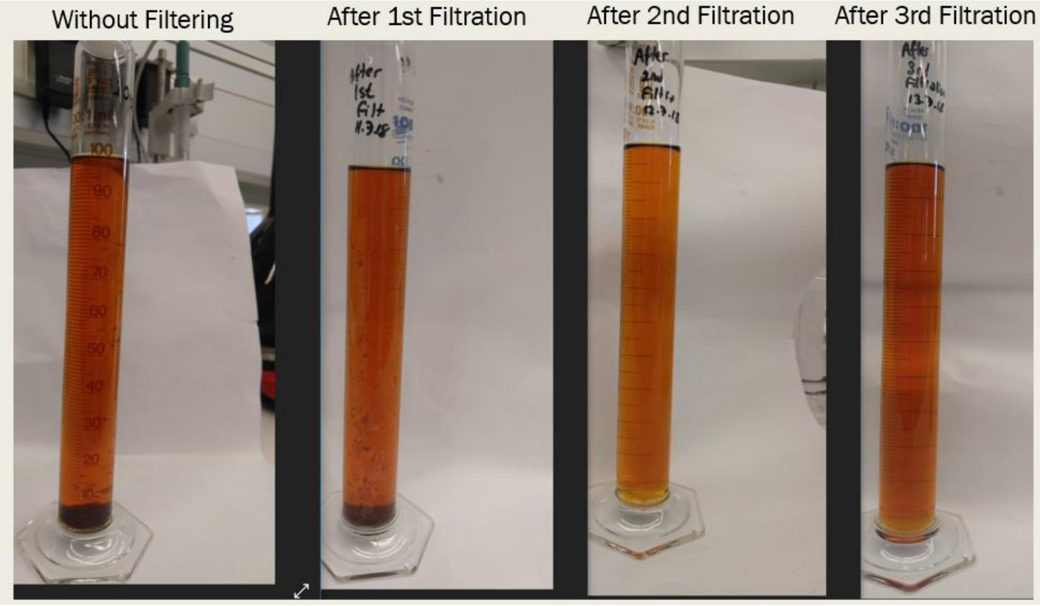


Figure 18: Pictures of 20% spent DES solution after each filtration

13.2.4 Characterization of DES

FTIR peaks of DES components and the DES itself are shown in Figure 19. Presented peaks in Figure 19, are not the original peaks for choline chloride and DES. For a better understanding of the FTIR graph, their absorbance values are shifted to 1 and 2 higher values, respectively for choline chloride and DES.

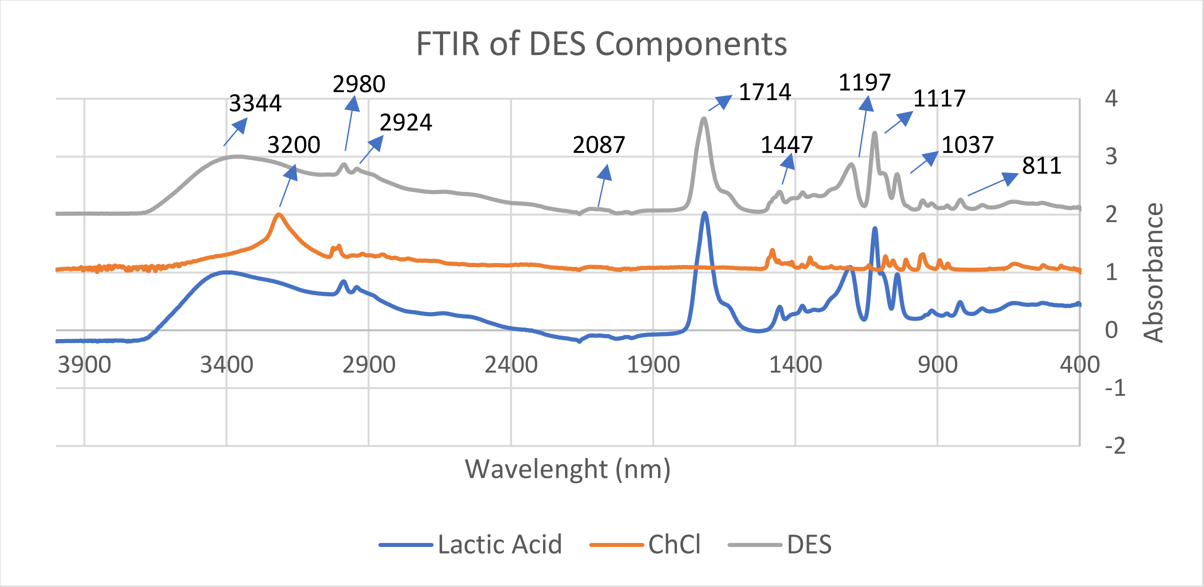


Figure 19: FTIR analysis of DES and its components by using the Perkin Elmer Frontier spectrometer with universal ATR module of diamond crystal at a resolution of 4 cm^{-1} in the absorbance mode

Choline chloride (ChCl) shows different peaks compared with lactic acid and with DES, while the same peaks are observed for DES and lactic acid. This result makes it tough to understand presence of any decomposition of DES by just looking at the peaks. Additionally, the reason behind DES and lactic acid have almost the same peaks may be due to high composition of lactic acid in DES solution i.e., 9 moles of lactic acid.

For the same purpose, FTIR peaks of non-diluted pure DES in the feed and permeate samples were compared. According to obtained same FTIR peaks as a result of a membrane filtration experiment with NF 270 membrane under 60℃ and 9.5 bar, it can be stated that there is not significant decomposition of DES caused by membrane filtration process.

UV-Vis analysis of non-diluted pure DES, diluted pure DESs and its components have been performed for better interpretation of lignin peaks in the feed, permeate and retentate samples of membrane filtration experiments. During UV-Vis experiments 280 nm was accepted as the wavelength where lignin peaks can be observed. However, DES compound and its components can also show peaks around the same wavelength with lignin. Therefore, for more accurate understanding of UV-Vis peaks, choline chloride, lactic acid and DES peaks were examined and represented in Figure 20.

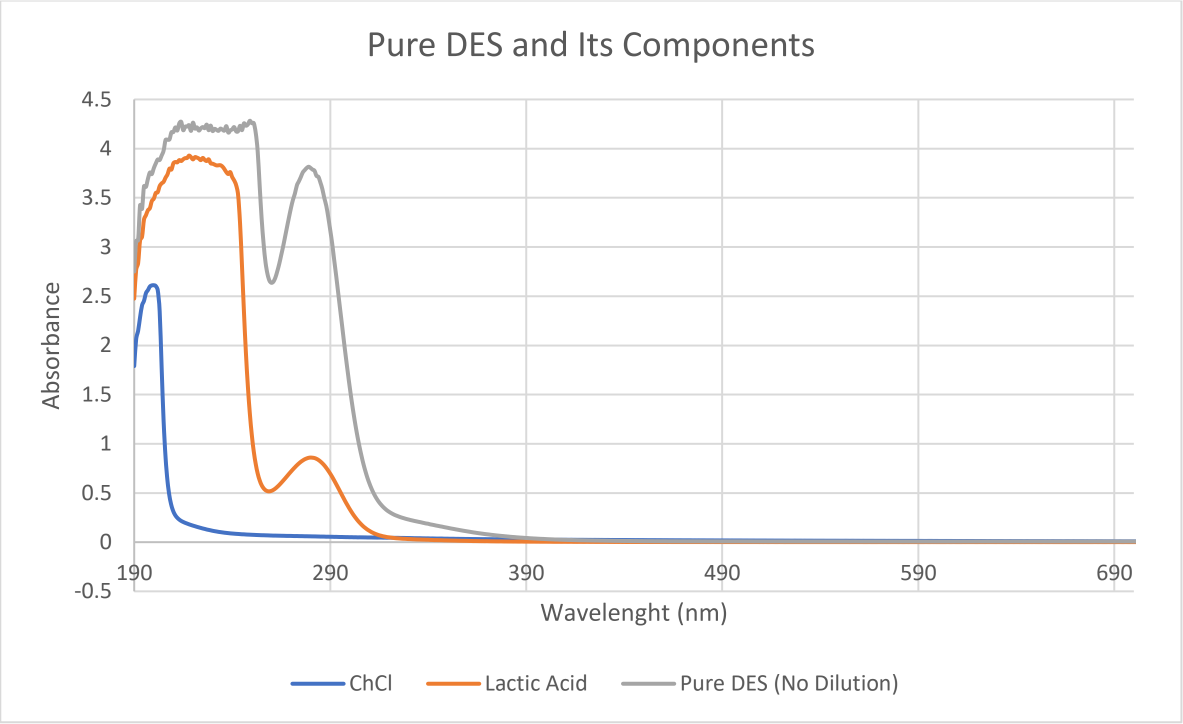


Figure 20: UV-Vis analysis of DES and its components where DI pure water used as a blank by using UV/Vis spectrophotometer (Jasco V-670 spectrophotometer, Japan) in the adsorption mode

As it is displayed in Figure 20, lactic acid and non-diluted pure DES show peaks around the same wavelengths i.e., 190 nm and 280 nm, but with different absorbance values, while choline chloride (ChCl) only shares the peak around 190 nm with lactic acid and DES, but again with a difference in the light absorbance value. In other words, both non-diluted pure DES and its components show absorbance values at the wavelengths where lignin molecule is also expected to display peaks i.e. 280 nm. However, it should be kept in mind that any dilution on utilized pure or spent DES as a feed solution will cause changes in the absorbance peaks. Thus, if a comparison of diluted utilized DES solution and its components are required to be done, then comparison should be performed based on diluted pure or spent DES solution as it was already represented in Figure 20.

