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COST-EFFICIENCY AND THE BENEFICIAL EFFECTS OF THE PROCESS TO RECOVER LIGNIN, HEMICELLULOSE, AND CELLULOSE WITH DEEP EUTECTIC SOLVENT

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ABSTRACT

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The processes in lignin, hemicellulose, and cellulose fractionation demand different chemicals, solvents, and equipment, which leads in absolute differences in their cost of production. In this research study cost-efficiency and the beneficial effects based on the DES fractionation process in separating lignin, hemicellulose, and cellulose were investigated and analysed.

For efficiently analysing of cost-efficiency, additional processes such as the sulphite process, Kraft process, and a process based on the use of ionic liquids (ILs) were studied. The CAPEX and OPEX data in fractionating lignocellulosic through pressurized hot water extraction (PHWE) was obtained from one industry in Finland. In addition, processes based on the use of deep eutectic solvents (DESs) were under examination and in them the use of four different DESs were evaluated in cost-efficiency analysis, which are ChCl:MA, ChCl:OXA, ChCl:Phenol and ChCl:LA, while ChCl:LA was utilized as a case study because it has been performed in the chemistry lab at LUT.

The Chemical Engineering cost index (CECI) was followed in analysing CAPEX and OPEX for the fractionation of biomass based on the processes mentioned

above. The design production capacity of lignin based on 220000 t/y was used and the estimated CAPEX and OPEX for DES (ChCl:LA) concept held as 131M€ and 105M€ respectively, while CAPEX and OPEX for Kraft are 111M€ and 93M€, and ILS is 145M€ and 122M€ for CAPEX and OPEX respectively.

In Addition, PHWE process is 115M€ for CAPEX and 88M€ for the OPEX, while DES (ChCl:OXA) concept are 105M€ and 83M€ for CAPEX and OPEX respectively. Revenue was analysed based on the yield output with a global lignin price of 6500 €/tonne for the Kraft process and DES (ChCl:LA) concept, while their revenue is 325M€ and 546M€ respectively.

Data envelopment analysis (DEA) method used for analysing cost efficiency, due to less prone to an error and required no further mathematics analysis, the SWOT analysis result showed several feasibilities for the DES fractionation process above the other fractionation methods such as sulfur-free. Based on the outcome of this research, the DES fractionation process can be more cost-efficient if the DES can be directly integrated into the existing pulp mills or upgraded to large or industrial scale.

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Oyinloye, Femi Adesola
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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS AND SYMBOLS

A	Acetamide
Aa	Acetic acid
AC	Administration cost
Adt	air dry tonne
C	Volume/mass of the used chemical [kg, L]
CA	Citric Acid
C_c	Total cost of the consumed chemical
CECI	Chemical Engineering Cost Index
ChCl	Choline Chloride
CNC	Cellulose nanocrystal
DC	Direct cost
DEA	Data envelopment analysis
DESs	Deep eutectic solvents
DI	De-ionized
DPC	direct production cost
EC	Equipment cost
FC	Fixed cost
HBA	Hydrogen bonding acceptor
HBD	Hydrogen bonding donor
H_w	Hourly wages $\left[\frac{€}{hr}\right]$
h	hour
GA	Glycolic acid
g	gram
IC	Indirect cost

IEA	International Energy Agency
IL	ionic liquid
ISPT	Institute for sustainable process technology
LA	Lactic acid
LC	Labor cost [€]
lg	Lignin
M	Million
MA	Malic acid
MAL	Malonic acid
MQ	Milli-Q water
MT	Metric ton
MWCNTs	multi-wall carbon nanotubes
mg	milligram
Na_2S	Sodium sulphide
Na_2SO_4	Sodium sulphate
NaOH	Sodium hydroxide
OXA	Oxalic acid
PHWE	Pressurized hot water extraction
P_H	Total production hours spent to produce the output [hr].
rpm	revolution per minutes
SFA	Stochastic Frontier Analysis
STc	Steam consumption
U	Urea
TA	Tartaric acid
TCIC	Total capital investment cost

TDC	Total direct cost
TDPC	Total direct production cost
TEG	triethylene glycol
TFCI	Total Fixed capital investment cost
TIC	Total indirect cost
t	Tonne
XOS	Xylo-oligosaccharides
$ZnCl_2$	Zinc Chloride
€	Euro
Ø	Energy consumption during the process [kW]
ΔT	Change in temperature in each process stage [K]

SUBSCRIPTS

a	after
b	before
c	consumption/consumed
H	hour
s	steam
u	unit
v	volume
w	wages

1   INTRODUCTION

Deep eutectic solvents (DESs) are green solvents that exhibit high potential for lignocellulosic biomass fractionation due to that they are capable to dissolve lignin. Thus, with them the recovery of high-quality sulfur-free lignin is possible in an environmentally benign approach. DESs have been developed by Abbot et al. (2003), and DES as solvent to recover lignin from biomass, and recovered lignin was tested as an additive in membrane matrix (Esmaeili et al. 2018) and as an additive composite (Anugwom et al (2019). There are several other studies have focused on using DESs as a solvent for the recovery of lignin from lignocellulosic biomass with more than 70 % recovery efficiency (Jablonský et al. 2015; Lalman et al. 2017).

The process based on DES could be an alternative fractionation method to recover lignin from lignocellulosic biomass (Hou et al. 2008). The major drawback of the Sulphite process and Sulphate (Kraft) process is that the lignin produced through these processes contains sulfur, which happened to be difficult in their further valorisation process, high-water pollution and odour which associated with sulphate and sulphite pulping is another concerns (Smink et al. 2019), while the high cost of ILs stands as a drawback for commercialization of ionic liquids as solvents for the fractionation of lignocellulosic biomass process.

1.1   Aim and objective of the thesis

In order to maximize revenues, all the three main components in the biomass, cellulose, hemicellulose and lignin must be utilized to the maximum feasibility. For example, carbohydrate could be used to produce ethanol, residual lignin could be used in production of high-value polymeric material. A new discovery on how to extract more than 60 % of lignin from fresh wood, woody waste or from woody biomass by fewer chemical adjustments enable lignin users to recognize the high-value proposition embedded in lignin.

 Deep eutectic solvents (DESs) would provide new insight towards lignin recovery and its possible applications. Therefore, the objective of this thesis is to analyze

cost efficiency together with the beneficial effects of a DESs based fractionation process for the recovery of lignin, hemicellulose and cellulose, and further make a comparison with the most common industrial fractionation processes for lignocellulosic biomass.

The literature part highlights some of the known industrial processes for the treatment of lignocellulosic biomass with their potentials. Hereafter, more details about the DESs based process and their potential in extract lignin will be discussed. Finally, the cost evaluation and cost-efficiency analysis for current processes and the process based on DESs will be explained in the result interpretation section.

LITERATURE REWIEW

2 THE MOST USED INDUSTRIAL PROCESSES FOR THE TREATMENT OF LIGNOCELLULOSIC BIOMASS

Lignocellulosic biomass is considered the most abundantly available naturally renewable resource in the world (Alén, 2011), Which composes of carbohydrates such as cellulose and hemicellulose, and an aromatic polymer (lignin). It is raw material for the pulp and paper industries.

There are various ways to fractionate lignocellulosic biomass, such as mechanical, physical, chemical, biological, thermochemical and thermophysical. This research is focused on chemical fractionation using alkaline (Kraft), dilute acid (sulphite), ionic liquid solvents and deep eutectic solvents.

Major stages and steps of pulping and papermaking are presented in Figure 1. These steps include pulping, where the fractionation takes place, chemical recovery, which involves recycling and recovery of dissolved materials from liquor, and the bleaching process, which is to remove residual lignin which often causes the colouration of the pulp.
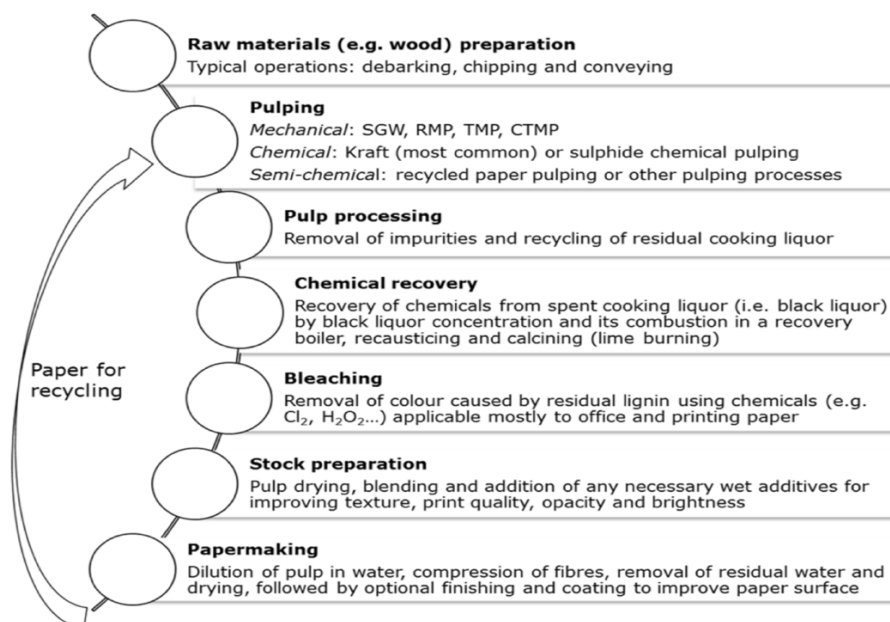
Figure 1. The major steps needed in manufacturing process in pulping and papermaking (Mayo & Pavel, 2018).

2.1 Sulphite process

Sulphite processing is a technique utilized in the separation of lignin, hemicellulose, and cellulose for further industrial use. This process is one of the traditional industrial methods for the treatment of lignocellulosic biomass. The sulphite process accounts for less than 10 % of the global total pulp production (Alén, 2011). During the sulphite pulping process, different types of salts and sulfuric acid are utilized for the fractionation of lignocellulosic biomass (wood chips) in digesters. For example, sulfite (SO_3^{2-}), bisulfite (HSO_3^-), sulfur dioxide (SO_2), and sulfuric acid (H_2SO_4) are added as sulfuric substances.

Furthermore, the method is operated at rather low pH due to the large volumes of sulphite added during the processing. In other words, bisulfite pulping operates at pH ranges from 3 to 5.5, while sulfur dioxide operates at pH of 1 – 2, and higher pH 6 – 8 sulfite pulping is done with sodium and ammonium counterions i.e. "counter" "ions" (Alén, 2011; Fardim, 2011; Prado et al. 2014). The temperature required for sulphite pulping depends on the chemical used. Typically, the temperature ranges between 130°C and 180°C. For example, bisulfite cooking is carried out at a temperature between 150°C and 170°C, while acid sulfite cooks temperature ranges from 130°C to 145°C, while, the cooking at neutral pH requires a higher temperature > 175°C (Deshpande, 2016; VTT).

The yields in sulphite are higher than the Sulphate Process (Kraft), for example, the yield in pine wood fractionation ranges from 55–60% in sulphite process, and 48–50% in Kraft process (Virkola et al. 1981; VTT). However, the fibers obtained from sulphite process are easier to bleach, but the fibers are weaker (Virkola et al. 1981). In addition, the lignin compounds obtained through sulfite processing are sulphonated, degraded and dissolved, and they are usually having close to 30wt % of impurities, like ash or some residual carbohydrates (Galkin et al. 2016).

In sulphite process, two types of lignin reactions are present, which are sulphonation and hydrolysis, both are responsible for delignification. Sulphonation produces hydrophilic sulphonic acid group, while hydrolysis breaks aryl ether linkage between the phenylpropane units. Furthermore, sulphonation and hydrolysis increases hydrophobicity of the lignin and facilitate its water-solubility (Alén, 2011).

The impurity or contamination by the cations used during pulp production, and separation is another drawback of sulphite process, the cation of sulfite and bisulfite salts used in the processing could be ammonium, calcium, magnesium, potassium, and sodium. For example, Holladay et al. (2007) reported that simplest separation method is to precipitate calcium lignosulfonate with excess lime. This method can separate up to 95 % of the lignin in a cooking liquor, but the process is not exercised commercially, because it is expensive.

One other method to recover lignin from the spent sulphite liquor is via the process by Borregaard Ligno Tech, Borregaard LignoTech is a lignin-based product industry that separates lignin in the form of lignosulfonates through the sulphite process for commercial use for over 70 years.

The traditional industrial process for recovery of lignosulfonates is referred to as Howard process, whereby lignosulfonate is precipitated in different stages from sulfite liquor by addition of lime. In the acid sulphite process, which is presented in Figure 2, the cooking liquor is applied under temperature between 130°C to 180°C, and 760 kPa pressure to dissolve lignin that binds the cellulose fibers together with wood in a digester. Hereafter, wood pulp is washed to further remove dissolved chemicals. The pulp may be bleached or not, which depends on the intended use of the product.
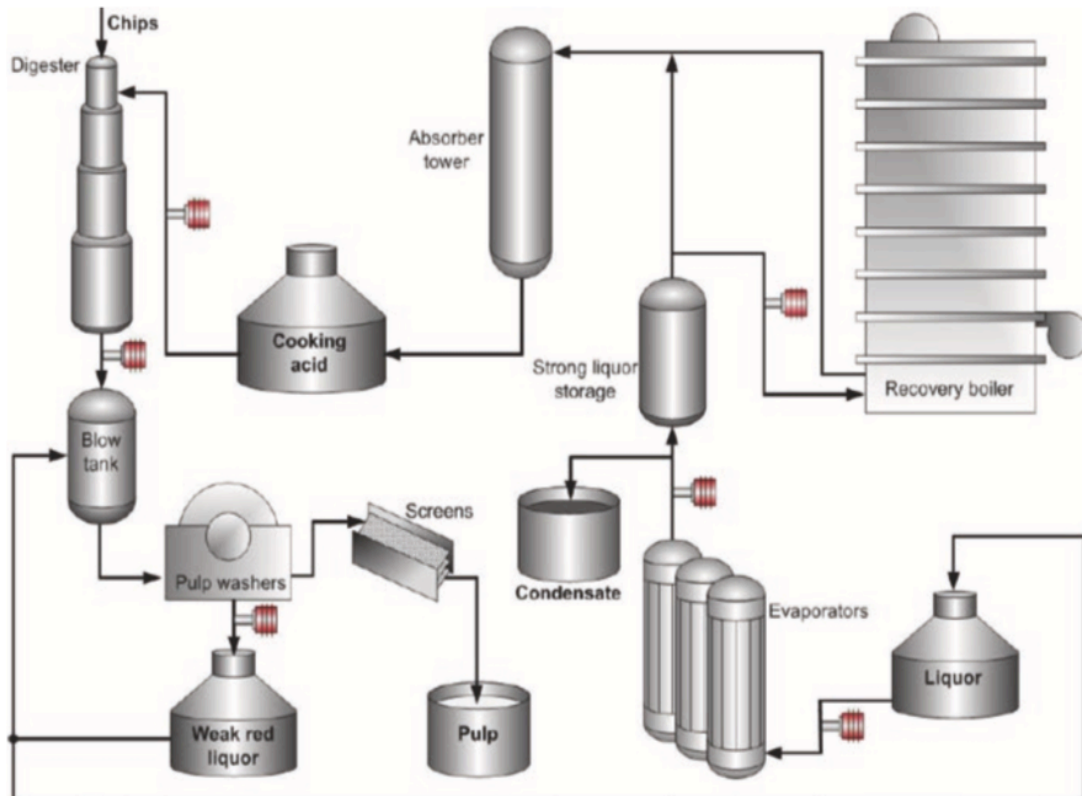
Figure 2. Process flow diagram for sulphite Fractionation process (Akpan & Adesosun, 2019).