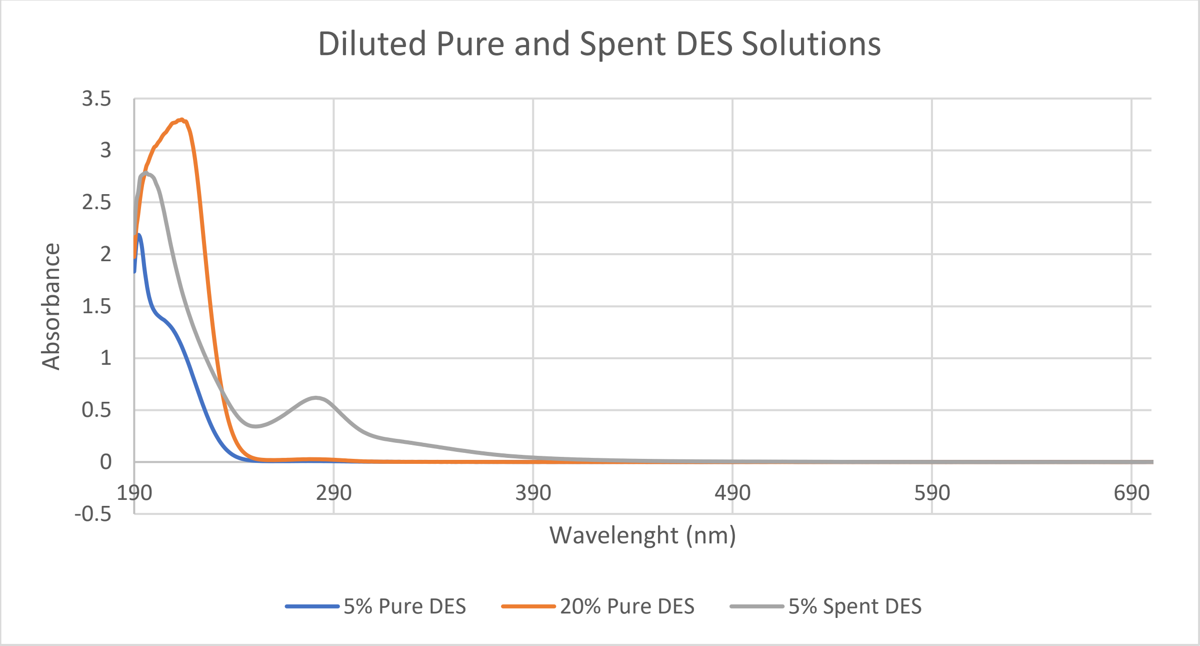


Figure 21: UV-Vis analysis of diluted pure and spent DES solutions where DI pure water used as a blank by using UV/Vis spectrophotometer (Jasco V-670 spectrophotometer, Japan) in the adsorption mode

According to performed UV-Vis analysis for this purpose where 20% is used as a feed concentration for utilized spent DES solution during membrane filtration process, lignin presence has been observed at wavelength of 280 nm. This wavelength was decided as an indication for a lignin presence, since diluted 20% and 5% pure DES does not display peaks at 280 nm. (Figure 21)

13.3 Study to Observe Tightening Effect of DES on Membrane Structure

In order for better understanding of observed very low flux of 20% spent DES, it was decided to study whether DES causes any tightening of the membrane structure which can lower the permeate flux. For this study, PEG (3000 g/mol) retention of the membranes was measured before and after the membrane filtration with 20% pure DES solution.

According to the results showed in Table 20 the observed increase in PEG solution (1 g/L) permeability i.e. 56%, and a decrease in water permeability i.e., 35%, after DES exposure, may be explained with following argument. If DES exposure makes the membrane softer which makes it easier to get damaged, applied higher DES filtration pressure after water flux i.e., 9 bar, could cause a compaction on the membrane which lowers the permeability compared with DES filtration after PEG flux. Additionally, observed permeability difference between PEG, water and DES permeabilities can also be arisen from the variations of the cut membrane pieces.

As an unexpected result, an increase in the PEG solution permeability which leads to an increase in the PEG retention after DES exposure of the membrane, can be given. Although there is an inverse relation between permeability of solution and observed retention, the same unexpected behaviour has been already observed with another ultrafiltration membrane with the same MWCO which is UFX5 membrane in Table 15.

Table 20: Average Flux and PEG retention results of UP005 before and after DES filtration measured in first 10 minutes
$T_{\text{PEG and Water Filtration}}$=25℃, $T_{\text{20\% Pure DES Filtration}}$=60℃
VRF of 20% pure DES for UP005 (with PEG) and UP005 (with water) are 53.6% and 39.0% respectively

UP005 (with PEG)		UP005 (with water)	
Pressurizing	T=25℃ and P=9.5 bar	**Pressurizing**	T=25℃ and P=9.5 bar
Before PEG Solution Permeability (kg/m^2.h.bar) at 4 bar	14.8	**Before Water Permeability (kg/m^2.h.bar) at 6 bar**	18
After PEG Solution Permeability (kg/m^2.h.bar) at 4 bar	23.1	**After Water Permeability (kg/m^2.h.bar) at 6 bar**	11.6
20% Pure DES Permeability (kg/m^2.h.bar) at 6 bar	40.0	**20% Pure DES Permeability (kg/m^2.h.bar) at 9 bar**	16.9
PEG Retention Before DES (%)	26.3	**No Retention Study**	
PEG Retention After DES (%)	74.1		

13.4 Purification of 20% Spent DES Solution

Insufficiently low flux of non-diluted spent DES during membrane filtration process makes dilution of utilized feed solution crucial. For this purpose, 20% spent DES solution was used. NF 270 membrane, whose resistibility against pure DES solution was already tested, and four different ultrafiltration membranes with different MWCO value i.e., UH004P, UP005, UP010 and UP020 membranes, were studied.

13.4.1 NF 270 Membrane

The effect of centrifugation, i.e. removal of solid material, on the flux and fouling of NF270 membrane was studied with 20% spent DES solution (Table 21) where any deformation caused on the membrane by the spent DES solution was understood by water fluxes. While the experimental conditions for water flux measurements were set as 20℃ and 19 bar, for spent

DES solution, the temperature was 50°C and pressure 25 bar. Experiments were carried out by using a dead-end filtration module which is described in Section 12.2.2

Table 21: Flux results of 20% spent DES with and without centrifuge by NF 270 membrane filtration

	Without Centrifuge	With Centrifuge
Before Water Flux (kg/m2.h)	178.2	163.2
After Water Flux (kg/m2.h)	132.8	140.2
Spent DES Flux (kg/m2.h)	3.76	3.37

According to shown results in Table 21, it can easily be concluded that centrifuge of 20% spent DES feed solution does not enhance the observed permeate flux. In order to understand the purification efficiency of NF 270 membrane on 20% spent DES solution, pictures of feed, permeate and retentate samples were shown in Figure 22.

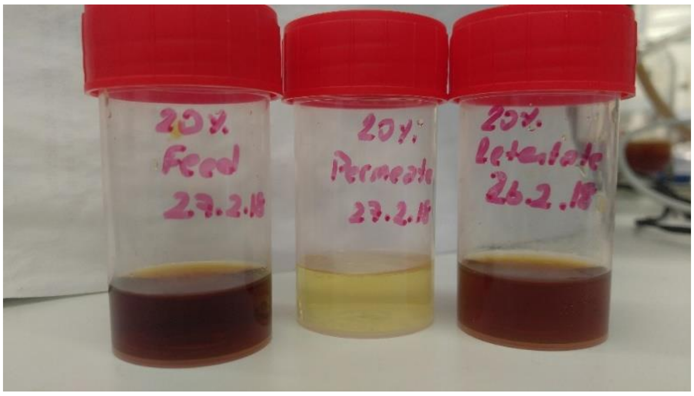


Figure 22: Pictures of feed, permeate and retentate samples of 20% spent DES solution by NF 270 membrane filtration

Based on Figure 22, it can be stated that separation of lignin from the spent DES solution was probably not fully effective yellowish colour of the permeate sample. In brief, due to very low permeate flux of NF 270 membrane on 20% spent DES, it has been decided to try utilization of higher MWCO ultrafiltration membranes in order to improve the process efficiency.

13.4.2 UH004P Membrane

As discussed in previous chapter the flux in nanofiltration was very low. Therefore, UF was tested prior to NF aiming to improve the flux in NF. For this purpose, UH004P membrane with MWCO of 4 kDa was used. However, surprisingly, obtained permeate flux which is 0.88 kg/m^{2}h under 50°C and 10 bar, was even lower than NF270 membrane whose MWCO is surely lower i.e., 400 Da. However, applied different experimental conditions and different production material of UH004P and NF 270 membranes can be the reason. Since, insufficient results were obtained with UH004P membrane, another series of ultrafiltration membrane with different MWCO values, has been studied.

13.4.3 UP005, UP010 and UP020 Membranes

The effect of MWCO on permeate flux of 20% spent DES solution was studied with three different ultrafiltration membrane whose MWCO values are 5 kDa, 10 kDa and 20 kDa for UP005, UP010 and UP020 membranes respectively. While utilized temperature for water flux was 25℃, during DES flux, 60℃ was used for each ultrafiltration experiments, in order to reduce the viscosity of DES. Obtained flux results were represented in Table 22.