2.2 Sulphate (Kraft) process

The Kraft process was started in 1854 by Hugh and Burgess, where the initial process was involved the treatment of wood with NaOH under higher temperature range between $165°C$ to $180°C$, this process was referred to as soda pulping due to NaOH obtained from caustic soda (Akpan & Adeosun, 2019). Presently, sulphate (Kraft) pulping is presently the dominant pulping process, with higher production capacity constituting about 90% of the global pulp production and 50 to 55 million metric tons of lignin are produced annually in the form of black liquor (Rodrigues et al.2018), while sulphite constituting less than 10 % (Herbert & Gabriele, 2009).

The principal objective of the sulphate process is to dissolve lignin, then release fibers, in which lignin is extracted without affecting the cellulose fiber, the application of cooking in high temperature in sulphate process shorten the residence time (Figure 4) (Andersson, 2014). Furthermore, the most desired aspect of the Kraft process is the recovery cellulose from wood, where the separation of lignin

and hemicellulose is achieved by breaking down the wood structure with NaOH and Na_2S.

The sulphate process applies NaOH and sodium sulfide (Na_2S), commonly known as white liquor. An exact calculated amount of an aqueous solution is brought into a pressure vessel known as digester, for an aqueous solution to react with wood chips, both contents are heated at a cooking temperature between 150°C and 175°C for roughly 2 to 3 h to allow the cooking to finalize the reaction. (Gillet et al.2017) During the cooking stage, NaOH helps to degrade lignin and Na_2S fastens the fractionation reactions and decreases the cellulose degradation caused through sodium.

Prado et al. (2014) published that Kraft cooking occurs in three stages which are initial, bulk and final stages (Figure 5), while the initial stage takes place at a temperature of about 150°C, which is controlled by diffusion. Then follows bulk phase at cooking treatment of 170°C and the rate of lignin separation is controlled by chemical reactions.

However, during the bulk phase a large amount of lignin is extracted, and the final stage is at the point where the rate of lignin separation is significantly decreased, and nearly 90 % of lignin is separated, which indicates the end of the sulphate process. Chakar and Ragauskas (2004) mentioned that the residual lignin amount at the end of a conventional softwood sulphate process is about 4 to 5 wt %. This residual can be removed during the several bleaching stages.

The significant benefit of the sulphate process is that the chemicals can economically be recovered, which close to 90 % for the recovery. One shortcoming, of this method is the use of alkaline chemicals, which resulted in metal corrosion and malodourous odors. Van Osch et al. (2017) also described that lignin extraction through the Kraft process is not sulphur-free, which elevates the challenge in valorization, furthermore, the obtained pulp often demands an extra need for bleaching.

The sodium hydroxide and sodium sulfide chemical reactions in cooking liquor based on the reaction are presented in equation below, while active and effective alkali in Kraft process are presented in Figure 3.

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$Na_2S + H_2O \rightleftharpoons 2Na^+ + OH^- + HS^-$$

$$Sulfidity\ (S) = \frac{NaS}{NaOH + Na_2S} * 100\%$$
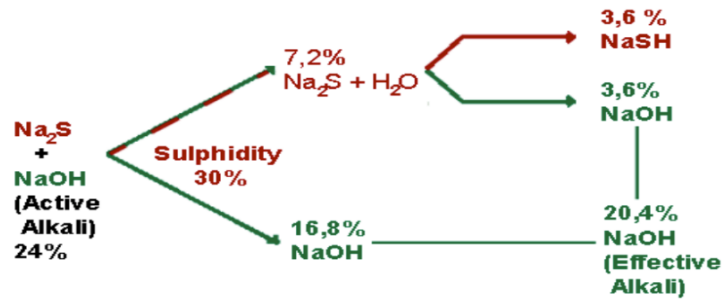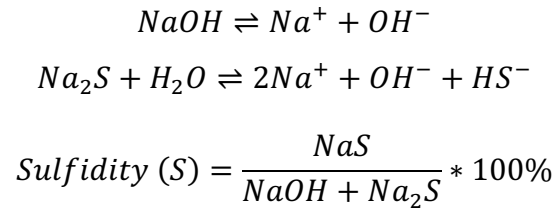
Figure 3. Example of active alkali (red colour) and effective alkali dependence (green colour) (Knowpulp.com).
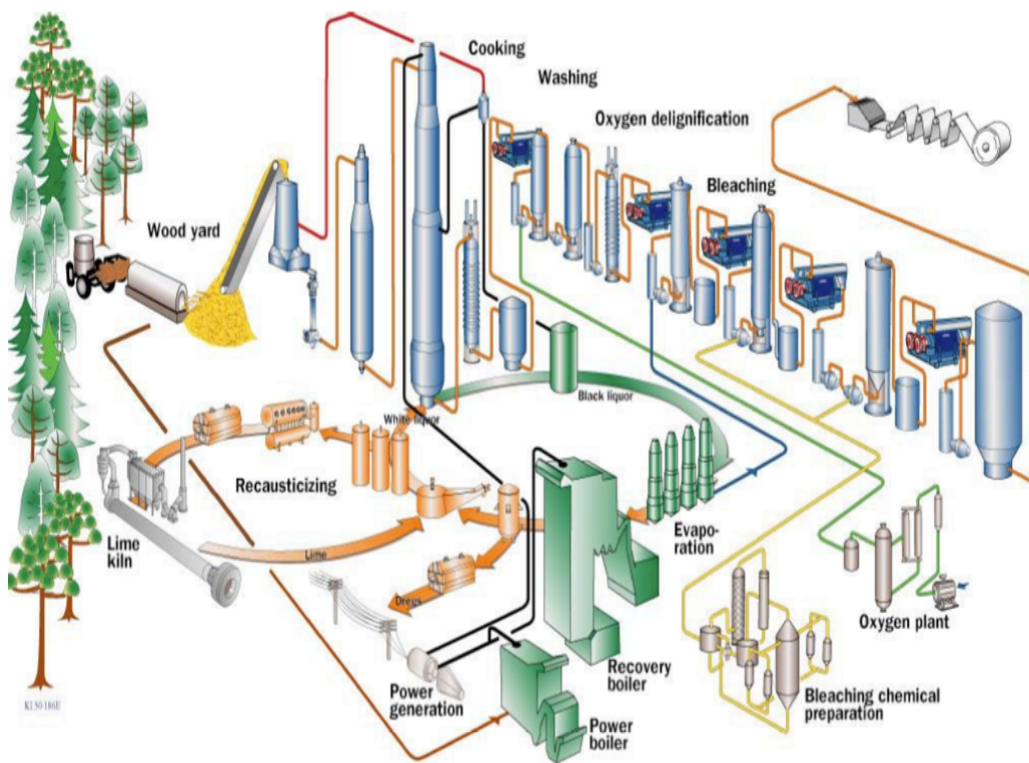
Figure 4. Sulphate (Kraft) process flow comprises the digester, recovery boiler, bleaching plant, lime kiln with NaOH and Na$_2$S (Andersson 2014).
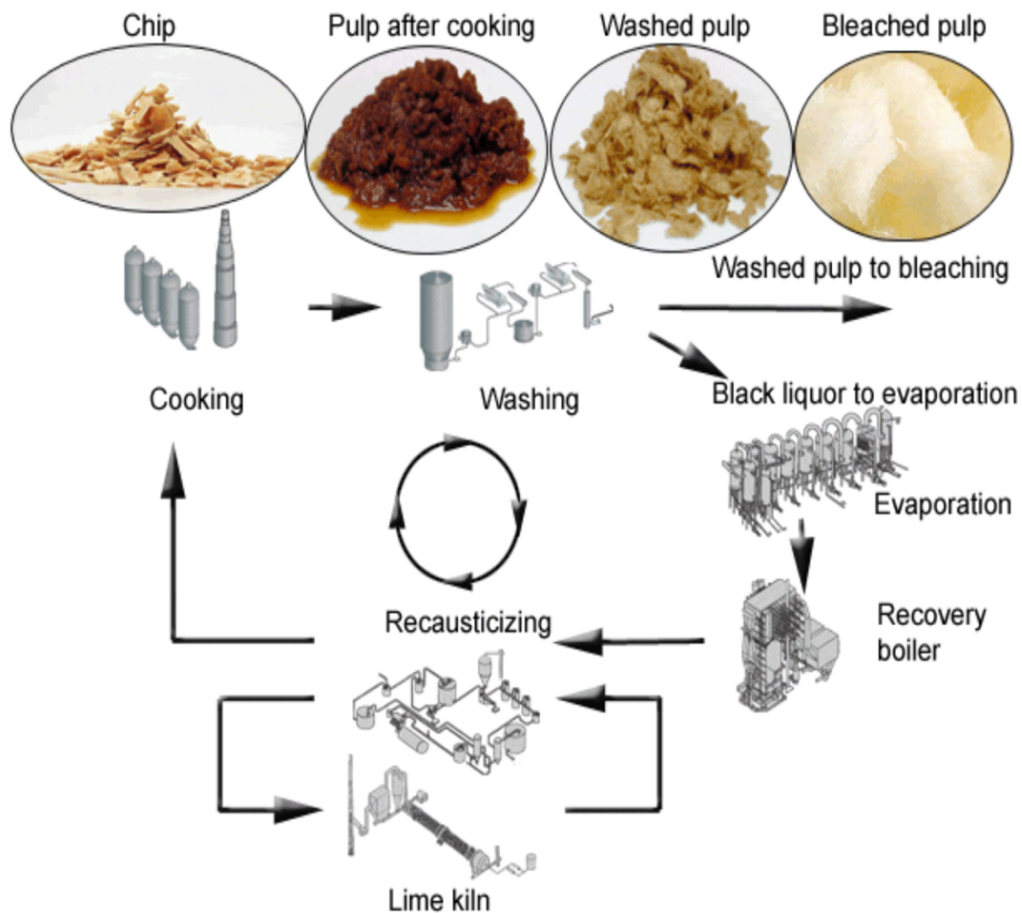
Figure 5. The outcome stages after fractionation from chip to the bleached pulp (Knowpulp.com).

2.3 Examples of methods used in the recovery of lignin from spent fractionation liquor.

2.3.1 LignoForce as a process in recovery of lignin

The LignoForce is utilized to recover high-quality lignin from Kraft black liquor (Figure 6). The LignoForce process involves the addition of a sufficient amount of oxygen at a temperature of about $80^{\circ}C$ to oxidize Kraft black liquor and to residual sulfide. This oxidation process is by improving the filterability of lignin, reduces the chemical consumption, and decreases the sulfur compound, which is outgassing potential from all the stages of the process. (Kouisni et al. 2016)

Hereafter, carbon dioxide is added at about 65°C to 75°C to decrease the oxidized liquor pH, then lignin slurry is subjected to coagulation at a temperature around 60°C under stirring to improve the filterability. At this point, the lignin slurry is filtered and washed with sulfuric acid, and water, then lignin cake is squeezed, dried, and a solid lignin product is obtained. LignoForce process is technically feasible to recover lignins from both softwood and hardwood. (Kouisni et al. 2016)

The lignin produced in LignoForce offers the possibility to us lignin in value-added products such as adhesives in wood products, surfactants and binders, thermoplastic composites, and green chemical alternatives (www.noram-eng.com).
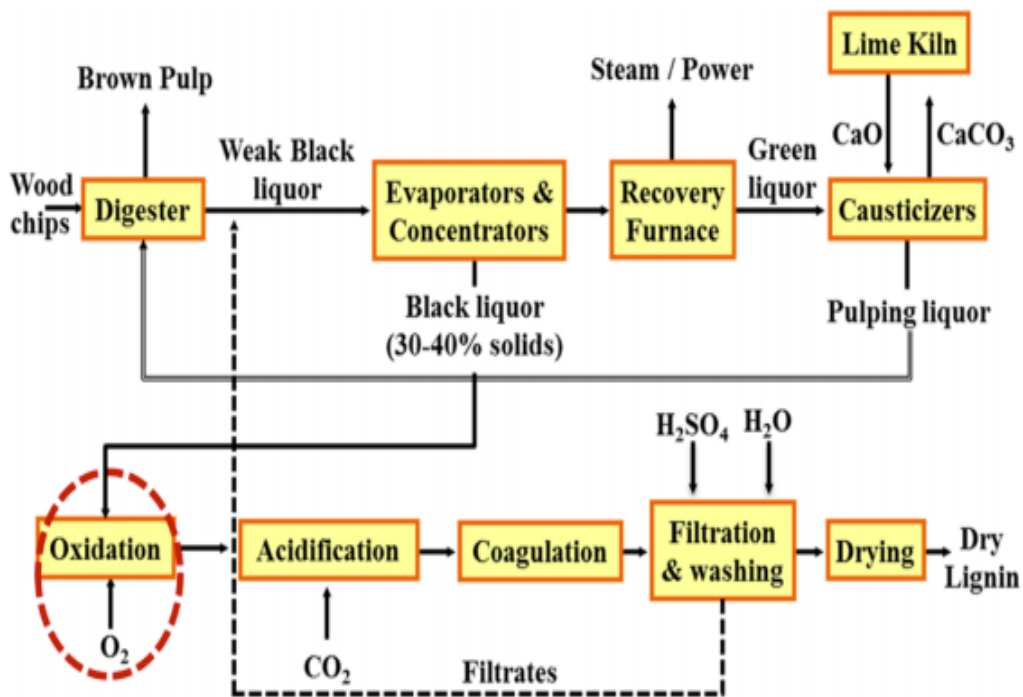
Figure 6. LignoForce system for lignin recovery from black liquor, process developed by NORAM and FPInnovations (Kouisni et al. 2016).