Table 22: Flux results of 20% spent DES for UP005, UP010 and UP020 membranes

	UP005	**UP010**	**UP020**
Pressurizing (30 min)	T=25°C, P=9.5 bar	T=25°C, P=5 bar	T=25°C, P=2 bar
Before Water Flux (kg/m2.h)	136.5 at P=6 bar	68.6 at P=1 bar	75.1 at P=0.5 bar
After Water Flux (kg/m2.h)	8.74 at P=6 bar	2.53 at P=1 bar	2.73 at P=0.5 bar
DES Flux (kg/m2.h)	1.04 at P=9.5 bar	1.42 at P=4 bar	1.66 at P=2 bar
Feed and Permeate Amounts (g)	Feed= 300 Permeate= 5.56	Feed= 300 Permeate= 5.48	Feed= 300 Permeate= 5.55
Lignin Retentions	23.2	27.9	8.55

As it can be clearly seen from Table 22, an increase in the MWCO of membranes results in a decrease in required applied hydrostatic pressure to achieve approximately the same flux. Therefore, pressurizing conditions as well as utilized pressures during water and spent DES flux filtration processes differs from each other. Based on measured pure water fluxes, it can be educed that spent DES filtration has a remarkable negative effect i.e., fouling, on all three ultrafiltration membranes which causes a dramatic decrease in water fluxes. Therefore, in case of utilization of one of these membranes during spent DES recycling processes, cleaning of used membrane will be of capital importance, for the lifetime of the process. In terms of effect of altered MWCO on spent DES flux, as membrane gets more open i.e., having higher MWCO, 20% spent DES flux increases. However, still even with the highest MWCO membrane i.e., UP020 membrane, observed permeate flux i.e., 1.66 kg/m^{2}h at 2 bar is very low. One of the reasons to this result can be osmotic pressure of 20% pure DES solution which is calculated as 11 bar based on Eq 7 (Pláteník, n.d.).

Despite of high osmotic pressure presence in solution, it should be kept in mind that, calculated osmotic pressure is a theoretical value for the conditions where 100% rejection is assumed. However, this assumption is not realistic in ultrafiltration experiments.

Even though slightly higher flux is observed with higher MWCO membranes, utilization of more open membrane means enabling of more lignin molecule penetration through the membrane which results in a decrease in the permeate purity. Thus, while deciding on a suitable membrane whose flux and separation efficiency is good enough, purity of permeate solution should also be placed an importance. For this purpose, as a good indicator of permeate purities absorbance of UV light and the retention values are calculated from absorbances (Table 22 and Table 23). Although lower lignin retention values were expected with increasing MWCO of membranes, calculated lignin retention results show that UP010 membrane has the highest lignin retention which results in the lowest lignin concentration in the permeate. The reason behind this result is because average of the feed and retention absorbance values are taken, to be represented as a feed absorbance values.

As another indicator of purity of feed, permeate and retentate samples of all three membranes which are diluted with dimethyl sulfoxide (DMSO), UV-Vis analysis was performed. UV-Vis analysis absorbance results which are measured at 280 nm were given in Table 23. During the analysis, a dilution for all samples was performed due to measured high absorbance peaks which are out of the limits of UV-Vis spectra.

Table 23: Absorbance values for UP005, UP010 and UP020 membranes at 280 nm after freeze-drying under 60°C and 9.5 bar, 4 bar and 2 bar, respectively for UP005, UP010 and UP020
* Represents average of feed and retentate absorbance values

ABSORBANCES	UP005	UP010	UP020
Permeate	241.2	258.9	317.7
Feed*	314.1	359.2	347.5

In this case, 280 nm as a specific wavelength where high absorbance values were observed, decided to be used as an indicator for lignin, due to nonexistence of large unsaturated aliphatic groups (Jingjing, 2011). Accordingly, permeate of UP020 membrane has the highest lignin content with the highest absorbance value and as MWCO of the membrane increases, lignin concentration in the membrane's permeate increases. Since increasing MWCO of the membrane causes a decrease in permeate purity, while deciding a suitable membrane for spent DES filtration process, highest cut-off membrane i.e., UP020 membrane, should not be chosen despite of its higher flux.

Additionally, picture of permeate samples for UP005, UP010 and UP020 membranes which are respectively displayed in Figure 23, indicates lower lignin retentions with increasing MWCO of the membranes as expected, due to darker colour of sample from UP005 membrane to UP020 membrane.

Figure 23: Pictures of permeate samples for UP005, UP010 and UP020 membranes respectively under the conditions mentioned in Table 22

While lightest permeate colour is observed by UP005 membrane, UP020 membrane has the darkest permeate colour which indicates that lignin concentration in UP020 membrane is higher compared with other lower MWCO ultrafiltration membranes, since lignin presence causes a brownish colour change in the samples.

As another lignin indication method in the filtration samples, concentration of lignin was calculated based on Eq 8 which is given in Materials and Methods in section 12.3.4 UV/Vis Analysis. Although it is more likely to have an interference due to carbohydrate decomposition products at 280 nm compared with 205 nm, analysis was performed at a wavelength of 280 nm. Since at 205 nm, 5% pure DES also displays a peak which can affect the accuracy of any calculations based on 205 nm.

For a better understanding of content of the feed, retentate and especially the permeate samples, HPLC analysis which indicates the lactic acid concentration was performed and represented in Table 24. Based on obtained results, it can be seen that surprisingly, lactic acid retentions are negative. However, filtration experiment with 20% pure DES feed solution does not show any negative lactic acid retentions.

Table 24: Lactic acid concentration in the samples of UP005, UP010 and UP020 membranes under the conditions mentioned in Table 22
VRF values were less than 1.1 and the same for all the tested membranes UP005, UP010 and UP020. Dilution factors for all the samples are the same.

Concentration (g/L)	UP005 Spent DES	UP010 Spent DES	UP020 Spent DES	20% Pure DES UP005
Permeate	252	255	212	122
Feed	174	194	177	190
Retentate	174	221	184	121

In terms of DES presence in the samples pH and conductivity measurements has been performed. Since pH value of non-diluted pure DES and 20% pure DES are 0.28 and 1.56 respectively, and it is known that DES has a high conductivity, observation of low pH and high conductivity were used as an indicator of DES presence in the samples (Table 25).

Table 25: UP05, UP010 and UP020 membranes sample's pH and conductivity results under the conditions mentioned in Table 22

	pH			Conductivity (ms/cm)		
	UP005	UP010	UP020	UP005	UP010	UP020
Retentate	1.7	1.6	1.7	33.1	31.9	33.9
Feed	1.6	1.6	1.6	32.2	32.2	31
Permeate	1.4	1.5	1.6	28.3	34.1	32.4

Based on pH results of permeate samples, as MWCO of membrane decreases pH of the samples decreases slightly which means DES permeation through membrane is more favourable than the other molecules present in spent DES. Thus, purity of the UP005 membrane permeate will be better than UP010 membrane and UP020 membrane. On the other hand, conductivity results does not have a clear trend. The reason behind this can be because conductivity does not linearly depend on the DES concentration, especially at higher DES concentrations.

Pictures of all feed, permeate and retentate samples and their colours which are belong to UP005, UP010 and UP020 membranes, as well as picture of these membranes after spent DES filtration, are given in Appendix 1-4 respectively.

As a result, although the permeability of the UP005 membrane was lower, it retained more colour (lignin) than other tested UF membranes and, therefore, it was chosen for further experiments.

13.5 Purification of 5% Spent DES Solution

Observed very low flux during the membrane filtration process with 20% spent DES, makes utilization of a more diluted spent DES solution necessary. Therefore, 5% spent DES solution was decided to be used as a feed solution for the ultrafiltration process which will be followed by nanofiltration and reverse osmosis membrane respectively. The reason behind utilization of three consecutive membrane is to enhance the separation efficiency as well as permeate flux which cannot be achieved by a single membrane filtration process.

13.5.1 Purification Process of 5% Spent DES Solution with UP005, NF 270 and AG Membranes

According to previously performed studies related with resistibility of membranes against pure DES and their performance in terms of separation efficiency and permeate flux, UP005, NF 270 and AG membranes were decided to be used in the respective order. Related process flow sheet is displayed in Figure 24 together with calculated lignin concentration of each stream. However, for better interpretation of Figure 24, DES loss in each process downstream due to non-zero DES retention, should be taken into account. The reason of using three consecutive membranes is to enhance efficiency of spent DES purification.

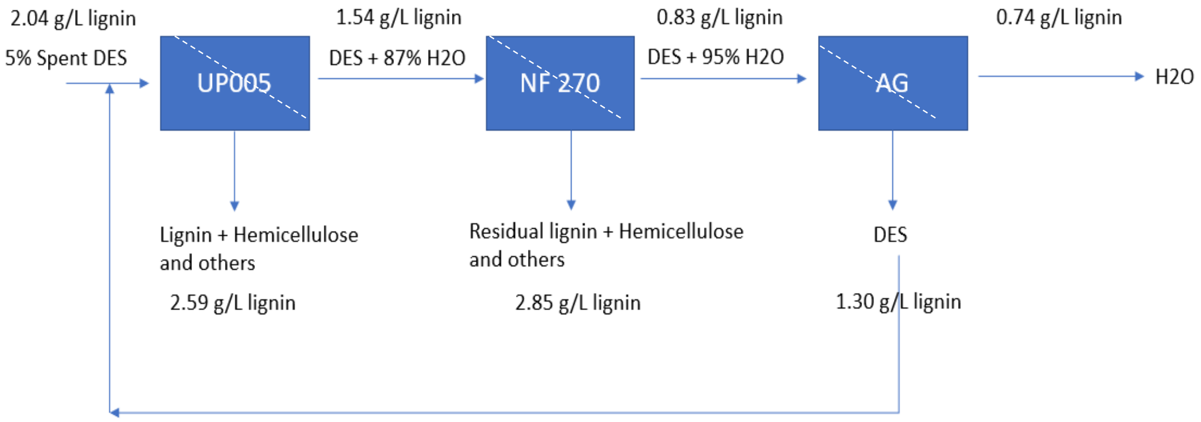


Figure 24: Process flow sheet of UP005, NF 270 and AG, where there is DES loss in each process downstream under the conditions mentioned in Table 26

Spent DES filtrations with UP005, NF 270 and AG membranes were performed at 60℃, 50℃ and 35℃ respectively, according to their maximum operating temperatures. Obtained flux results and calculated lignin retentions were represented in Table 26.

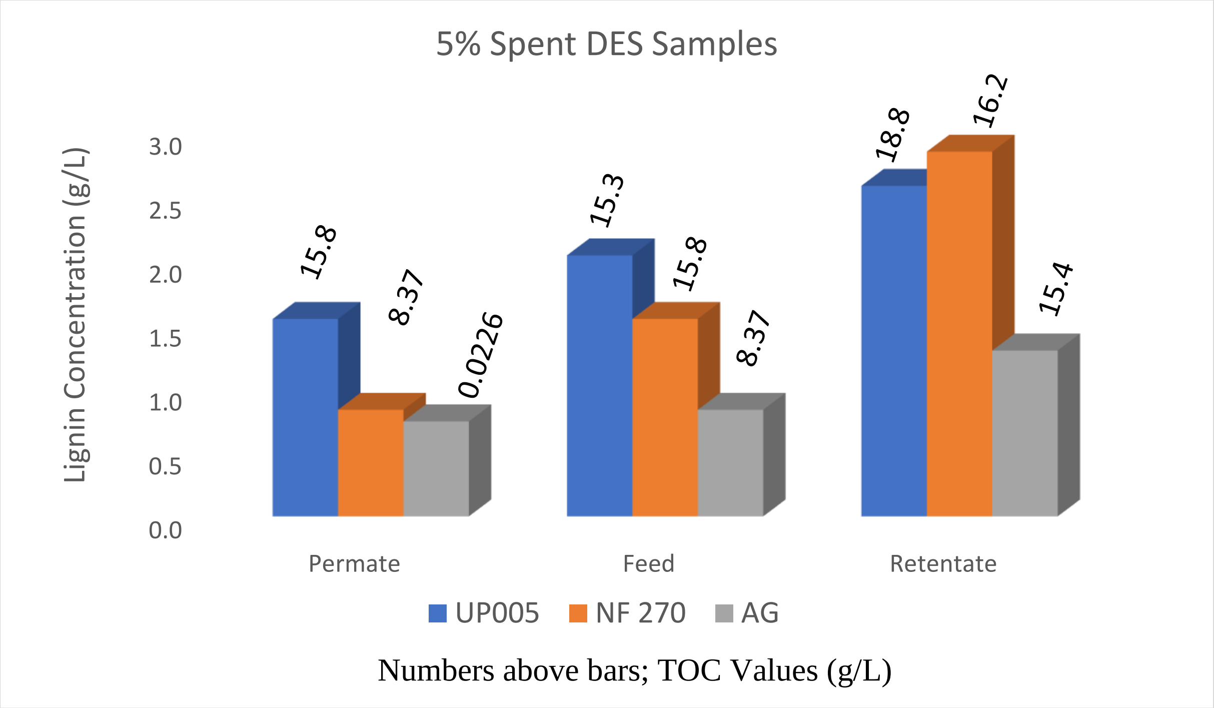
Table 26: Flux and retention results of UP005, NF 270 and AG membranes (VRF values in Table 27).

	UP005	**NF 270**	**AG**
5% Spent DES Flux (kg/m^2.h)	17.4 at P=9.5 bar	28.8 at P=20 bar	11.4 at P=25 bar
Lignin retention of 5% Spent DES (based on absorbance)	24.3	46	10.9
20% Spent DES Flux (kg/m^2.h)	1.33 at P=9.5 bar	-	-

It can be clearly seen from Table 26 that an increase in the dilution of spent DES solution from 20% to 5% enhance the flux nearly 13 times. Therefore, it has been decided to use 5% spent DES as a feed solution for the continuation of the experiments. In terms of lignin retentions, calculated based on absorbances, most effective separation actualizes by NF 270 membrane. This result is also matching with the colour of the NF 270 membrane's feed, permeate and retentate samples which are presented in Appendix 6, since there is a considerable colour change in between feed and permeate sample of NF 270 membrane.

In respect of recycled 5% spent DES purity, TOC analysis results of each sample which belong to each three membranes, are represented in Figure 25 above the bars which represents lignin concentrations. According to Figure 25 results, it can be concluded that retentate of reverse osmosis membrane which is aimed to be re-used for lignin dissolution from birch, is almost 5% pure DES, due to having similar carbon content with 5% pure DES i.e., 15.1 g/L. Additionally, due to observed very low carbon concentration, it can be stated that permeate of reverse osmosis membrane with TOC value of 0.0226 g/L is nearly pure water as expected. Thus, based on TOC results, it is concluded that excellent separation efficiency of water and DES was achieved with the reverse osmosis membrane (AG).

Besides lignin retention and carbon content of the samples, lignin concentrations of feed, permeate and retentate samples for all three membranes were calculated based on beforementioned Eq 8 and given in Figure 25.



Numbers above bars; TOC Values (g/L)

Figure 25: Lignin concentrations and TOC concentrations of UP005, NF 270 and AG membranes under the conditions mentioned in Table 26 (VRF values in Table 27).

Figure 25 shows that lignin concentration decreases from UP005 membrane to AG membrane in all feed and permeate samples as expected which proves the efficiency of the separation process. For each membrane lignin concentration is lower in the permeate compared with their feed solution and concentration of lignin is higher in the retentate in comparison with its feed. However, the values in Figure 25 show that the equation (8) used to calculate lignin amount in the samples is not valid for permeate samples.

In order to have a better comparison of separation efficiencies for filtration processes where 5% and 20% spent DES solutions were used as a feed for UP005 membrane, Figure 26 displays a comparison. The Figure 26 shows that only small amounts of lignin were retained with the UP005 membrane and tighter membrane is needed to purify the spent DES. Furthermore, the lignin concentration in the permeate of UP005 membrane when the 20% DES solution has been used is higher than in the spent DES used as feed (blue bars). The reason for this is not known.

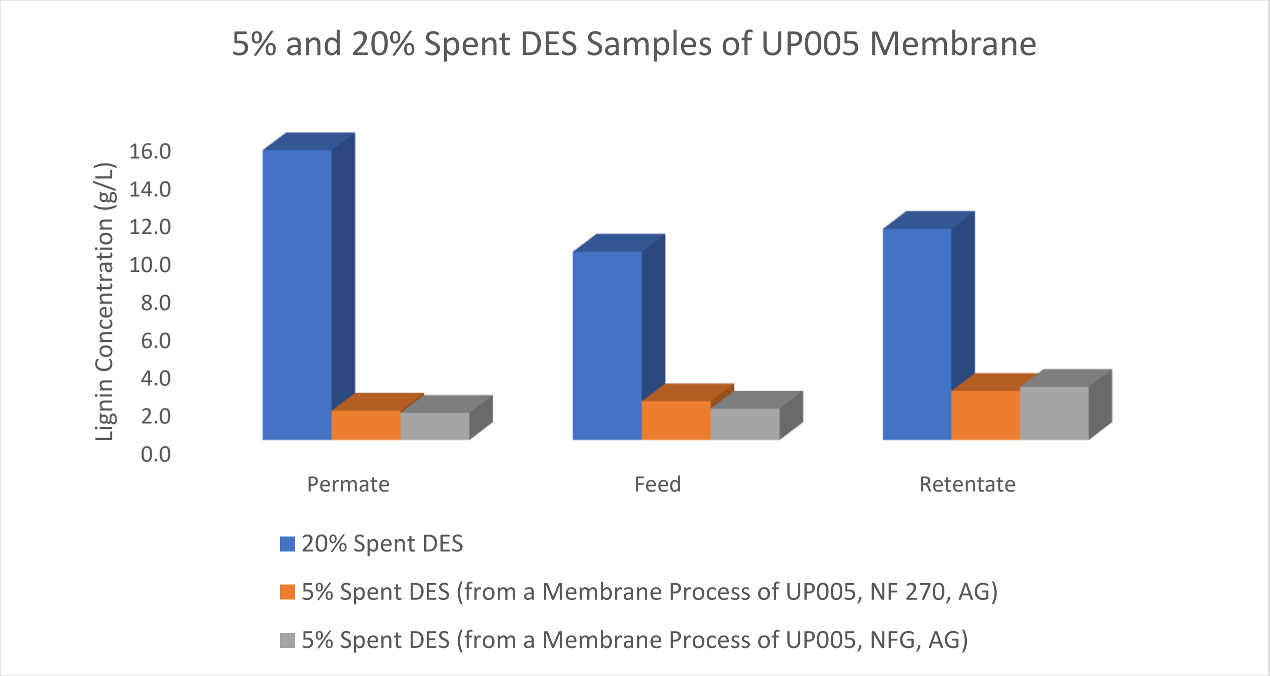


Figure 26: Lignin concentrations of feed, permeate and retentate samples for the UP005 membrane where 5% and 20% spent DES were used as feed solutions under the conditions mentioned in Table 22, Table 26 and Table 29

In terms of permeate flux of each membrane, a decrease in flux values was observed. In Table 27, flux reductions, as well as volume reduction values of UP005 and AG membranes were displayed. For UP005 membrane, volume reduction value at the end of the 2nd day was calculated. Based on represented results, there is a dramatic flux decrease in both cases. Although it was not represented, same dramatic decrease is also observed in NF 270 membrane.