2.3.2   LignoBoost as a Potential process in recovery of lignin

LignoBoost process is another well proven process to recover quality Kraft lignin. The demonstration plant started in 2007, and it became to full-scale operation in 2013 at North Carolina mill. Another LignoBoost plant situated at Sunila in Finland also became a commercial production plant in 2015 with 50 000 t/y of dry lignin

production.
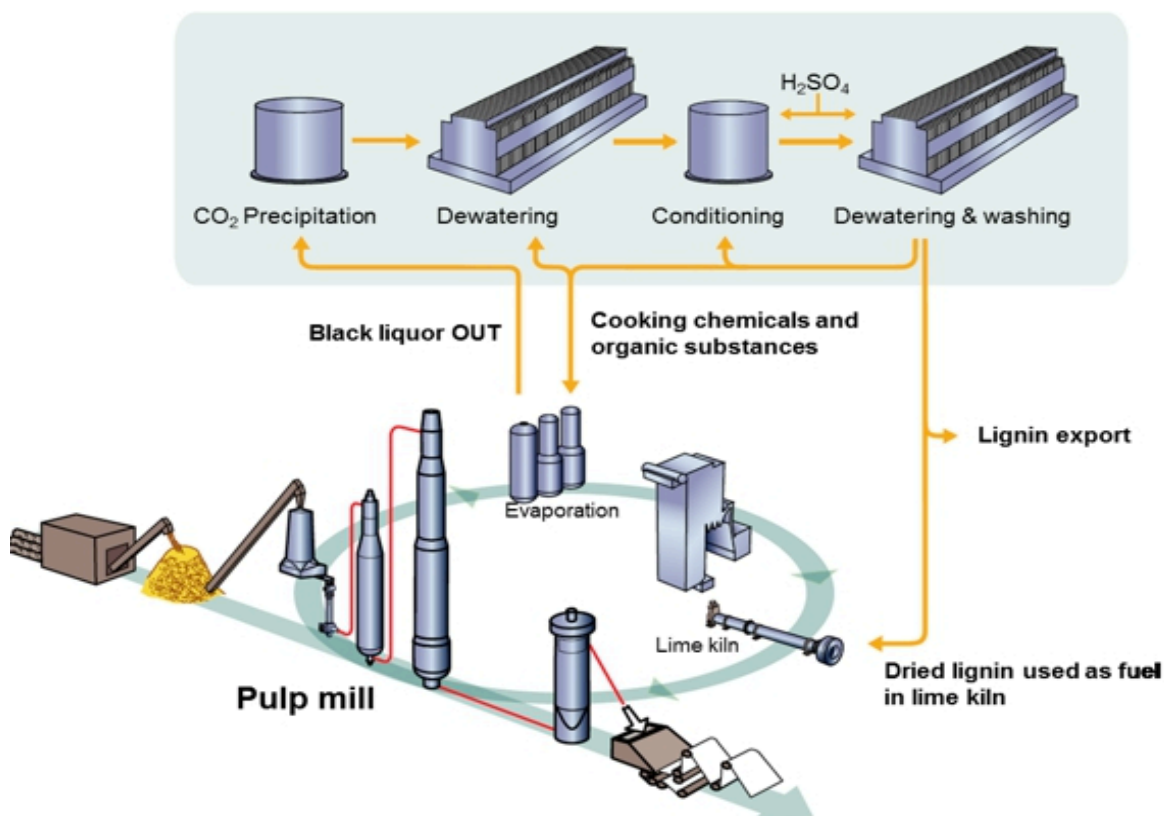
Figure 7. LignoBoost system for lignin recovery from black liquor, process developed by Valmet (Valmet.com).

The LignoBoost process involves the precipitation of lignin in the black liquor by using carbon dioxide to lower the pH, followed by dewatering the precipitated lignin with a filter press, then re-dissolving the lignin in spent wash water and acid, and again lignin slurry is dewatered and washed with sulfuric acid to produce pure lignin cakes (Valmet.com). The process of LignoBoost and LignoForce are similar processes, where both are using Kraft black liquor as raw material, but in the LignoBoost process, acidification takes place and enhanced by applying CO_2, while LignoForce process first oxidizes black liquor with oxygen (O_2) which is then followed by acidifying (CO_2) (EUCALIVA.eu).

3 NOVEL SOLVENTS IN THE TREATMENT OF LIGNOCELLULOSIC BIOMASS

3.1 Ionic liquids

Ionic liquid (ILs) are salts which are nonvolatile liquids at ambient temperature. They have melting point under 100°C and they can be used as solvents for biomass fractionation (Drapcho et al. 2008). It has been indicated that ILs which are capable of dissolving cellulose generally consist of imidazolium[+,] pyridinium[+], morpholinium[+] based cations, and anions that can form strong hydrogen bonds with hydroxyl groups such as carboxylate, dialkyl phosphates. (Hou et al. 2017)

However, not all anions that contain strong hydrogen bonds are capable of dissolving cellulose, for example, IL with 1-methylimidazolium acetate ([Mim]Ac) is unable to dissolve cellulose (Hou et al. 2017), while ILs with moderate hydrogen bonding anions are capable solvents for lignin, for example, IL which including Pyridinium acetate ([Py][Ac]). Therefore, it is extremely important to choose the correct and suitable combination of anions and cations for Ionic liquid in the dissolution of lignocellulose.

Typically, many ionic liquids such as 1-butyl-3-methylimidazolium cation are capable of dissolving lignin, cellulose, and hemicellulose simultaneously. While, some ILs are capable of dissolving one of lignocellulosic biomass major components, and some ILs are not capable of performing such processing. In ILs fractionation process, ILs disrupt and solubilize the three main compounds of lignocellulose, whereby the interaction of ILs with lignocellulose involves ionic and hydrogen bonding interactions (Fort et al., 2007; Muhammad et al.,2012).

In the experiment performed by Brandt-Talbot et al. (2017), Ionic liquid (triethylammonium hydrogen sulfate [TEA][HSO4]) was utilized to fractionate miscanthus X giganteus into lignin, cellulose-rich pulp, and distillate, close to 85 % lignin and 100 % hemicellulose were reported to have been solubilized into ILs, and about 99 % of the ILs was recovered after each cycle. Furthermore, they reported to have reused same ILs for about four cycles.

Yan et al. (2015) reported that 1,3-dimethylimidazolium methylsulfate ([Mmim] $MeSO_4$), 1-butyl-3-methylimidazolium methylsulfate ([Bmim] $MeSO_4$), 1-butyl-3-methylimidazolium acesulfamate ([Bmim] Ace), and 1-ethyl-3-methylimidazolium xylenesulfonate ([Emim] ABS) are suitable for lignin recovery from biomass. Furthermore, the reutilizing of IL solvent in several times without further purification stands as a reduction in the process cost, but the temperature $> 120^{\circ}C$ required for lignin fractionation in IL process (Tan et al. 2009), toxicity, weak biodegradability, the price of ILs, the possibility of contamination after reusing the IL stands as a limitation to the effectiveness in fractionation process, (Prado et al. 2016; Mohtar et al. 2017).

Furthermore, Anugwom et al. (2014) reported a new class of ILs called switchable ionic liquid (SIL) to recover or extract lignin from birch wood, the process is done by using an alkanol amine (monoethanol amine [MEA]) and an organic superbase (1,8-diazabicyclo-[5.4.0]-undec-7-ene [DBU]) with CO_2 and SO_2 as a trigger. They established that the solvents could extract over 50 wt% and 80 wt% of lignin after applying MEA-CO_2-SIL and MEA-SO_2-SIL respectively.

The lignocellulosic biomass fractionation process with ILs are summarized in Figure 8, whereby lignin-rich material, carbohydrate-rich material, together with hemicellulose-rich material were obtained when ionic liquids (1-ethyl-3-methylimidazolium acetate) mixture of 5000 mg together with 250 mg of wheat straw were heated in continuous stirring for 6 h at 120ºC.
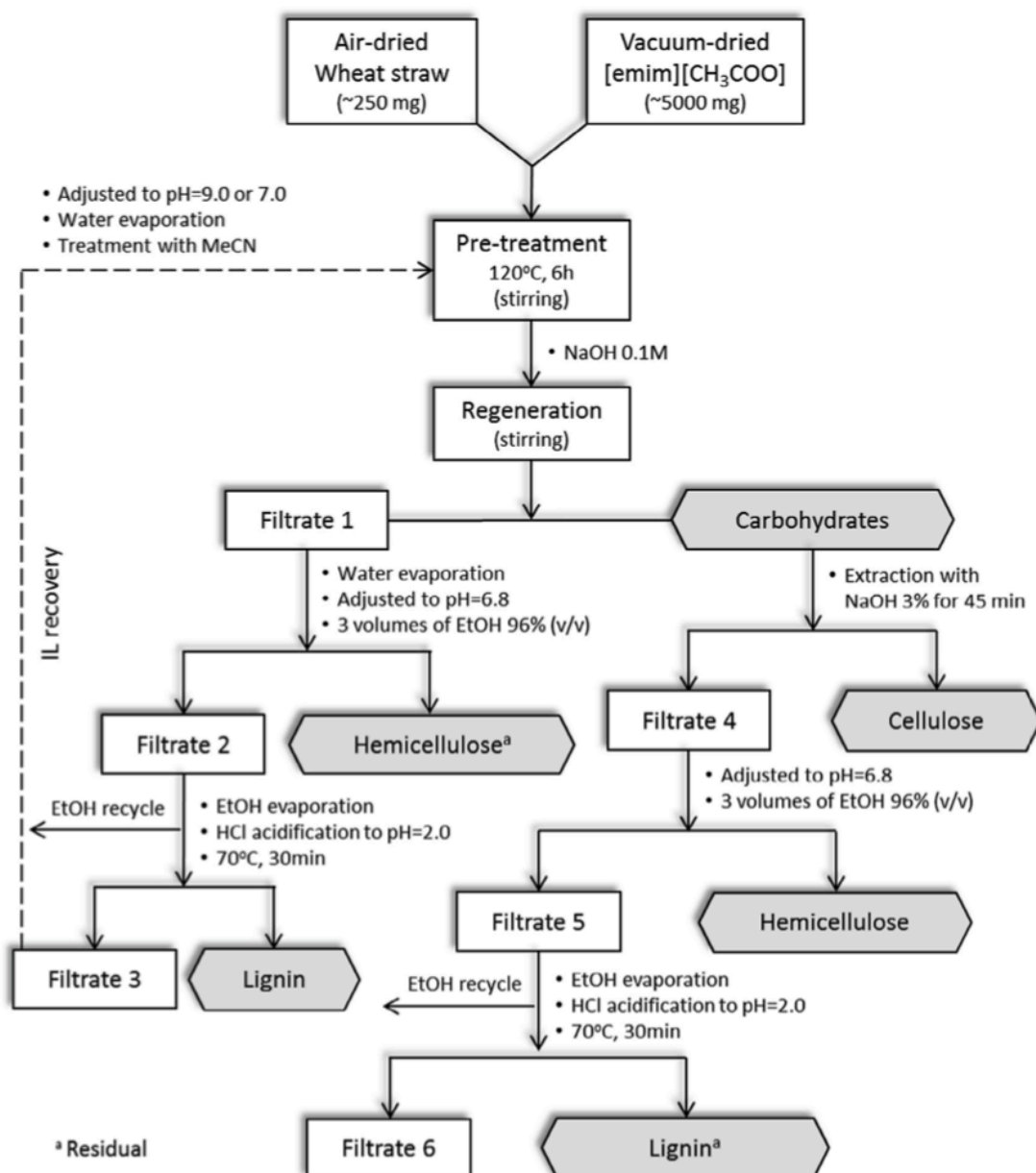
Figure 8. Process flow diagram for Fractionating of lignocellulosic biomass with ILs (1-ethyl-3-methylimidazolium acetate) (Da Costa Lopes et al. 2013).

3.2 Deep eutectic solvents

The Deep eutectic solvents are green solvents that exhibit deep eutectic behavior upon mixing the constituents of these solvents. Schuur et al. (2019) reported that the mixtures melting points reduce considerably, usually (>50°C) that would not be the case for ideal mixtures. (Smink et. al. 2019). DESs are commonly prepared by the interaction between a hydrogen bonding donor (HBD) and a hydrogen bond

acceptor (HBA), Figure 9 is presented the HBD and HBA that are used in the preparation of DESs.
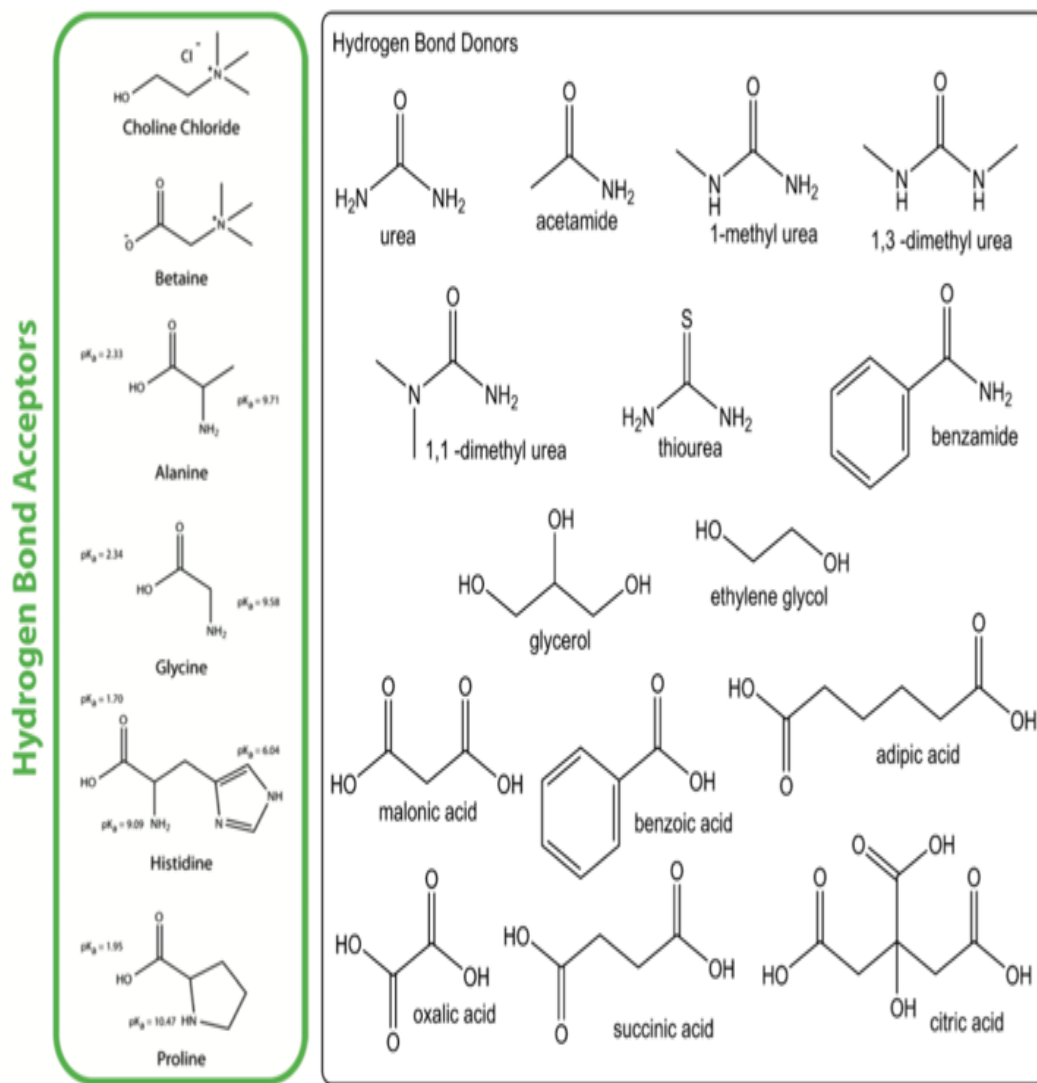
Figure 9. Chemical structure of hydrogen bond donors (HBD) (Smith et al. 2014), and hydrogen bond acceptors (HBA) (Francisco et al. 2012) used in composition of DESs.

DES consists of non-symmetric ions that have low lattice energy, and low melting point (Marcus 2019), for example, a mixture of ChCl and Urea gives the freezing point at 12°C which is lower than the melting point in ChCl and Urea components at 302°C and 133°C respectively (Abbott et al. 2003). DES is currently recognized as a solvent in extraction a substantial amount of lignin, from biomass, and could be used in replacing conventional solvents, because of many advantages associated

with DESs such as easily synthesized, environmentally friendly (non-toxic), (Satlewal et al. 2018).
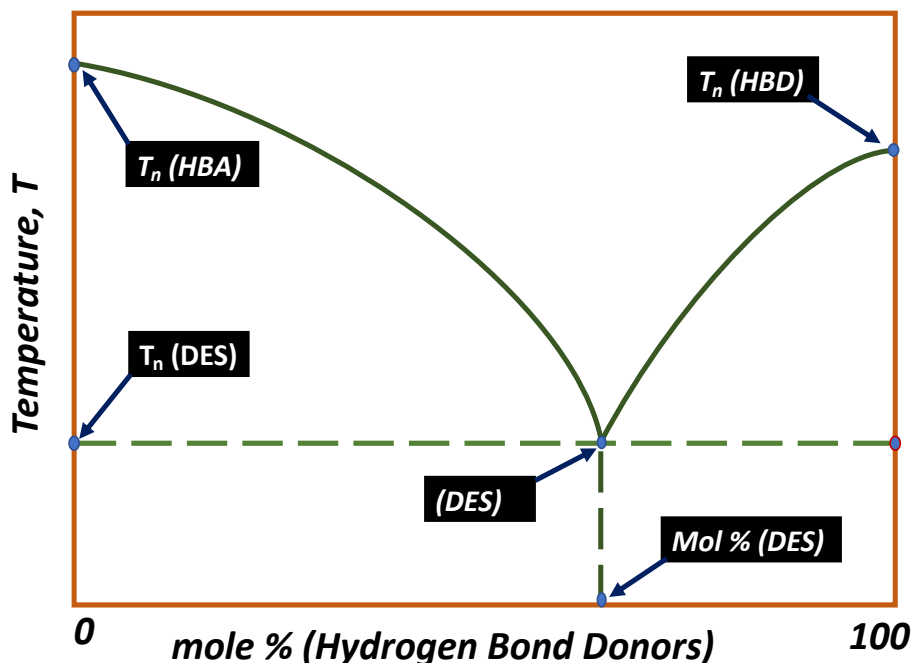
Figure 10. Diagram for eutectic mixture between hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD). Solid line (–) shows melting point and dashed line (--) represent the temperature and composition of the eutectic, Temperature (T_n) (Garcia et al. 2015).

Furthermore, deep eutectic solvents are extensively being utilized in organic synthesis, in electrochemical areas, and currently, biorefinery has shown a deep interest in DESs application due to physicochemical properties associated with them (Tang et al., 2017). DESs have been reported as solvent in several other applications, such as, in biodiesel production, electrodeposition of metals, electro-polishing, nanotechnology, in the separation of aliphatic-aromatic (Marcus, 2019).

DESs have the potential as solvent to impact positively the environment condition (benign) and can extract at a high yield of lignin averagely between 60 and 70 % and lignin recovered through process based on the use of DES is highly pure which are solely depends on the source of biomass and purity of starting material (Oliveira et al. 2013; Jablonský et al. 2015). The main reason why DESs could dissolve

biomass compounds is that DESs are capable of breakdown the complex structure in biomass and destroy the intra- and intermolecular interaction of biomass polymers (Chen & Mu, 2019).

The solubility of lignin in different DESs differ from each other, Satlewal et al. (2018) reported that lignin solubility improved with the increase in the acid content. For instance, 51% to 60 % of lignin solubilization was observed when acid content increases in ChCl:LA from a molar ratio of 1:2 to 1:5 upon using rice straw as a substrate. (Satlewal et al. 2018)

Furthermore, the DES process compared to the traditional or conventional chemical pulping processes can be performed at a lower temperature and pressure, which enables the implementation of DESs as a value-added process in the industry. Deep eutectic solvents as a low carbon, less energy demanding process, could be an alternative to the next-generation reagents for sustainable industrial development, due to easy recycling of DESs, and less energy required when DES is used as a chemical agent for dissolving lignin, hemicellulose, and cellulose (Oliveira et al. 2013).

3.2.1 Preparation of deep eutectic solvents.

DESs are grouped into four types based on the combination of their chemical components (Table 1) and they can be prepared via the following four procedures: The first procedure for DES preparation is by heating and mixing method. The compounds were heated at nearly 100°C under continuous stirring till homogeneous liquid (clear liquid) was formed. The second procedure is the grinding process, it involves the mixture of the compounds at ambient temperature, then followed by grinding the compounds until a pure liquid is produced (El Achkar et al. 2019).

The third procedure is based on evaporation. The DES components are dissolved in water, then water is evaporated at temperature about 50°C. The liquid obtained is then stored in a desiccator until the steady mass is achieved (Yii et al. 2016). The fourth method is based on the freezing drying. An aqueous solution of individual DES components is freeze-drying at 65°C, the technique is rarely used in comparison with the aforementioned method (Alvarez-Vasco et al. 2016).

Table 1. General description for the classification of deep eutectic solvents (Smith et al. 2014, Satlewal et al .2018)

Type	Components	General formula	DESs example
I	Metal salt + organic salt	$Cat^+ X- zMClx$; M = Zn, Sn, Fe, Al, Ga, In	$ChCl + ZnCl_2$
II	Hydrate metal salt + organic salt	$Cat^+ X- zMClx.yH_2O$; M = Cr, Co, Cu, Ni, Fe	$ChCl + CoCl_2.6H_2O$
III	Hydrogen bond donor + organic salt	Cat+ X- zRZ; Z = $CONH_2$, COOH, OH	ChCl + U
IV	$Zn/AlCl_3$+HBD	$MClx + RZ = MCl_{x-1}{}^{+\cdot} RZ + MCl_{-x+1}$; M = Al, Zn and Z = $CONH_2$, OH	$ZnCl_2 + U$

Cat^+ could be any of these: ammonium, phosphonium or sulfonium cation, X halide anion, z number of y molecules that interact with the anion

3.2.2   Properties of DESs

The application of DESs in processes depends on the properties of the DESs. The main properties of DESs are density, viscosity, thermal behavior, surface tension, and conductivity. Therefore, density, viscosity, and surface tension were discussed in detail in this section.

3.2.2.1   Density (ρ)

The combination of HBA and HBD compounds has an essential role in the density of DES, where density relates to the water content in the said mixture (DES), in such a way that by increasing the percentage of water leads to decreases in density (Veronika, 2015). For instance, the density of ChCl:Urea in 1:2 molar ratio at 25°C is about 1.25 [g/cm^3], which means that the density of DES is higher than the density of water. The density of DESs are mostly within the range of 1.1 to 1.3 [g/cm^3] (Marcus, 2019).

The density needs to be measured in order to know the extensive role and behavior of DESs (Garcia et al. 2015). Satlewal et al. (2018) reported that decreases in densities affect increasing in temperature. The density is often applied for analyzing

the changes of DESs against water supplement and to determine excess molar volume. (Ma et al. 2018)

3.2.2.2 Viscosity

Viscosity is another significant property needed to be considered, when DES is to be used in a process, due to the possible problems in filtering, stirring and handling of the process streams. Viscosity of DES is determined by various factors such as the components that constitute the HBD and HBA, temperature, molar ratio of DES components and water content or ratio.

The viscosity of DESs follows the Arrhenius expression, whereby viscosity decreases with increasing in temperature (Marcus, 2019). Furthermore, in some cases, by increasing the molar ratio of DES components, the viscosity of the synthesized DESs decreased. For instance, adding glycerol at 50 °C, the viscosity of ChCl: glucose at molar ratio 1:1 decreased from 34.4 to 0.93 [Pa]. (Sarmad et al. 2016)

3.2.2.3 Surface tension

Surface tension is another essential property which must be taken into consideration in processes based on the use of DES. The existence of crystal water in the salt component of DESs leads to decrease in its surface tension. Also, when the surface tension of DESs increased, the water mole fraction is > 0.9. Another important aspect in DESs surface tension property is that an increasing in temperature leads to decrease in surface tension of DESs. (Chen et al. 2019[a])

3.3 Presentation of the major constituent of lignocellulosic biomass (lignin, hemicellulose, and cellulose).

Lignocellulose comprises from three significant fractions or compounds namely from cellulose, hemicelluloses, and lignin. These compounds are presented in Figure 11 carried dry weight of 30–50 %, 14–35 %, and 10–30 % from cellulose, hemicellulose and lignin respectively, which based on wood, bark and forest residue (Alén, 2011). Likewise, the proportion of different compounds differ from each other which depending on the biomass specie.
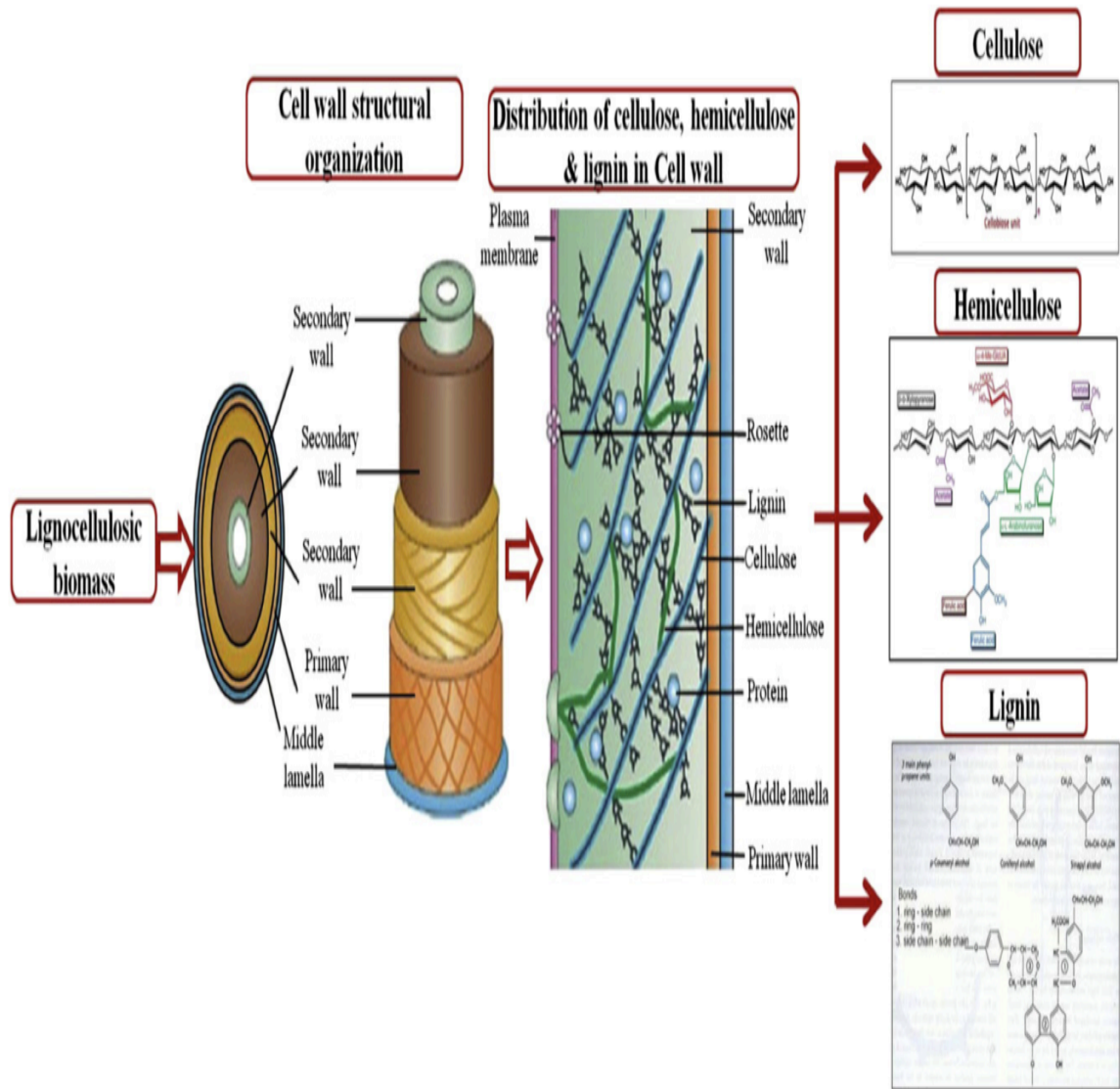
Figure 11. Composition of lignocellulose (Menon & Rao, 2012).

4 METHOD AND DATA COLLECTION

There are two approaches about cost analysis which related to one another both have a distinct meaning, first is cost efficiency analysis and second is cost-effectiveness analysis. The cost-efficiency analysis is a systematic approach to analyze the cost per output of a product and enables to compare the product which produces the same output, and to determine the benefits which provide the value against the decision concern the cost. The cost-effectiveness analysis is a form of analysis which compares the related costs and outcomes of different products. Therefore, lignin, hemicellulose, and cellulose separation concepts will be analyzed by the cost-efficiency analysis, because the cost-efficiency analysis provides a good measure of operational execution.