Table 27: Volume reduction values and decrease in flux of UP005 and AG membranes by time under the conditions mentioned in Table 26

UP005	**Flux ($kg/m^2.h$)**	**Volume Reduction (%)**	**AG**	**Flux ($kg/m^2.h$)**	**Volume Reduction (%)**
1st Day	17.4	60	**10 min**	11.4	5.86
2nd Day	5.73		**4 hour**	3.17	29.9
			7 hour	2.12	35

As another analysis method for filtration samples, water content of permeate samples for UP005, NF 270 and AG membranes were analysed, and results are presented in Table 28. This analysis is performed under 50 ℃ where each sample were waited in the oven for three days.

Based on Table 28, an increase in the water content of permeate samples as utilization of membranes from ultrafiltration to reverse osmosis is observed. This result is expected, since as smaller cut-off membranes were used, it is likely that almost only water penetration through membrane is allowed. In the ideal scenario, most lignin should be removed from the 5% spent DES feed solution in ultrafiltration and nanofiltration steps and by reverse osmosis membrane, separation of water from pure DES should actualized.

Table 28: Water content in permeate samples of UP005, NF 270 and AG membranes under the conditions mentioned in Table 26

	Water in 25 mg Samples (%)
Permeate UP005	87.6
Permeate NF 270	95.6
Permeate AG	98.4

Represented results and pictures of 5% spent DES feed, permeate and retentate samples for all three membranes which are displayed in Appendices 5-7 are corroborative results to ideal case.

13.5.2 Purification Process of 5% Spent DES Solution with UP005, NFG and AG Membranes

In order to increase flux and DES concentration in the permeate of nanofiltration membrane i.e., NFG membrane, which aims to enhance filtration process yield by increasing DES concentration in the retentate of reverse osmosis membrane which will be re-used, utilization of higher MWCO nanofiltration membrane instead of NF 270 membrane is preferred. Related process flow sheet is displayed in Figure 27 together with calculated lignin concentration of each stream where feed and permeate stream of NFG membrane show a negligibly slight decrease in lignin concentration. Thus, it can be stated that almost no lignin separation is achieved by NFG membrane.

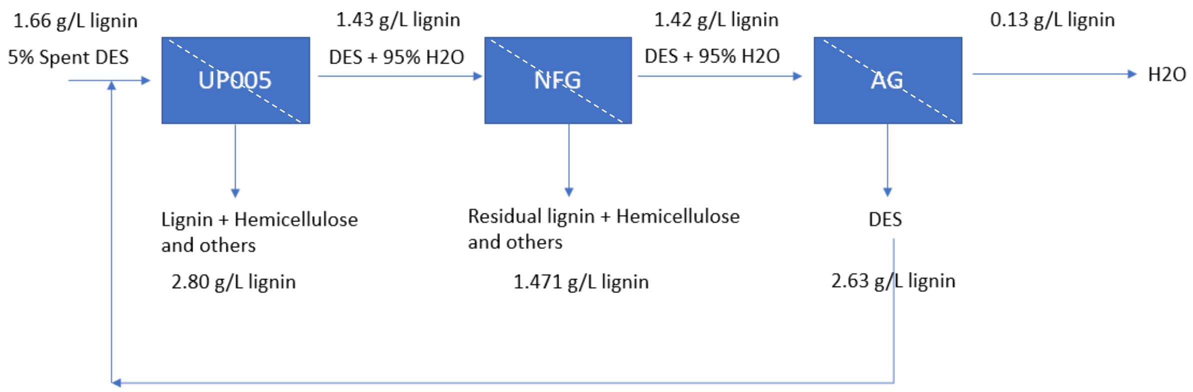


Figure 27: Process flow sheet of UP005, NFG and AG membranes under the conditions mentioned in Table 29

Utilized temperatures for 5% spent DES filtration process for UP005, NF 270 and AG membranes were 60℃, 40℃ and 35℃ respectively, according to their maximum operating temperatures. Obtained flux results and calculated lignin retentions were represented in Table 29.

In terms of absorbance-based lignin retention results, unlike previously mentioned filtration process where NF 270 membrane was used as a nanofiltration membrane, reverse osmosis membrane i.e., AG, displays the highest lignin retention. Additionally, almost nine times higher lignin retention of AG membrane after NFG membrane utilization, in comparison with AG membrane lignin retention value after NF 270 membrane utilization was observed. Since, feed concentration of AG membrane after NFG membrane utilization is approximately 1.5 times higher than the AG feed concentration after NF 270 membrane utilization. However, this result was expected, because of bigger average molecular size of feed due to higher pore size of NFG membrane compared with NF 270 membrane, which results in better separation. Similarly, absorbance-based retention results also prove that almost no lignin separation is achieved by NFG membrane utilization.

Table 29: Flux and retention results of UP005, NFG and AG membranes (VRF are represented in Table 30).

	UP005	**NFG**	**AG**
5% Spent DES Flux (kg/m^2.h)	3.70 at P=9.5 bar	107 at P=15 bar	10.6 at P=25 bar
Lignin retention of 5% Spent DES (based on absorbance)	12.9	0.57	91.1

In respect of recycled 5% spent DES purity, TOC analysis results of each sample which belong to each three membranes, are represented in Figure 28 above the bars which represents lignin concentrations. According to Figure 28 results, TOC values for AG membrane's retentate and 5% pure DES respectively as 27.0 g/L and 15.1 g/L, are not close to each other. The reason behind this can be because DES solution was more concentrated in the retentate of reverse osmosis membrane when NFG was used as a nanofiltration membrane. Thus, it can be concluded that when a higher MWCO nanofiltration membrane used, more DES is observed in the final retentate and permeate samples.

Besides TOC values, lignin concentrations of feed, permeate and retentate samples for all three membranes were calculated based on beforementioned Eq 8 and given in Figure 28.

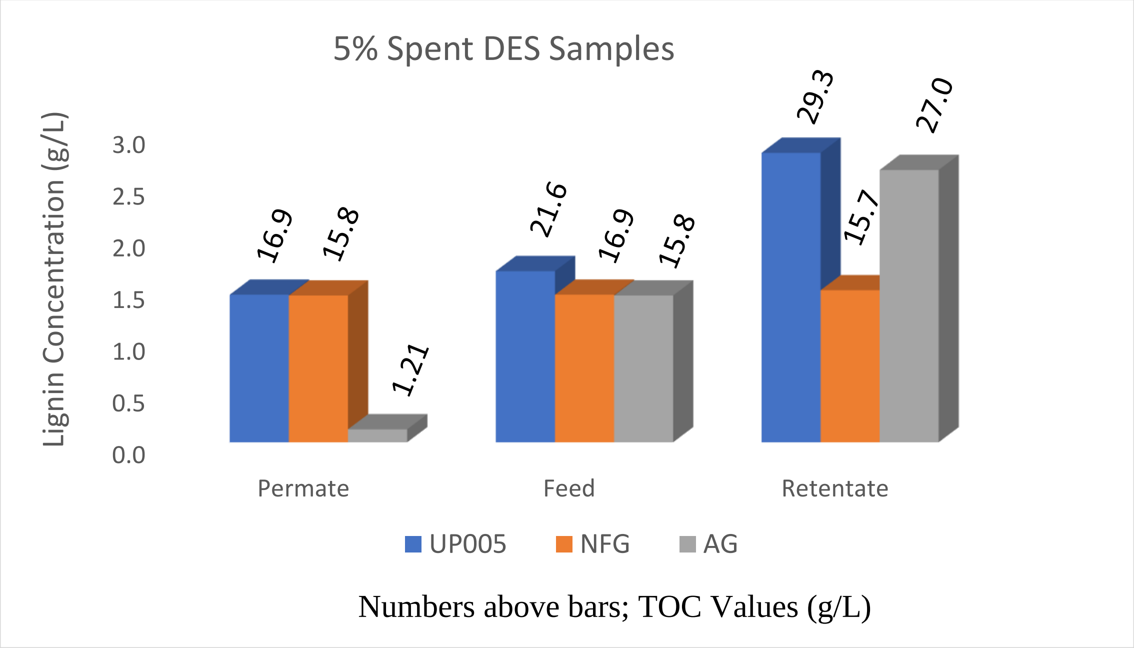


Figure 28: Lignin concentrations and TOC concentrations of UP005, NFG and AG membranes under the conditions mentioned in Table 29

Figure 28 shows that lignin concentration decreases from UP005 membrane to AG membrane in all feed and permeate samples except NFG membrane which almost does not show any change in the lignin concentrations. For UP005 membrane and AG membrane lignin concentration shows lower value in the permeate compared with their feed and retentate as expected.