Furthermore, the idea of cost-efficiency analysis is to evaluate the ability on how to achieve immediate production at a more economical and minimal cost. Though, there may be some circumstances that may impose change on prices and costs such as the area of availability of materials (chemical, raw materials), exchange rates, tax rate, and location, these factors cannot be controlled by individual industries.

4.1 Steps to measure cost efficiency

The first step in measuring cost efficiency is by calculating each of the cost components. The metrics to apply in estimating the cost need to be selected, as well as a complete list of appropriate cost need to be compiled. Besides, it essential to ascribe monetary values to each stage of the processing, which means, direct cost should be assigned with monetary value, then the equation needs to be decided.

The second step in measuring cost efficiency is by summing up each segment cost component. In assigned monetary values to the cost, the cost needs to be summed up and determined the numerical equation to use for outweighing the cost and compare the cost side by side.

Another step is by comparison and verification of total cost. After the aforementioned steps, then the total cost for other process has to be compared with the principal process chosen for the cost efficiency analysis (cost based on DES

process).To establish an unbiased comparison, the total cost requires to be checked with a few longer processing times or periods either in a day, a month or a year.

However, cost efficiency needs to employ these following procedures and reflects on them. First, studying the different separation method for lignin, hemicellulose, and cellulose, and second, by analyzing the chemical applied for fractionation in different stages and operation modes. The third aspect is by analyzing the proportion of quality yield achieve as an output in each processing method.

Cost efficiency is usually measured by applying parametric or nonparametric approach (Linna et al. 2006). There are several cost-efficiency analysis methods used in literature (Linna et al. 2006), such as data envelopment analysis (DEA) which is nonparametric, and stochastic frontier analysis (SFA), thick frontier approach (TFA), distribution free approach (DFA) which are parametric.

Data envelopment analysis (DEA) and stochastic frontier analysis (SFA) will be further explained. Hereafter, the appropriate method will be chosen for the cost-efficiency analysis.

4.2   Data envelopment analysis method

Data envelopment analysis (DEA) is a well-known method which was introduced by Charnes et al. (1978) and adopted by operation research and management science for analyzing the cost efficiency (Liu et al. 2013). Data envelopment analysis (DEA) is using for comparable performance output in various industries which producing the related product with the multiple input and output, several inputs, and single output (Nataraja & Johnson, 2011; Rogge & Jaeger, 2013).

DEA is described as nonparametric, which means DEA does not require prior assumption on what result would likely be, rather implies that the result can be retrieved from the data which was analyzed. DEA linear model equation is aligned with purpose of this research and the equation stated below (Jain et al. 2011).

$$P = \sum_{j=1}^{D} W_j \qquad\qquad (1)$$

$$\sum_{i=1}^{C} Y_i, \quad i = 1, \ldots\ldots n \qquad\qquad (2)$$

$$\sum_{j=1}^{D} W_j, - \sum_{i=1}^{C} Y_i \qquad\qquad (3)$$

Where

(c)	inputs cost components required
(D)	output number of cost component required for cost efficiency,
(i)	inputs to produce cost component required
(j)	number of industries data were used for analysis
(P)	indicate overall cost efficiency under the evaluation method.
(W)	overall cost efficiency score for the separation/Extraction of lignin
(Y)	overall cost for the comparison for the separation of lignin.

In simple term for DEA, there are n industries which is ($j = 1, \ldots.$, n) which use c inputs Y_i ($i = 1, \ldots.$, n) to achieve D outputs W_j ($j = 1, \ldots.$, n).

4.3 Stochastic Frontier Analysis

Stochastic Frontier Analysis (SFA) is another cost analysis used in measuring Cost efficiency and technical inefficiency. SFA usually presents a way to maximize production and minimize cost and is characterized as parametric analysis. SFA is used to estimate pre-specified functional form under the econometric approach.

In the stochastic frontier analysis approach, there can be used various model such as estimation model (which generalized least square model), method of moments, maximum likelihood estimation model. The main functionality of SFA methods is to model a firm's behavior, and SFA can be fathomed to suit the comparisons of similar products to make meaningful output (Balliauw et al. 2018).

Stochastic frontier analysis (SFA) uses input and output function, where one output variable is considered, and the input variable can be many for example, labor cost, materials costs, capital cost, and energy costs (Balliauw et al. 2018). To achieve a good result in the Stochastic Frontier Analysis approach, further mathematical analysis is required.

4.4 Data envelopment analysis versus Stochastic frontier analysis

The scope of the analysis is to reveal how the DES fractionation process has had an impact on cost and output efficiency on separation lignin, hemicellulose, and cellulose. The DEA approach is more flexible, does not discriminate among inefficiency and random disturbance, no prior constraints on data, and functions accurately with smaller sample sizes (Nataraja & Johnson, 2011).

Stochastic Frontier Analysis requires ad hoc hypothesis on the efficiency component distribution, and SFA deals mostly with firms and involves a production function that has an error term which included two factors, while one dealt with random effects and another with technical inefficiency. The stochastic frontier analysis needs behavioral hypotheses for cost minimization, and the models are non-specified. In addition, SFA can be error terms and tend to have biased in estimating the parameter. (Linna et al. (2006)

Therefore, for assessing cost efficiency in the separation of lignin, hemicellulose, and cellulose, the data envelopment analysis model in equation (1) to (3), which employs linear approach techniques, and serves as the reference in the efficiency evaluation shall be applied. DEA is less prone to this kind of specification error, sensitive to variable selection, and no matter the number of variables added to the model, the model will continue to be efficient in terms of cost analysis and thus not required further mathematical analysis (Jain et al. 2011).

4.5 Key cost components

In analyzing the cost efficiency for fractionation process, the essential cost component requires to be identified and understood. The cost model categorized under the key cost components is based on Capital expenditure and operational expenditure.

Capital expenditure (CAPEX) is those fixed costs connected with the actual equipment employing in fractionating process (Culbertson, 2017). CAPEX does not depend on the volume of the production and does not change over the short time, while the OPEX tends to be the variable costs that are relatively proportional to the volume of the product. OPEX is classified as a direct cost and indirect cost, the direct cost can individually be described to cost objects, and indirect cost cannot be clearly traced to cost objects, for example, quality control cost, insurance, and tax.

The direct costs under operational and manufacturing cost classified into three-segment, they are direct material cost, direct labor cost, and overhead. In this research, they are classified as chemical costs (reagents cost), direct labor cost (Operators cost), and utility cost (energy consumption, water consumption).

Total production cost will be determined with equation (4)

$$TPC = CC + DLC + U \qquad (4)$$

Where TPC Total Production cost

CC Chemical cost

DLC Direct labor cost

U Utilities cost

The operating cost of the DES fractionation process will be compared with the most used industrial process such as Kraft process. The energy consumption can be determined according to the temperature implemented in every stage of the process to the final output. Energy consumption can be determined by equation (5), but in this study it is based on Chemical Engineering Cost Index (CECI) and Kangas et al. (2014).

$$\emptyset = (q_{m,P} * C_p * \Delta T) \qquad (5)$$

Where $Ø$ Energy consumption during the process [kW]

                       $q_{m,p}$ Mass flow in each stage of process $\frac{kg}{s}$

                       C_p Specific heat capacity in each stage (water and Chemical) $\left[\frac{KJ}{kgK}\right]$

                       ΔT Change in temperature in each process stage [K]

The steam consumption during the processes can be determined by equation (6)

$$ST_c = \left(\frac{\left(\frac{Ø}{h'_s - h'_w} \right)}{extraction\ Fraction} \right) \qquad (6)$$

Where ST_c Steam consumption during the processing $\left[\frac{L}{t\ of\ fraction\ component} \right]$

                       h'_w Enthalpy of water in the heating process $\left[\frac{KJ}{kg} \right]$

                       h'_s Enthalpy of steam in the heating process $\left[\frac{KJ}{kg} \right]$

Labor cost would be determined by equation (7)

$$LC = H_w * P_H \qquad (7)$$

Where LC Labor cost [€]

                       H_w Hourly wages $\left[\frac{€}{hr} \right]$

                       P_H Total production hours spent to produce the output [hr] or [adt]

Chemical cost is determined by equation (8)

$$C_C = \frac{\sum_{i=1} C_{1_i} * P_{1u}}{P_{1v}} + \frac{\sum_{i=1} C_{2_i} * P_{2u}}{P_{2v}} , ... \frac{\sum_{i=1} C_{N_i} * P_{Nu}}{P_{Nv}} \qquad (8)$$

Where C_c Total cost of chemical consumed

               C Volume of chemical used [kg, L]

               P_u Unit price for the chemical [€]

               P_v Volume of the whole chemical [kg, L]

There are n same chemicals (C) used in different processing stages which are (i=1…., n), then Pu is the unit price of each different chemical from (1….N) applied in the process and Pv is the quantity of the whole different chemical purchased for the production from type (1….N).

Total annual cost can be calculated with equation (9)

$$TAC = ACC + OC + MC \qquad (9)$$

Where ACC annual capital cost

               TAC Total Annual cost

               OC the operation cost

               MC maintenance cost

The annual capital cost can be determined or calculated based on the equation (10) according to Humphreys & Engush (1993).

$$ACC = TCC * \frac{i*(1+i)^n}{(1+i)^n - 1} \qquad (10)$$

Where TCC Total capital cost

	i	the interest rate
	n	the number of annuities (economic life of the equipment)

The required adjustment for inflation was calculated by equation (11) based on Chemical Engineering Plant Cost Index (CEPCI)

$$C_p = C_1 \left(\frac{I_2}{I_1} \right) \qquad\qquad (11)$$

Where	Cp	the present purchase cost
	C_1	Initial purchase cost
	I	the actual cost index point
	1	subscript 1, based on time when initial value is determined
	2	subscript 2 desired period for the cost estimated

The cost estimation model analysis shown in Table 2 which based on the chemical engineering cost index, has been proved by more than 100 researchers (Fornell et al. 2012). The Plant Design and Economics for Chemical Engineers modelling book (Peters & Timmerhaus, 1991), including Project and cost engineer's handbook (Humphreys & Engush 1993) used the model in their cost estimation. Therefore, the procedure will be followed appropriately in analysing the capital cost investment (CAPEX) and operating cost (OPEX) for DES.

The pulp production and lignin production data used in this analysis is updated to the current data. The data has been obtained from Chen et al. (2014) and the research record by the VTT Technical Research center of Finland (Kangas et al. 2014). Data used were supplied by Finnish Pulp departments to VTT. Kangas et al. (2014) mentioned that some experts from Stora Enso, Metso, Andritz, and UPM-

kymmnene guided the work, and the investment cost in this research were initially estimated by Pöyry Oy Finland and their prices were based on assumption.

Table 2. The cost estimation analysis for the capital investment cost, total operation cost and maintenance cost based on the large-scale production (industrial production) for DES Fractionation.

Total capital investment cost (TCC)		Annual operational cost and maintenance cost	
Direct Cost (DC)	**EC (%)**	**Fixed cost (FC)**	
EC (equipment cost)	100	Local taxes	2 % on TFCI
Installation of equipment	42	Insurance	1 % on TFCI
Instrumentation + control	35	Total Fixed cost (TFC) = local taxes + insurance	
Pipe connection	65	**Direct production cost (DPC)**	
Electrical cost	8	Maintenance cost (MC)	3 % on TFCI
Building and service in building	27	Labour cost (LC)	
Facilities services	20	Supervisors (S)	15 % on LC
Total for direct cost (TDC) 297		Lab cost	15% on LC
Indirect cost analysis (IC)	**EC (%)**	Operating supplies	15 % on MC
Contingency cost	30	Overhead	15 % on (MC+LC+S)
Legalization cost	4	Electricity	
Engineering cost	30	Total direct product cost (TDPC)	
Contractors' cost	20	**Other cost**	
Expenses based on construction	41	Administration cost (AC)	20 % of LC
Total indirect cost (TIC) 125		Marketing	2 % of (OC+MC)
Total Fixed capital investment cost (TFCI) =TDC+TIC (422)		Research cost	2 % of (OC+MC)
Working capital expenses 15% of TCIC		*Total other cost*	
DES/IL cost		Solvent recycling cost (SRC)	
Total capital Investment cost (TCIC)=TFCI + WC+ DES/IL cost)		Depreciation cost (DC)	
		Operational cost and maintenance cost = TFC+ TDPC +TOC + SRC + DC)	

5 RESULTS AND ANALYSIS

The capital investment cost (CAPEX) and operational cost (OPEX) for biomass fractionation processes such as the Kraft process, sulphite process, and the Ionic liquid process is scarce, and there are no references for industrial-scale operation. It was discovered that most of the CAPEX and OPEX data in the literature review base their analysis on the assumption data, and most of the contacted companies refused to release their data as at the time of writing this thesis due to confidentiality. Therefore, the cost estimation is done based on the equipment costs analysis in the chemical engineering cost index with few modifications. The utility cost, solvent cost, and chemical cost were based on the current online cost value.

5.1 Cost data analysis for Kraft processing to fractionate lignin, hemicellulose and cellulose

The capacity for the production of Kraft pulp was based on 2000 adt /day and 620000 adt /year, the annual production for lignin was based on 220000 t/year (UPM.com). OPEX and CAPEX are presented in Table 4 and Table 5 respectively, also analysis based on chemical engineering cost index (CECI) is presented in Table 3.

The cost data from Kangas et al. (2014) which was estimated by Pöyry Oy showed the high cost in the capital investment and annual operational cost with 770M€ in Table 5 and 152M€ in Table 4 respectively for pulpwood compared with cost analysis based on chemical engineering cost index in Table 3 which is 111M€ and 93M€ for CAPEX and OPEX respectively. Though the analysis result on the chemical engineering cost index excluded the wood handling and water treatment cost from the figure, if these values are included, the new estimated CAPEX is 199M€ based on the chemical engineering cost index.

In Kangas et al. (2014), the recovery boiler takes the highest percentage of the capital investment cost due to its functionality and purpose to convert or generate steam through the processing by burning the lignin. If the recovery boiler and everything linked with the processing can be removed in the Kraft lignin process, the CAPEX will reduce drastically.

However, the recovery boiler cannot be excluded in the Kraft process due to a crucial role in chemical recovery. If such happened, there would be an increase in chemical costs, then leads to a situation whereby chemicals cannot be recycled. The chemical consumption value was obtained from literature (Kangas et al. 2014), while the price based on the current figure in the market, which resulted in 23M€ for the chemical consumption by the Kraft process.