In order to have a better comparison in terms of separation efficiencies of the processes where NF 270 and NFG were used as nanofiltration membranes, Figure 29 displays a comparison of reverse osmosis membrane i.e., AG, feed, permeate and retentate samples. In overall, better lignin purification efficiency was achieved with the membrane process where NF 270 was used as a nanofiltration membrane rather than the process where NFG was used. The reason behind this result is due to utilization of higher MWCO membrane as a nanofiltration i.e., NFG, which almost does not achieve any lignin removal, thus results in higher concentration in the feed, permeate and retentate of the reverse osmosis membrane.

As it can be seen, the use of reverse osmosis membrane with the process where NFG was used as a nanofiltration membrane lead to considerably higher lignin concentration in the RO retentate compared with the process where the NF 270 was used. This result is expected, since NFG membrane did not retain significantly lignin.

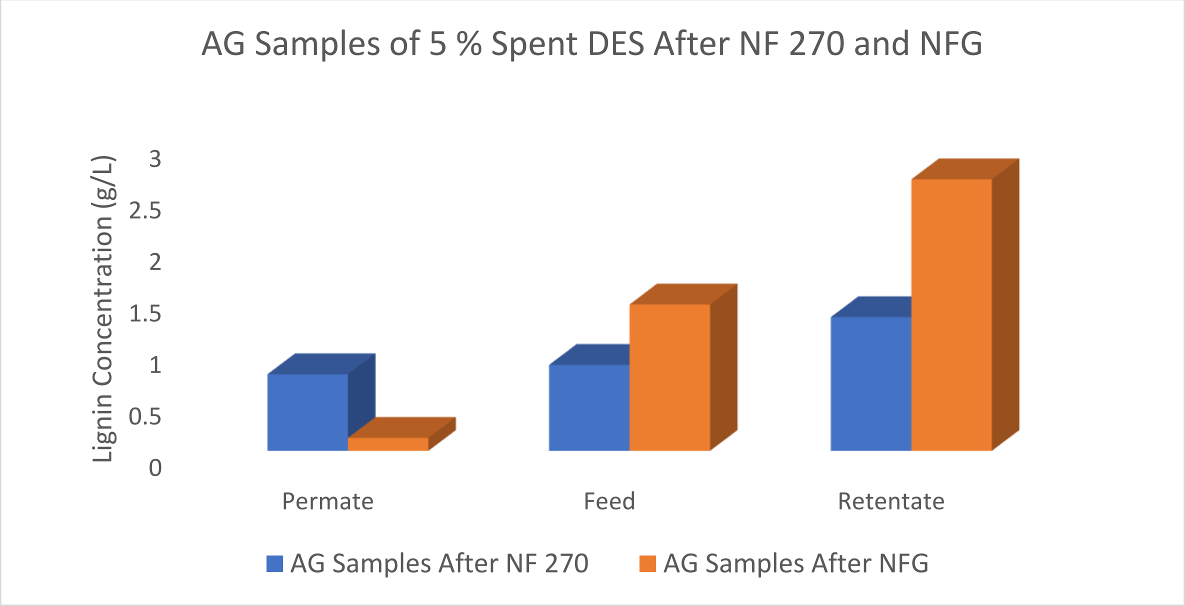


Figure 29: Lignin concentrations in AG membrane samples for the processes where NF 270 and NFG membranes are used as nanofiltration membranes under the conditions mentioned in Table 26 and Table 29

Permeabilities of each membrane were represented in Table 29 as 0.389, 7.13 and 0.424 kg/m^{2}hbar for UP005, NFG and AG respectively. A decrease in the permeate flux of AG membrane compared with the beforementioned process (NF270 as the NF stage), is also observed. However, this time reason can be explained due to more concentrated feed solution which can enhance fouling, as well as the higher osmotic pressure of the solution. Regarding to this, decrease of flux by time, as well as volume reduction values of each membrane were displayed in

Table 30. In each membrane, there is a considerable flux decrease observed, including NFG membrane which has the lowest decrease with the volume reduction (VRF) of 59.5%, compared with UP005 and AG whose VRFs are 63.8% and 48.8% respectively. As a comparison of membrane filtration durations, NFG membrane performed the fastest filtration

by far. This can be because NFG membrane do not retain components due to its high MWCO, thus there is not any concentrating of components occurred during the filtration as well as no increase in the osmotic pressure, which leads to a faster membrane filtration.

Table 30: Volume reduction values and decrease in flux of UP005, NFG and AG membranes by time under the conditions mentioned in Table 29

UP005	Flux (kg/m^2.h)	Volume Reduction (%)	NFG	Flux (kg/m^2.h)	Volume Reduction (%)	AG	Flux (kg/m^2.h)	Volume Reduction (%)
1 hour	15.7	3.6	**1 min**	186	7.4	**1 hour**	8.04	14.1
10 hour	4.23	42.1	**10 min**	99.4	24.8	**3 hour**	5.92	35.0
20 hour	2.12	63.8	**40 min**	73	59.5	**5 hour**	4.02	48.8

For better determination of spent DES filtration process efficiency, DES and water content of permeate and retentate samples of reverse osmosis membrane is analysed and represented in Table 31. This experiment was performed in the same way for the process where NF 270 membrane is used as a nanofiltration membrane. According to represented results, water content is lower and DES concentration is higher in both permeate and retentate samples, compared with the beforementioned process with NF 270 membrane usage. This result is expected due to higher MWCO of NFG membrane compared with NF 270 membrane, which allows more penetration of DES molecules. However, from the purification point of view, filtration process with NF 270 membrane is better, since there is more lignin presence in the retentate sample of AG membrane from the membrane process where NFG was used.

Table 31:DES and water content of permeate and retentate of AG membrane under the conditions mentioned in Table 29

UF, NFG, AG Membranes	DES + Lignocellulosic Materials (%)	Water (%)
AG Permeate	20.8	79.2
AG Retentate	28.6	71.4

Pictures of 5% spent DES feed, permeate and retentate samples from UP005, NFG and AG membranes are represented in Appendices 8-10.

13.6 Efficiency of Purified Spent DES in Wood Extraction

Lignin dissolution efficiency of recycled i.e., purified, 5% spent DES is analysed, in order to close the spent DES purification cycle by its re-use. Thus, comparison of extraction efficiency of purified 5% spent DES which is concentrated to 100% by evaporation, with efficiency of fresh DES become a matter of importance. If lignin dissolution efficiency of purified spent DES is close to efficiency of fresh DES i.e., pure DES before any wood treatment, overall efficiency and applicability of the process will be proven. Additionally, by this way it is possible to determine detrimental effect of increasing lignin concentration in purified spent DES on lignin extraction efficiency. For this purpose, performed experiment results which represent lignin concentration in untreated birch and purified spent DES treated birch from the membrane filtration process where consecutive usage of UP005, NFG and AG membranes takes place, was given in Table 32. Lignin concentrations in Table 32, were represented as two fractions which are acid insoluble lignin (AIL) that contains the higher lignin concentration and acid soluble lignin (ASL). However, extraction efficiency of purified spent DES from filtration process of UP005, NF 270 and AG membranes, could not be analysed, due to insufficient amount of purified spent DES.

Table 32: ASL and AIL content of untreated birch and recycled spent DES treated birch

	AIL (%)	ASL (%)	Total Lignin (%)
Untreated Birch	18.2	3.7	21.9
Recycled Spent DES Treated Birch from Filtration Process with NFG	12.5	2.3	14.8

Based on the presented results, lignin dissolution efficiency by purified spent DES is 32.6%, while lignin dissolution efficiency of fresh DES is 60% based on previously performed experiment where water content in both purified and fresh DES is approximately the same. It can be concluded that, lignin dissolution efficiency decreases approximately by half, due to presence of biomass degraded compounds in purified spent DES or due to the changes in DES composition.

14. CONCLUSION

Purpose of this thesis was to find out if DES used in the extraction of birch can be purified with membrane technology. Moreover, it was evaluated if the purified spent DES solution can be reused in extraction of birch. Recycling of DES from different process solutions is still a developing research area where not many researches have been performed, since DESs are new class of solvents.

Experimental part of this work was divided into three sections as preliminary experiments, spent DES purification experiments and experiments to determine efficiency of purified spent DES. In the first section the used DES and spent DES were characterized and membrane resistances against the DES were evaluated. The results from the first section show that 1) the used DES solution is a Newtonian fluid, of which viscosity decreases with temperature, 2) Non-diluted spent DES displays a very low permeate flux due to its high viscosity which can be decreased by dilution and 3) Membrane filtration did not cause significant changes in FTIR spectra of DES samples. For membrane resistances against pure DES, cross-flow membrane filtration experiments for four ultrafiltration and nanofiltration membranes and SEM analysis of specific ultrafiltration, nanofiltration and reverse osmosis membranes i.e., UP005, NF 270 and AG, were performed. These experiments showed that regenerated cellulose did not withstand DES, while polyamide and polyethylene sulfone (PES) membranes seemed to be more stable in DES filtration experiments.