By applying DEA analysis equation (1) to (3) for analyzing cost-efficiency in Kraft process in both Kangas analysis and Chemical Engineering Cost Index (CECI) for CAPEX and OPEX, then electricity consumption is decreased in CECI and resulted to less cost input and more extra profit output in CECI analysis.

Table 3. Summary of capital investment cost and operation cost based on the Kraft processing calculated on the equipment costs analysis in the chemical engineering cost index.

Items	Chemical cost (M€)	Total capital investment cost (M€)	Total operation Cost (M€)
Kraft processing	23	111	93

Table 4. Total production costs (Operating cost) for Kraft process in fractionation processing (Variable costs +Fixed costs) in € per air dry tonne at 90% solids and operating cost in Million € per annum, the original data retrieved from Kangas et al. (2014) (details presented under appendices in Table A 8–1 to Table A 8–8).

Material	€/ adt	M€/y
Pulpwood	97	21
Chemicals consumption	103	23
Utilities	75	17
Electricity consumption	76	17
Waste	102	22
Labour cost	8	2
Maintenance	48	11
Depreciation	136	30
Other indirect costs	15	3
Logistics	30	7

Total	690	152

Table 5. Total capital investment cost in Kraft pulp in fractionation processing with pulpwood, the original data retrieved from Kangas et al. (2014) with few modifications, share investment cost detail presented under Appendices in Table A 8–2.

Processing stages	M€
Wood handling	57
Delignification	113
Bleaching	52
Pulp drying processing	118
Evaporation stage	50
Recovery boiler	168
Re-causticizing and lime kiln	52
Turbine plant	59
Water treatment section	31
Infrastructure	70
Total (Million €)	770

5.2 Cost data analysis for ILs processing

The economics cost data based on ionic liquid process with 1-ethyl-3-methyl imidazolium acetate ([Emim] Ace), 97% were selected based on the price of common ionic liquid solvent. The capacity for the ILs were based on 220000 t /year for the lignin production. The details about the ILs calculation are presented under appendices in Table A 8–9 and Table A 8–11, while OPEX and CAPEX are presented in Table 6 and Table 7 respectively.

The cost data of ILs fractionating process with consumption analysis presented under appendices in Table A 8–9 by using 1-ethyl-3-methyl imidazolium acetate 97% purity, with the same production capacity as Kraft and DES process resulted to 122M€ for OPEX in Table 6 and 146M€ for CAPEX in Table 7. When studying the breakdown analysis of operating cost for ILs fractionation, the ionic liquid solvent is the significant cost factor accounting for 43% of operating cost, followed by crude material (pulpwood) which also accounted for 18%, while the total cost for others is below 39% of operating cost.

Table 6. The estimated annual operating and maintenance costs for ionic liquid fractionation processing with 1-ethyl-3-methyl imidazolium acetate, 97% IL based on 220000 ton/year lignin production.

Cost items	Cost (M€)
Pulpwood	23
Ionic Liquid (ILS)	53
Chemicals (other)	2
Other costs	9
Maintenance (Mc)	2
Labour cost (LC)	6
Supervisors (S)	1
Operating supplies cost	0.3
Laboratory cost	1
Overhead cost	5
Depreciation	7
Utilities	4
Electricity consumption	0.04
Local taxes	1.4
Insurance cost	0.7
Admin Cost (AC)	1.2
Advertisement	2
Research Cost	2
Total (M€/y)	122

Table 7. The total capital investment cost for ILs Fractionation process based 1-ethyl-3-methyl imidazolium acetate, 97% IL with 220000 t/year of lignin production.

Total capital investment cost (TCC)		Cost in millions of euro
Direct Cost (DC)	**EC (%)**	**(M€)**
EC (equipment cost)	100	16.83
Installation of equipment	42	7.07
Instrumentation + control	35	5.89

Pipe connection	65	10.94
Electrical	8	1.35
Building and building service	27	4.55
Facilities services	20	3.37
Total for direct cost (TDC)	297	50.00
Indirect cost analysis (IC)	**EC (%)**	
Contingency cost	30	5.05
Legalization cost	4	0.67
Engineering cost	30	5.05
Contractors' cost	20	3.37
Expenses based on construction	41	6.90
Total indirect cost (TIC)	125	21.04
Total Fixed capital investment cost (TFCI) =TDC+TIC (422)		71.04
Working capital expenses 15% of TCIC		21.89
IL cost		53.00
Total capital Investment cost (TCIC)=TFCI + WC + IL cost		145.93

To make the ILs concept to be cost efficiency according to the cost summary, the ionic liquid should be produced from economical and inexpensive feedstocks, which is also suggested by Drapcho et al. (2008). Furthermore, ILs must be recycled according to Brandt-Talbot et al. (2017), for more than 5 to 6 times to be cost-efficient and sustainable.

5.3 Cost data analysis for fractionation based on DES process

To bring value of equipment cost to current value based on analysis from Chen et al. (2014) and Peters et al. (2003) with the initial calculation which based on 2002 cost for an industrial fractionation process. Equation (11) on Chemical engineering Plant Cost Index (CEPCI) was utilized to determine the current purchase cost for the equipment.

The capacity was updated to 220000 t/year, details about the initial data are presented under appendices in Table A 8–10 and Table A 8–12. The relevant cost data based on the DES fractionation processes are scarce, therefore the cost

estimated data were based on the experimental analysis done in the chemistry laboratory at Lappeenranta-Lahti University of Technology (LUT) in the Department of Chemical Engineering with few modifications using ChCl with LA, and comparison with OXA, MA and phenol in molar ratio 1:9.

The cost analysis based on the process used in DESs fractionation prepared using ChCl with MA, OXA, and Phenol, including the total capital investment cost and total operation cost, are summarized in Table 8. The cost analysis of the DES fractionation process based on Lactic acid is stated in detail in Table 9 and Table 10.

Based on the cost analysis for DES fractionation process in four different categories, the cost for deep eutectic solvent took a significant factor in each DES application. In studying the breakdown of CAPEX and OPEX in Table 8 – Table 10, the lowest CAPEX with 105M€ and OPEX with 83M€ was achieved from ChCl:OXA, followed by ChCl:Phenol with 120M€ for CAPEX and 95M€ for OPEX, and the DES with ChCl:LA which was performed in LUT Laboratory resulted to 131M€ for CAPEX and 105M€ for OPEX.

The ChCl:MA received the highest cost in CAPEX with 149M€ and OPEX with 121M€, assumption on if they all undergone the same molar ratio. Therefore, to know the cost-efficiency of processes based on the use of DESs and the beneficial aspect of it, the yielded output by-product needs to be analyzed, which are going to be discussed in the next subchapter 5.4.

Table 8. Summary of DES cost, capital investment cost and operation cost based on the process used in DES fractionation prepared using ChCl with Malic acid, Oxalic acid and Phenol.

Items (9:1)	DES cost (M€)	Total capital investment cost (M€)	Total operation Cost (M€)
Malic Acid: ChCl	56	149	121
Oxalic acid: ChCl	19	105	83
Phenol: ChCl	31	120	95

Table 9. Total production costs (Operating cost) based on the process used in DES fractionation prepared using ChCl and Lactic acid

Cost items	Cost (M€)
Pulpwood	23
DES cost	40
Chemicals (other)	2
Other costs	7
Maintenance (Mc)	2
Labour cost (LC)	6
Supervisors (S)	1
Operating supplies cost	0.3
Laboratory cost	1
Overhead cost	5
Depreciation	7
Utilities	2
Electricity consumption	0.04
Local taxes	1.4
Insurance cost	0.7
Admin Cost (AC)	1.2
Advertisement	2
Research Cost	2
Total (M€/y)	105

Table 10. The total capital investment cost for the DES (ChCl/Lactic acid) fractionation process.

Total capital investment cost (TCC)		Cost in millions of euro
Direct Cost (DC)	EC (%)	(M€)
EC (equipment cost)	100	16.83
Installation of equipment	42	7.07
Instrumentation + control	35	5.89
Pipe connection	65	10.94
Electrical	8	1.35
Building and building service	27	4.55
Facilities services	20	3.37
Total for direct cost	297	50.00
Indirect cost analysis (IC)	EC (%)	
Contingency cost	30	5.05
Legalization cost	4	0.67
Engineering cost	30	5.05
Contractors' cost	20	3.37
Expenses based on construction	41	6.90
Total indirect cost (TIC)	125	21.04
Total Fixed capital investment cost (TFCI) =TDC+TIC (422)		71.04
Working capital expenses 15% of TCIC		19.60
DES cost		40
Total capital Investment cost (TCIC)=TFCI + WC + DES cost		131

5.4 Cost comparison and benefits for DESs based process and Other processes for lignin production.

Another data for CAPEX and OPEX is obtained from another company situated in South-western Finland who focused on lignin, hemicellulose, and cellulose fractionation through Pressurized hot water extraction (PHWE), which practically is chemical-free with the production capacity of 100,000 MT/year (pilot-scale). The obtained data is updated to 220000 t/year with an approximate result of 200M€ and 88M€ for CAPEX, and OPEX respectively.

In applying equation (3) about the DEA method for analyzing the capital investment cost for different fractionation method for lignin production are presented in Figure 12, the Kraft process and DES based process on ChCl: OXA stood as the most economical method in fractionating processing, followed by the PHWE process. In terms of chemical cost, malic acid (MA) has a costly rate of about 50% than lactic acid (LA), in Figure 13, upon analyzed the ChCl:LA as an index factor due to its regular processing in LUT Lab, there are other DESs process apart from DESs process based on ChCl/LA, which is more economical and cost-efficiency in terms chemical cost are presented in Figure 13.

However, before conclusion, the purity and high quality of lignin produced from each process needs to be considered, for instance, are the lignin obtained, suitable as a polymeric substitute and other suitable product manufacturing? The answer can determine if the process is cost-efficient or not. Besides, the reflection of material based on chemicals makes some capital investment cost could influence the process, thus, making it more expensive than the other, the benefit of each processing has to be investigated, which is coming up in the next subchapter.
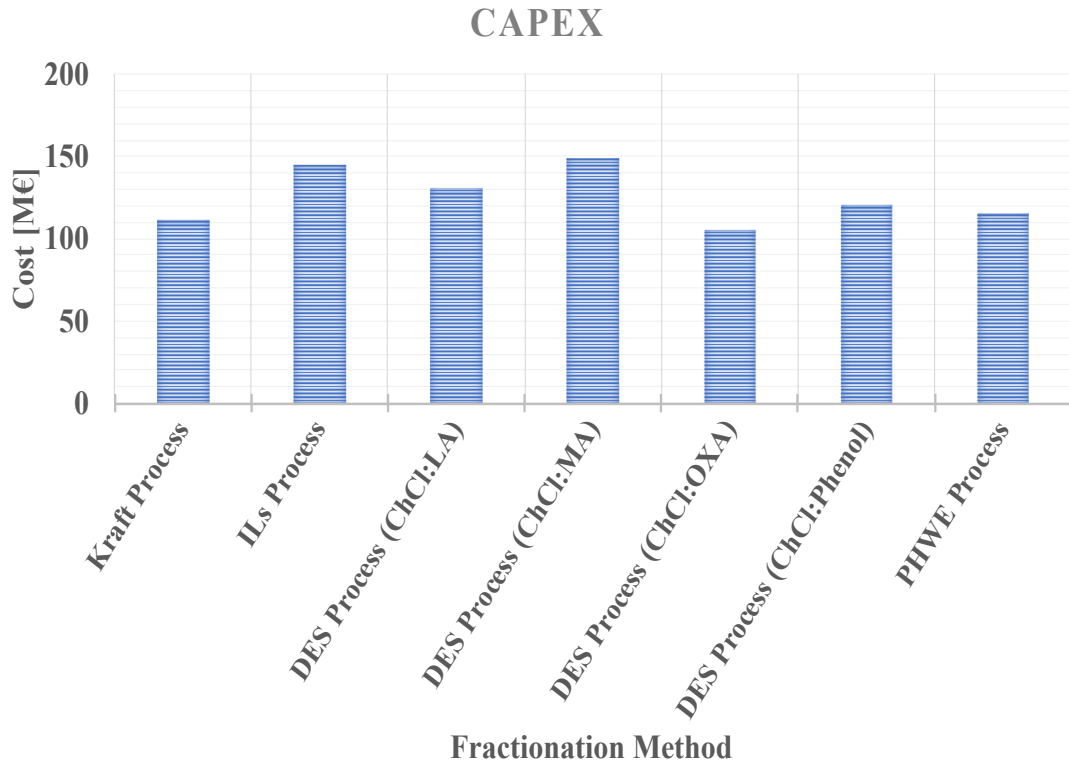
Figure 12. The analysis of Capital investment cost based on different fractionation method for lignin production.

Figure 13. ChCl:LA as index base for the DEA analysis for Capital investment cost (CAPEX) based on different fractionation method for lignin production.

The cost of materials such as feedstocks, solvents, and chemicals in operational cost analysis presented in Figure 14 shows a significant role in fractionating process. In analyzing OPEX in different fractionating process, the costs for raw material such as wood was calculated to be 23M€/y, which is the same for all the fractionation processes because all the processes estimated by using the same input of 220000 t/year. However, the chemicals made from fossil material standout as more economical material, but it demanded higher utility due to the number of the separation process required.

In addition, there are some materials made from renewable material that competes with non-renewable materials in fractionating process such as oxalic acid. Zhang et al. (2020) & Li et al. (2018) reported that deep eutectic solvent is possible to reuse, and the reusable or recyclability of DES up to 5 or 7 times, gives DES potential to reduce the input of OPEX and produce more output (revenue). The cost for reusability of DES consumption did not reflect in analyzing operational cost, due to insufficiency data about the reusable cost.

However, in the report by Li et al. (2018), the process based on the use of DES (ChCl:LA) was repeated for five cycles without purification and fresh solvent was added between the batches. Hence, the structure of ChCl:LA changed after five reuses. Besides, Zhang et al. (2020) reported that reusability of DESs after the first cycle resulted in a decrease of $\pm$ 0.2 % of yield output.