Purpose of the second part of the experiments which includes membrane filtration experiments with two different feed concentrations of spent DES as 20% and 5%, was to examine the membrane based recycling process for spent DES. Based on the performed experiments it can be concluded that 1) Centrifuging the 20% spent DES solution does not provide any development in the permeate flux; 2) On the contrary to expected, UH004P membrane shows lower flux value than NF 270 membrane, despite of its higher MWCO; 3) Among ultrafiltration membranes the UP005 membrane was selected to be used for lignin removal in the purification of the spent DES for reuse due to its better lignin retention. To purify the spent DES for reuse a three-stage membrane process was studied. The membranes tested in the processes were 1) UP005 (UF), NF 270 (NF), AG (RO) and 2) UP005 (UF), NFG (NF), AG (RO). According to performed experiments, it can be concluded that purity of recycled spent DES by a filtration process where NF 270 membrane was used as a nanofiltration membrane, was considerably better compared with the purity of the recycled spent DES by a filtration process where NFG membrane is used. On the other hand, the NF270 membrane also retained partly DES, which leads to DES losses in the recycling process.

Purpose of last part of the experiments was to evaluate recyclability of the purified spent DES in terms of its efficiency to dissolve lignin from birch. According to performed experiment, two following conclusions can be drawn: 1) Lignin dissolution efficiency of purified spent DES where NFG membrane was used as a nanofiltration membrane, is 32.6%. 2) Lignin dissolution efficiency of purified spent DES by beforementioned process, falls approximately by half, compared with fresh DES extraction efficiency, due to presence of remained biomass degraded compounds in purified spent DES or possibly changes in DES composition.

Herewith, set objective of the thesis has been attained. However, possible improvements of the process in terms of notably slow solvent permeate flux, energy requirement of the process by three consecutive membrane utilization and lower lignin extraction efficiency by half, can be considered as further studies.

15. FURTHER RECOMMENDATIONS

Although effectiveness of a membrane filtration process with sufficient spent DES purification which results in reasonable lignin dissolution efficiency of birch has been proven, still some improvements can be achieved in terms of low permeate flux, lignin extraction efficiency, concentration of utilized spent DES feed solution and membrane resistibility. As one of the possible enhancements of the process, utilization of centrifuge followed by vacuum filtration which is prior to membrane filtration process can be considered, for the purpose of increasing flux. By this means, utilization of higher concentrated feed solution than 5 % spent DES may also be enabled. From the point of lignin extraction efficiency, purer recycled spent DES utilization which contains less lignin, should be studied to see whether any improvements can be achieved. For this purpose, membrane filtration process where NF 270 was used as a nanofiltration membrane, can be repeated in order to obtain sufficient amount of purified spent DES which is enough to determine lignin extraction efficiency. As another approach, rotary evaporator utilization instead of a reverse osmosis membrane can be considered, depending on the efficiency of evaporation and also the lignin content of the feed solution. In the sense of membrane resistibility, ceramic or metallic membrane usage as an ultrafiltration membrane can be taken into consideration.

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APPENDICES

Appendix 1: Feed, permeate and retentate samples of UP005 experiment where 20% spent DES is filtrated under 60℃ and 9.5 bar when VRF is 1.85%

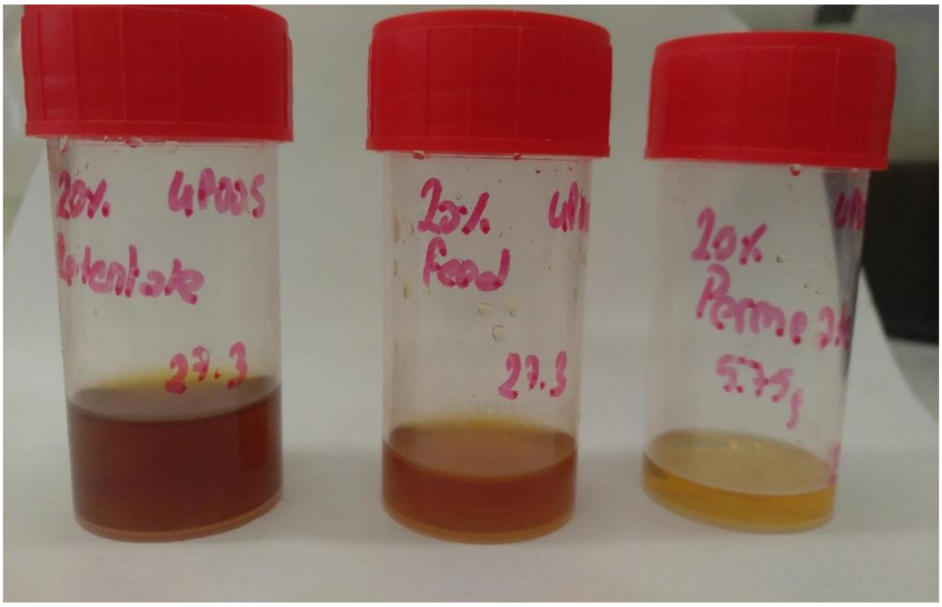

Figure 30: Pictures of retentate, feed and permeate samples of UP005 respectively

Appendix 2:Feed, permeate and retentate samples of UP010 experiment where 20% spent DES is filtrated under 60℃ and 4 bar when VRF is 1.83%

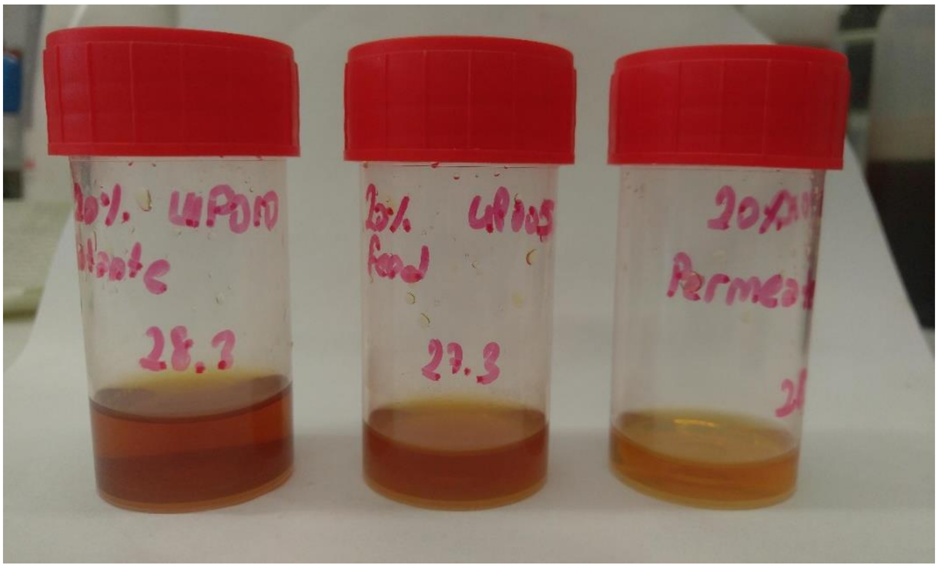

Figure 31: Pictures of retentate, feed and permeate samples of UP010 respectively

Appendix 3:Feed, permeate and retentate samples of UP020 experiment where 20% spent DES is filtrated under 60℃ and 2 bar when VRF is 1.85%

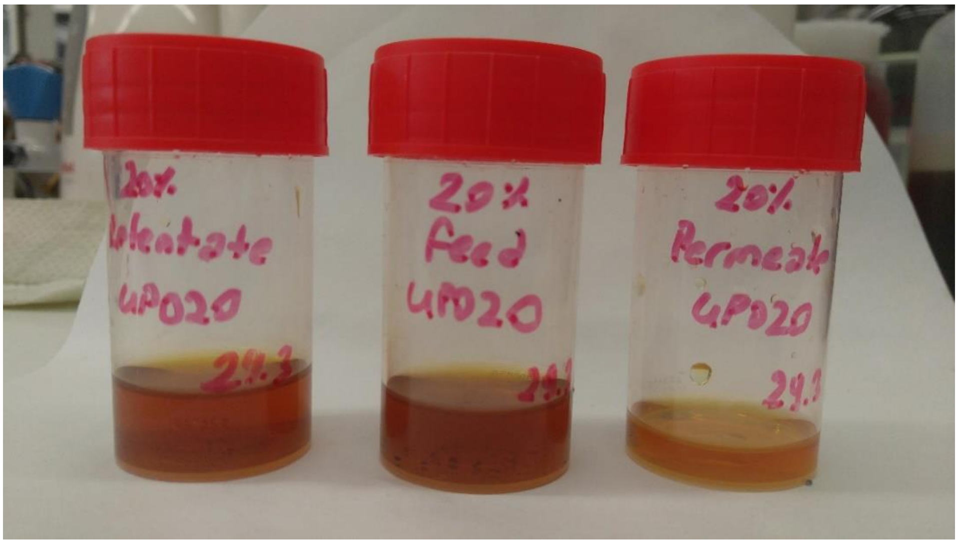

Figure 32: Pictures of retentate, feed and permeate samples of UP020 respectively

Appendix 4:Membranes after 20% spent DES filtration with UP005, UP010 and UP020 under 9.5 bar, 4 bar and 2 bar respectively, at 60℃