In Figure 15, when ChCl:LA utilized as cost index, it can be understood that Cost input in OPEX comparison offered more reduction in cost input for some of processes based on the use of DES such as ChCl:OXA with 22M€ decrease and 10M€ for ChCl: Phenol. The yield of the production output from each fractionation process differ and show clear advantages upon each other in Table 11, which signifies another important aspect in review cost-efficiency in the processes based on the use of DESs.
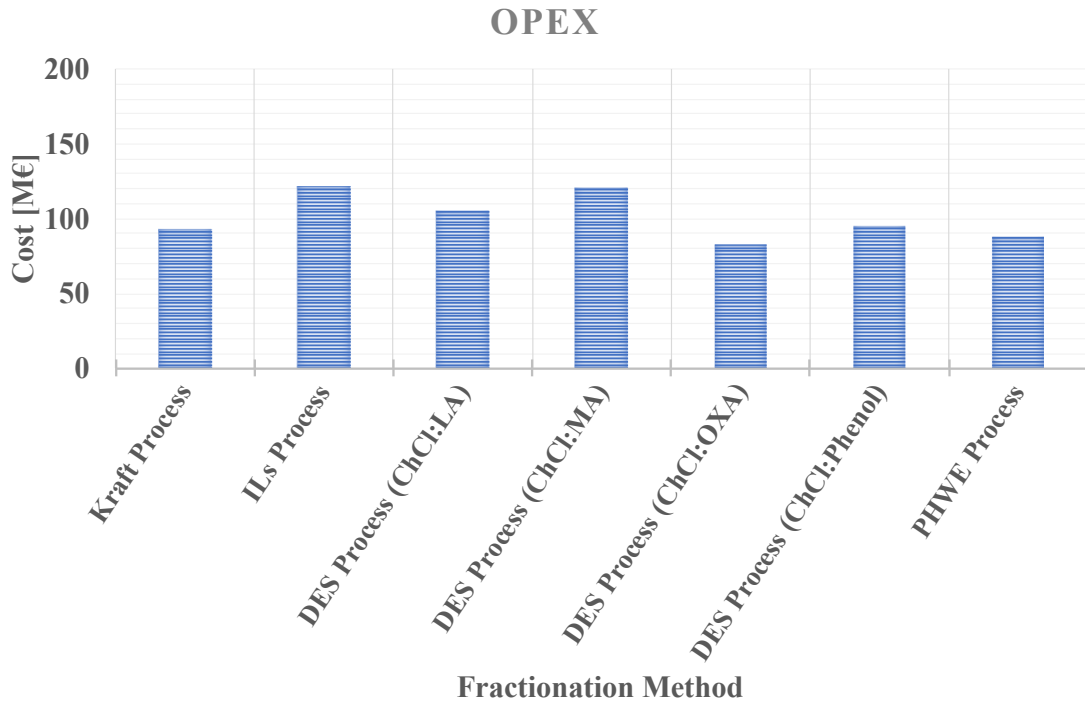
OPEX

Figure 14. The analysis of annual operating cost based on different fractionation method for lignin production.
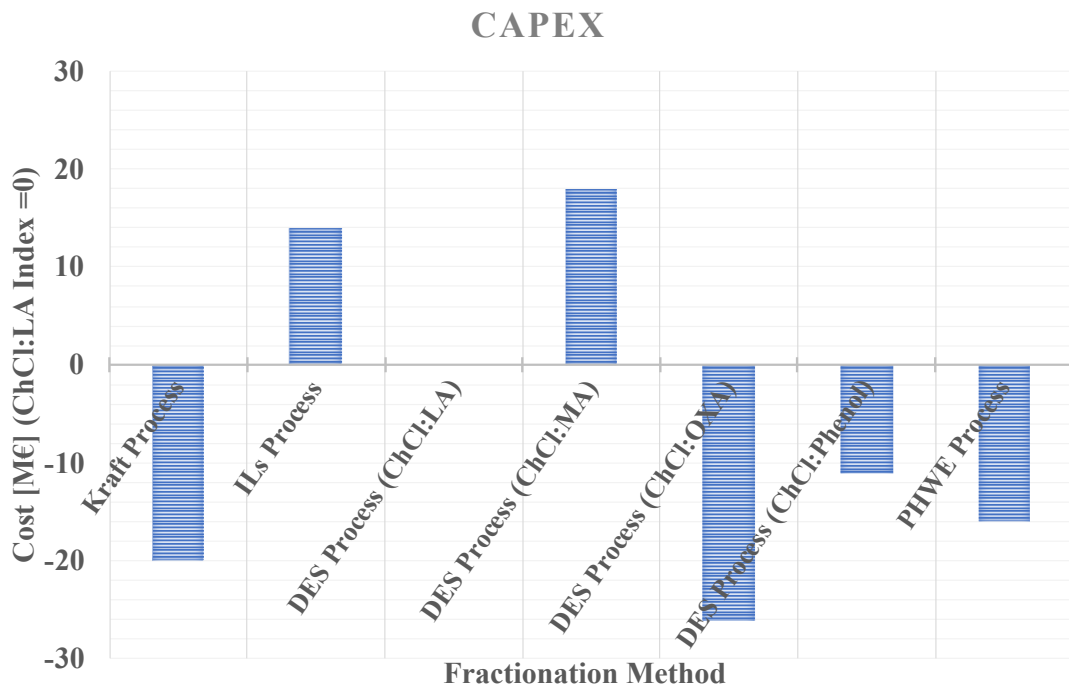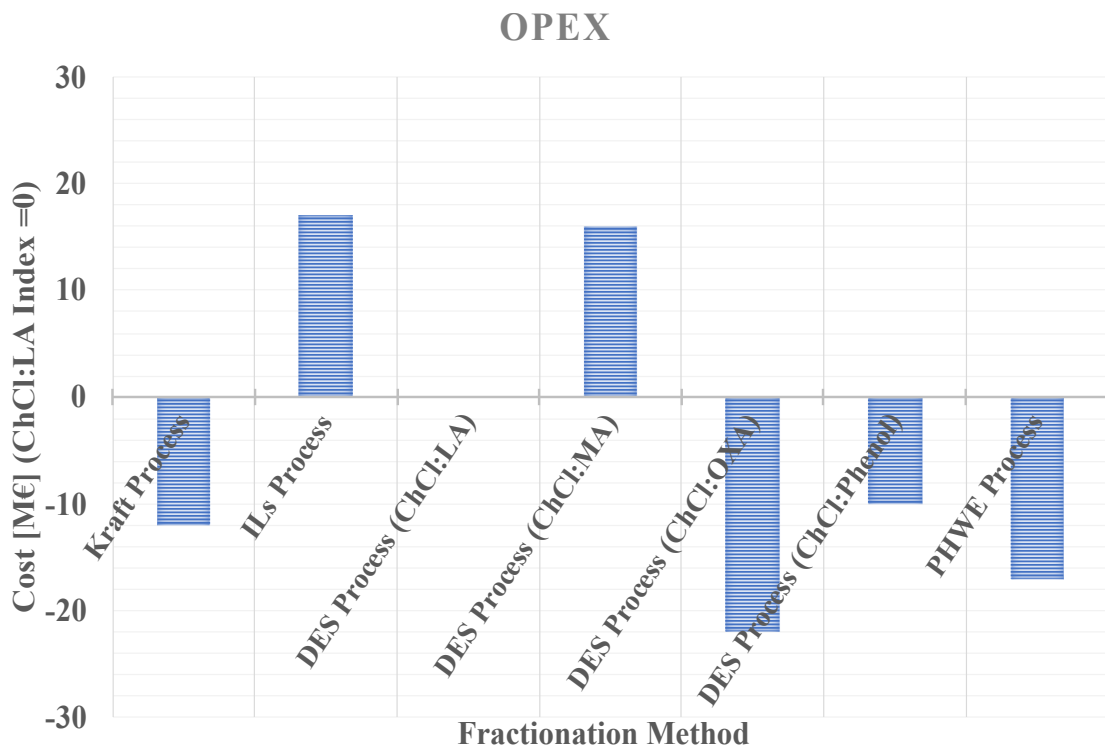
OPEX

Figure 15. ChCl:LA as index base for the DEA analysis for annual operating cost (OPEX) based on different fractionation method for lignin production.

UPM reported that their lignin UPM BioPiva 300 costs about 60 €/kg, and its produced as 100% bio-based. Also, Stora Enso on specified in their website that their lignin is renewable, wood-based and non-toxic made from Kraft pulping process from Nordic softwood, pine, and spruce, and stated further that their annual capacity for lignin production is 50kt and 370kt for the annual pulp production. In addition, Lignolproduktion AB, a joint company owned by RenFule and Preem said, their plant is assumed to generate about 25k–30k tonnes of lignin per annum.

For this project, the lignin revenue cost was analyzed with global lignin price which is 6500 €/tonne and lignin classification based on the yield output in Table11. Stora Enso's revenue was estimated to be 325M€, and Lignolproduktion AB revenue is 195M€, while the DES-based on (ChCl:LA) would result in 546M€ which are presented in Table 12.

 However, if the UPM lignin price is used as a yardstick for assessing lignin cost with the yield output production of lignin in Table 11, then Stora Enso would have revenue of €3 billion based on their lignin product, while the revenue for the lignin obtained through the DES (ChCl: LA) estimated as €5 billion with UPM price for lignin. In 2019 under the UPM business area, UPM reduced the capacity of their 620,000 tonnes operation by 240,000 tonnes, the UPM other operations such as biochemicals, biocomposites, biomedicals, and forest, and UPM biorefining such as pulp, biofuels, and timber categorized as major products banged revenue of €2.354 billion in total. The UPM capital expenditure in 2019 was totalled 378M€ excluding leased assets (source: UPM annual report 2019, UPM Financial Results 2019).

Table 11. The classification and characteristics of different fractionation process for lignin products in wood (Rodrigues et al. 2018).

Processing	Suitability for various biomass	Yielding content (%)	Sulphur content	Purity	Scale of production
Kraft process	hard wood and softwood	35–50	Moderate	Moderate	Industrial
Sulphite	hard wood and softwood	55–60	High	Low	Industrial
ILs	hard wood, softwood and non-wood crops	N/A	Free	High	Pilot/Demo
DESs	hard wood, softwood and non-wood crops	60–75	Free	High	Pilot/Demo
PHWE	hard wood and softwood	N/A	Free	Moderate	Pilot/Industrial

N/A: Not available/applicable, – cannot be ascertained.

Table 12. The annual revenue based on the yield content on the recovery of lignin from Kraft and DES based process

Processing	**Annual Revenue for production (Billion €)	Yielding content selected (%)	Annual Production capacity (k/tonne)	*Annual Revenue for production (Million €)
Kraft process	3	40	50	325
ILs	–	N/A	–	–
LA:ChCl	5	67	84	546
MA:ChCl	–	N/A	–	–
OXA:ChCl	–	N/A	–	–
Phenol:ChCl	–	N/A	–	–
PHWE	–	N/A	–	–

*Global market price (6500€/tonne), **UPM price (60€/kg) N/A: Not available, – cannot be ascertained.

5.5 Value proposition and SWOT on DESs based process in fractionating lignin, hemicellulose, and cellulose over Sulfite, Kraft, and ILs process.

The summary of the necessary business model canvas for the processes based on the use of DESs are presented in Table 13, also it provides an extensive overview for any industry wishing to integrate DES process into their processing.

Table 13. The summary of key aspect of the business model canvas on the processes based on the use of DESs and output.

Key Partners (8)	Key Activities (7)		
The key partners on the processes based on the use of DESs could be achieved through these following factors: • Biorefineries Industries • Universities • Other lignin producers • Other hemicellulose producers • Other cellulose producers • Pharmaceutical industries	• The activities to recover Lignin, hemicellulose, and cellulose to increase production efficiency. • Selection of feedstocks (wood or non-wood). • Selection of right DES mixture for the selected feedstocks. • Way to achieve high purity lignin product and evaluation such as level of purity. • Development of suitable fractionation method and modification of chemical when deemed necessary.		
Customer relationships (4)	**Key resources (6)**	**Customer segments (2)**	
• Partnership in a project (partner with current industries who are into the recovery of lignin, hemicellulose, and cellulose). • A bilateral agreement in the co-financing grant to increase the usability of the DESs process.	• Expertise's • Pilot and Demo facilities for the fractionation • Right tools and apparatus for characterization process **Channels (3)** The channel to create awareness can be through these following avenues.	The target customer will be those involves in the following segments. • Automotive producers • Energy industries • Forest industries • Composites producers • Construction industries • Pharmaceuticals industries • Water treatment industries • Furniture industries • Other end users	
Cost structure (9)	• Advertisement through partner's website • Trade fairs • Regular publicity • Visit to pulping industries		
• Capital investment cost • Operating and manufacturing cost • Transport and travel cost • Overhead cost • Research and development			

Value Proposition (1)	Revenue streams (5)
Other features to make the process based on the use of DESs attractive to those industries who are interested. • Cost efficiency advancement by integrates the DESs process into the existing process as blended or substitute. • The ability to decrease dependence on fossil-based feedstocks. • DESs is excellent as renewable chemical /solvents • Availability of Lignin, Hemicellulose, and cellulose research expert consultant. • The DESs process can reduce pollution (water pollution).	Revenue can be generated through these following factors: • Lignin • Cellulose • hemicellulose • Loan /public funding

The perspective concerning the processes based on the use of DESs was analyzed in Table 14, which provides beneficial effects and feasibility for integrating the concept into the existing process and reduced the capital investment cost. Furthermore, revenue through the lignin production and ability to reduce carbon footprint, simple preparation, sulfur-free, and reusability of deep eutectic solvents up to 5 times render the DES fractionation process more profitable, promising, and hopeful.

Table 14. The summary of SWOT analysis of DES fractionation process over sulphite, Kraft (sulphate) and ILs based process

Strength

- The processes based on the use of DESs have a potential high yield grade product and non-toxic than other processes such as Kraft, sulfite process.
- More lignin content can be extracted with high purity in processes based on the use of DESs than other processes due to more than five-time of the recycling process.
- Less electricity consumption can be achieved compared to other methods, due to low melting point and lower temperature $< 120^{\circ}C$ required for the processing.
- DESs as a solvent has a wide range of usability (Wide enrichments factor), for instance, DESs as a solvent has been used in the biomedical industry for drugs solubilization such as ibuprofen.
- The processes based on the use of DESs is simple to prepare, environmental sustainability and it is sulfur-free
- The DESs based process such as ChCl: LA is Capable of fractionating wood biomass in waste streams (construction and building waste).
- The DES fractionation process has low extraction time, and the process is typical salts also without a non-charged hydrogen bond donor (HBD).

Weakness

- The processes based on the use of DESs is high production cost due to the price of the DESs components.
- Insufficiencies awareness to bigger industries.
- The processes based on the use of DESs consuming large volume of water.
- It will require more persistence, and valuable result, in order for existing industries to adopt the process based on the use of DESs into pilot or industrial scale.

Opportunities

- The process based on the use of DES can replace or substitute the traditional and sulphate method in the fractionation process in the nearest future.
- More revenue can be generated from the lignin production output in process based on the use of DES due to the amount lignin extracted and quality (sulfur-free).