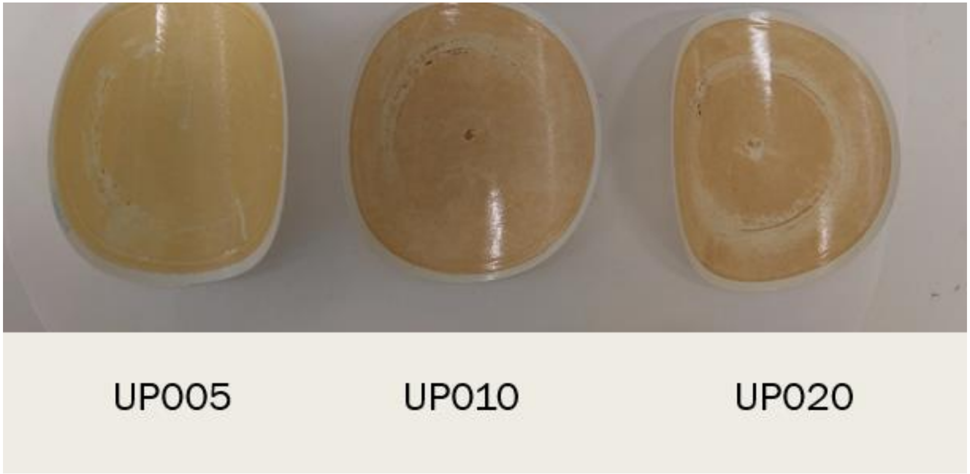

Figure 33: Pictures of UP005, UP010 and UP020 membranes after spent DES filtration

Appendix 5:Feed, permeate and retentate samples of UP005 experiment where 5% spent DES is filtrated under 60℃ and 9.5 bar

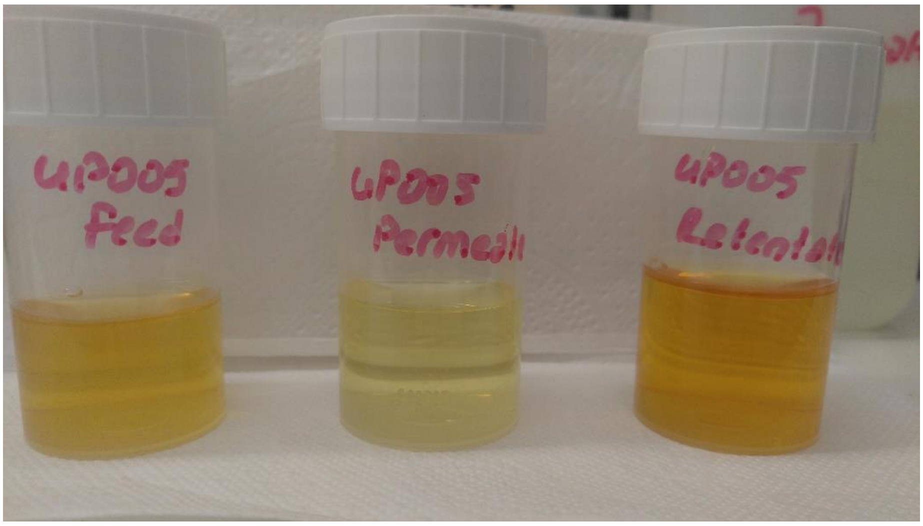

Figure 34: Pictures of feed, permeate and retentate samples of UP005 respectively

Appendix 6:Feed, permeate and retentate samples of NF 270 experiment where 5% spent DES is filtrated under 50℃ and 20 bar

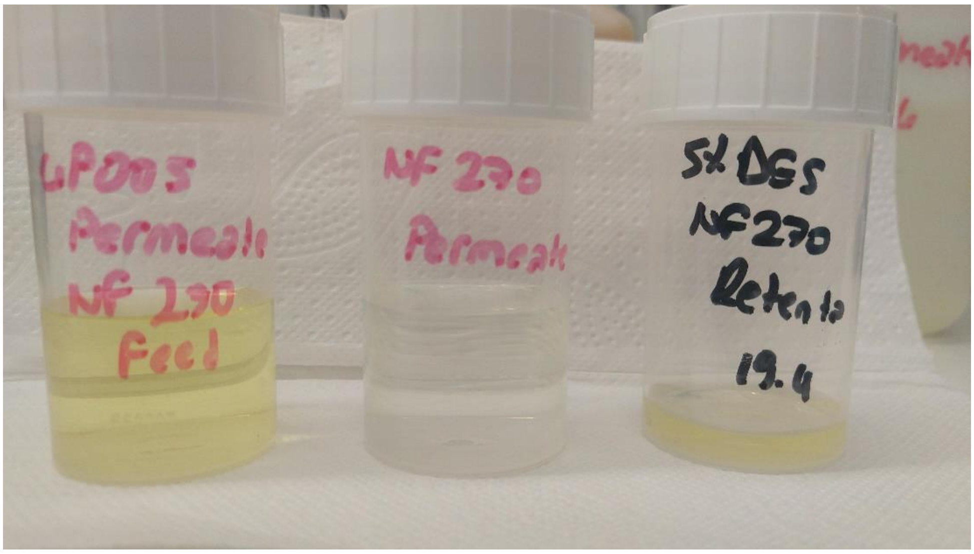

Figure 35: Pictures of feed, permeate and retentate samples of NF 270 respectively

Appendix 7:Feed, permeate and retentate samples of AG experiment where 5% spent DES is filtrated under 35℃ and 25 bar when VRF is 35%

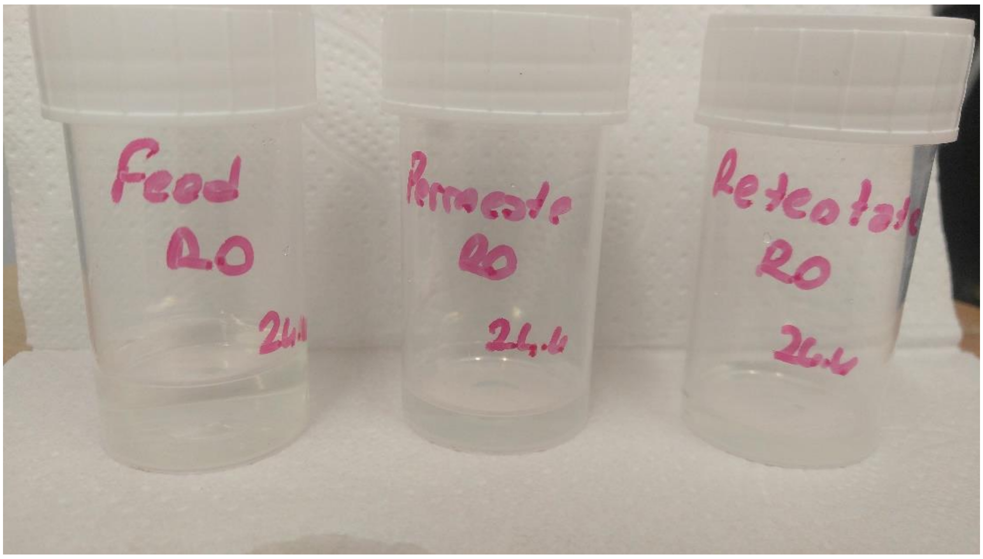

Figure 36: Pictures of feed, permeate and retentate samples of AG respectively

Appendix 8:Feed, permeate and retentate samples of UP005 experiment where 5% spent DES is filtrated under 60℃ and 9.5 bar when VRF is 63.8%

Figure 37: Pictures of retentate, feed and permeate of UP005 respectively

Appendix 9:Feed, permeate and retentate samples of NFG experiment where 5% spent DES is filtrated under 40°C and 15 bar when VRF is 59.5%

Figure 38: Pictures of retentate, feed and permeate samples of NFG respectively

Appendix 10:Feed, permeate and retentate samples of AG experiment where 5% spent DES is filtrated under 35°C and 25 bar when VRF is 48.8%

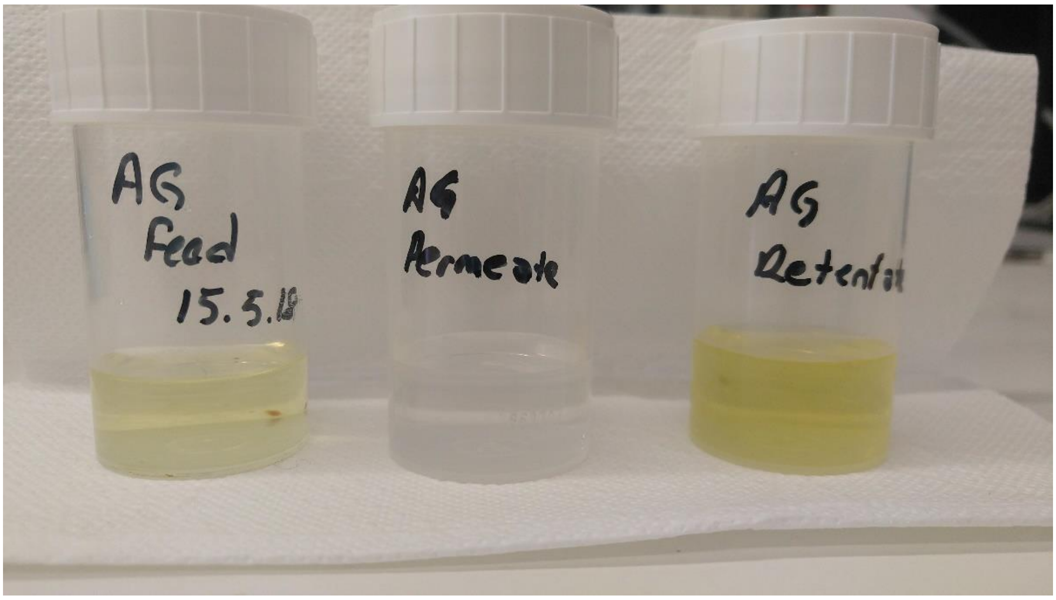

Figure 39: Pictures of retentate, feed and permeate samples of AG respectively