- The lignin output produced through the process based on the use of DES can increase the availability of feedstocks for composite producers and automotive.
- The processes based on the use of DESs can create jobs for specialists (DESs expertise) has a result of consultancy (R&D consulting).
- The DESs based fractionation process is capable of decreasing the carbon footprint and contribute to 100 % uses of biomass.
- Suitability for membrane technology (membrane additives).
- The process based on the use of DES, does not require a completely new factory, it can integrate into existing or current process lines (lignin production set up industry).
- It creates a market for those industries that producing DES components, which could result in competition in the DES components cost aspects.

Threats

- Decreasing pulp demand and make pulp capacity less important due to more lignin extraction.
- Regulation and policy

6   CONCLUSIONS

First, it was observed that the lignin yield from each of the DES processes for biomass fractionation differs for each other. For instance, the level of biomass compatibility is not the same in every DES component. The molar ratio between its components can be varied to obtain the eutectic solvent, and it can reflect in the revenue perspective.

The recycling of the chemicals from the DESs based processes is another significant characteristic that makes the process cost-efficient and sustainable. Besides that, the production of sulfur-free lignin through this process added more benefits for the DES process over other methods.

Furthermore, DESs as solvent for biomass fractionation could be used to reduce carbon footprint due to its green in nature, less energy requires in mixing and heating, low vapor pressure, and environmentally benign. Therefore, when industries that specialize in recovery or extracting lignin and hemicellulose take up the process based on the use of DES as an alternative or blended method for biomass fractionation process, it could help in reducing the carbon footprint.

In analyzing the proportion of quality output obtained through different fractionation methods, it happened that process based on the use of DES showed cost efficiency characteristic, if it can be integrated into the existing pulp mills or upgraded to large or industrial-scale. ILs process is the most extremely capital and operational cost intensive fractionating systems, due to the expensive cost of ILs.

Furthermore, upon applying the chemical engineering cost index (CECI) concept and SWOT analysis approach in analyzing the chemical and solvent used in fractionating process. The Kraft process is the lowest and most affordable in terms of chemical cost, since the Kraft process is mature process that is well established, but it lags in the lignin purity, usually high sulfur content. Finally, in considering the revenue through the separation or extraction method, the processes based on the use of DESs generated more profits than the other approaches due to the amount of lignin product obtained and opportunity to make uses of different biomass in full contexts such as waste wood from construction and forest residual.

7   RECOMMENDATIONS AND FUTURE WORK

Any industries which involve in the Fractionating processes, desire better production, economical, and minimization of the cost should integrate the DES process into their processing.

To implement the DESs fractionating process into a pilot scale, it would be appropriate to target those companies experiencing a weak or struggling with economy or experience downturn. For instance, it may be a challenge in their process scheme or an increase of the competitors, a rise of the chemical cost, these kinds of industries are to be targeted and concentrate on, by offering new prospects for those industries.

Moreso, it would be important due to confidentiality that this type of project should be done in collaboration with industries that are still doing their fractionation processes based on the current and well-known system in order to receive or obtain appropriate data which are suitable for the confidence of this project, therefore the data would not be biased. It would be more important and advisable that the several ranges of DESs system based approach should be performed at a small scale or lab scale level with the same parameter, the same personnel, and the same equipment to determine the actual yielding, the separation or fractionation of lignin, hemicellulose, and cellulose, also to have an excellent cost-efficiency comparison. Finally, to give DES more opportunity over other processes, DES needs to be produced at a large or industrial scale for availability as affordable green solvents.

8 REFERENCES

Abbott, A., Boothby, D., Capper, G., Davies, D. & Rasheed, R. 2004. Deep eutectic solvents formed between choline chloride and carboxylic acids: Versatile alternatives to ionic liquids. Journal of The American Chemical Society, 126(29), pp. 9142-9147. doi:10.1021/ja048266

Abbott, A. P., Capper, G., Davies, D. L., Munro, H. L., Rasheed, R. K. & Tambyrajah, V. 2001. Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains. Chemical Communications, 1(19), pp. 2010-2011. doi:10.1039/b106357j

Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K. & Tambyrajah, V. 2003. Novel solvent properties of choline chloride/urea mixtures. Chemical Communications, 9(1), pp. 70-71. doi:10.1039/b210714g

Abo-Hamad, A., Hayyan, M., Alsaadi, M. A. & Hashim, M. A. 2015. Potential applications of deep eutectic solvents in nanotechnology. Chemical Engineering Journal, 273, pp. 551-567. doi:10.1016/j.cej.2015.03.091

Agbor, V. B., Cicek, N., Sparling, R., Berlin, A. & Levin, D. B. 2011. Biomass pretreatment: Fundamentals toward application. Biotechnology Advances, 29(6), pp. 675-685.

Alibaba.com (Chlorine dioxide) [cited 23-03-2020]. Available: https://www.alibaba.com/product-detail/Chlorine-Dioxide-powder-Clo2-for-Disinfectant_60770984435.html?bypass=true&spm=a2700.7735675.normalList.23.786d74cdHGHVaU&s=p

Alex, O & Simons H. Energy generation and use in the Kraft pulp industry [cited 24-03-2020]. Available: https://www.aceee.org/files/proceedings/1995/data/papers/SS95_Panel1_Paper04.pdf

Alvarez-Vasco, C., Ma, R., Quintero, M., Guo, M., Geleynse, S., Ramasamy, K. K., . . . Zhang, X. 2016. Unique low-molecular-weight lignin with high purity

extracted from wood by deep eutectic solvents (DES): A source of lignin for valorization. *Green Chemistry, 18*(19), pp. 5133-5141. doi:10.1039/c6gc01007e

Alén, R. 2011. Papermaking science and technology: Book 20, Biorefining of forest resources. Helsinki: Paperi ja puu. Ch 2. Pp 56-115

Andersson, P. 2014. A dynamic Na/S balance of a Kraft pulp mill: Modeling and simulation of a Kraft pulp mill using WinGEMS.

Anugwom, I., Eta, V., Virtanen, P., Mäki-Arvela, P., Hedenström, M., Hummel, M., . . . Mikkola, J. 2014. Switchable Ionic Liquids as Delignification Solvents for Lignocellulosic Materials. *ChemSusChem, 7*(4), pp. 1170-1176. doi:10.1002/cssc.201300773

Anugwom, I., Lahtela, V., Kallioinen, M., Kärki, T., LUT, L. t. y., LUT, L. U. o. T. & Science|, f. o. E. S. o. E. Lignin as a functional additive in a biocomposite: Influence on mechanical properties of polylactic acid composites. Elsevier.

Balliauw, M., Meersman, H., Onghena, E. & Van de Voorde, E. 2018. US all-cargo carriers' cost structure and efficiency: A stochastic frontier analysis. Transportation Research Part A, 112, pp. 29-45. doi:10.1016/j.tra.2018.01.005

Benavides, P. T., Salazar, J. & Diwekar, U. 2013. Economic Comparison of Continuous and Batch Production of Biodiesel Using Soybean Oil. Environmental Progress & Sustainable Energy, 32(1), pp. 11-24. doi:10.1002/ep.11736

BISLEY, the people who know material [cited 09-06-2020]. Available [https://bisley.biz/products/detail/lignosulfonates]

Borregaard sustainable lignin products [cited 09-06-2020]. Available: [https://lignotech.com/About-us]

Brandt-Talbot, A., Gschwend, F. J. V., Fennell, P. S., Lammens, T. M., Tan, B., Weale, J. & Hallett, J. P. 2017. An economically viable ionic liquid for the fractionation of lignocellulosic biomass. Green Chemistry, 19(13), pp. 3078-3102.

CEPCI 2019, Chemical Engineering Plant Cost Index annual average [cited 02-04-2020]. Available: https://www.chemengonline.com/2019-chemical-engineering-plant-cost-index-annual-average/

Chakar, F. S., Ragauskas A. J., (2004). Review of current and future softwood Kraft lignin process chemistry. Industrial Crops and Products. 20, 131-141.

Charnes, A., Cooper, W.W., Rhodes, E., 1978. Measuring the efficiency of decision making units. European Journal of Operational Research 2 (6), 429–444 (cross ref.)

Chen, J., Li, Y., Wang, X. & Liu, W. 2019. Application of Deep Eutectic Solvents in Food Analysis: A Review. *Molecules, 24*(24), . doi:10.3390/molecules24244594

Chen, L., Sharifzadeh, M., Mac Dowell, N., Welton, T., Shah, N. & Hallett, J. P. 2014. Inexpensive ionic liquids: [HSO 4] -based solvent production at bulk scale. *Green Chemistry, 16*(6), pp. 3098-3106. doi:10.1039/c4gc00016a

Chen, Y., Chen, W., Fu, L., Yang, Y., Wang, Y., Hu, X., . . . Mu, T. 2019[a]. Surface Tension of 50 Deep Eutectic Solvents: Effect of Hydrogen-Bonding Donors, Hydrogen-Bonding Acceptors, Other Solvents

Chen, Y. & Mu, T. 2019. Application of deep eutectic solvents in biomass pretreatment and conversion. *Green Energy & Environment, 4*(2), pp. 95-115. doi:10.1016/j.gee.2019.01.012

Chen, Z., Reznicek, W. D. & Wan, C. 2018. Deep eutectic solvent pretreatment enabling full utilization of switchgrass. Bioresource Technology, 263, pp. 40-48. doi:10.1016/j.biortech.2018.04.058

Chen, Z., Bai, X., Lusi, A. & Wan, C. 2018. High-Solid Lignocellulose Processing Enabled by Natural Deep Eutectic Solvent for Lignin Extraction and Industrially Relevant Production of Renewable Chemicals. ACS Sustainable Chemistry and Engineering, 6(9), pp. 12205-12216. doi:10.1021/acssuschemeng.8b02541

Coz, A., Llano, T., Cifrián, E., Viguri, J., Maican, E. & Sixta, H. 2016. Physico-Chemical Alternatives in Lignocellulosic Materials in Relation to the Kind of Component for Fermenting Purposes. Materials, 9(7), . doi:10.3390/ma9070574

Culbertson, C. 2017. Commercialization of Sustainable Bio-Refinery Projects for the Pulp and Paper Industry.

Cvjetko Bubalo, M., Vidović, S., Radojčić Redovniković, I. & Jokić, S. 2015. Green solvents for green technologies. Journal of Chemical Technology & Biotechnology, 90(9), pp. 1631-1639. doi:10.1002/jctb.4668

Da Costa Lopes, A. M., João, K. G., Rubik, D. F., Bogel-Łukasik, E., Duarte, L. C., Andreaus, J. & Bogel-Łukasik, R. 2013. Pre-treatment of lignocellulosic biomass using ionic liquids: Wheat straw fractionation. Bioresource Technology, 142, pp. 198-208. doi:10.1016/j.biortech.2013.05.032

Deshpande, R. 2016. The initial phase of sodium sulfite pulping of softwood: A comparison of different pulping options.

Digman, M. F., Shinners, K. J., Casler, M. D., Dien, B. S., Hatfield, R. D., Jung, H. G., . . . Weimer, P. J. 2010. Optimizing on-farm pretreatment of perennial grasses for fuel ethanol production. Bioresource Technology, 101(14), pp. 5305-5314.

Drapcho, C. M., Nhuan, N. P. & Walker, T. H. 2008. Biofuels engineering process technology. New York: McGraw-Hill.

Du, B., Sharma, L. N., Becker, C., Chen, S., Mowery, R. A., Van Walsum, G. P. & Chambliss, C. K. 2010. Effect of varying feedstock–pretreatment chemistry combinations on the formation and accumulation of potentially inhibitory degradation products in biomass hydrolysates. Biotechnology and Bioengineering, 107(3), pp. 430-440.

El Achkar, T., Fourmentin, S. & Greige-Gerges, H. 2019. Deep eutectic solvents: An overview on their interactions with water and biochemical compounds. Journal of Molecular Liquids, 288, p. 111028. doi:10.1016/j.molliq.2019.111028

Equihua-Sánchez, M. & Barahona-Pérez, L. 2019. Physical and Chemical Characterization of Agave tequilana Bagasse Pretreated with the Ionic Liquid 1-Ethyl-3-Methylimidazolium Acetate. Waste and Biomass Valorization, 10(5), pp. 1285-1294. doi:10.1007/s12649-017-0150-4

Esmaeili, M., Anugwom, I., Manttari, M. & Kallioinen, M. 2018. Utilization of DES-Lignin as a Bio-Based Hydrophilicity Promoter in the Fabrication of Antioxidant Polyethersulfone Membranes. *Membranes,* *8*(3), . doi:10.3390/membranes8030080

Espino, M., de Los Ángeles Fernández, M., Gomez, F. J. & Silva, M. F. 2016. Natural designer solvents for greening analytical chemistry. *Trends in Analytical Chemistry, 76*, pp. 126-136. doi:10.1016/j.trac.2015.11.006

EUCALIVA.eu Lignin and polyurethane extraction from black liquor [cited 17-02-2020]. Available: [https://eucaliva.eu/project-concept#:~:text=Two%20procedures%20can%20be%20used,then%20acidified%20(CO2).

Fardim, P. 2011. Papermaking science and technology: Book 6, Chemical pulping. Part 1, Fibre chemistry and technology. 2nd ed. totally updated version. Helsinki: Finnish Paper Engineers' Association : Paperi ja puu.

Florindo, C., Oliveira, M. M., Branco, L. C. & Marrucho, I. M. 2017. Carbohydrates-based deep eutectic solvents: Thermophysical properties and rice straw dissolution. Journal of Molecular Liquids, 247, pp. 441-447.

FOEX Indexes Ltd, Bioenergy and wood Indices. [cited 23-03-2020]. Available: https://www.foex.fi/index.php?page=biomass

Fornell, R., Berntsson, T. & Åsblad, A. 2012. Process integration study of a kraft pulp mill converted to an ethanol production plant – part B: Techno-economic analysis. *Applied* *Thermal* *Engineering,* *42*, pp. 179-190. doi:10.1016/j.applthermaleng.2012.02.043

Fort, D. A., Remsing, R. C., Swatloski, R. P., Moyna, P., Moyna, G. & Rogers, R. D. 2007. Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1- n -butyl-3-methylimidazolium chloride. *Green Chemistry, 9*(1), pp. 63-69. doi:10.1039/b607614a

Francisco, M., Van Den Bruinhorst, A. & Kroon, M. C. 2012. New natural and renewable low transition temperature mixtures (LTTMs): Screening as solvents for lignocellulosic biomass processing. Green Chemistry, 14(8), pp. 2153-2157. doi:10.1039/c2gc35660k

Galkin, M. V. & Samec, J. S. M. 2016. Lignin Valorization through Catalytic Lignocellulose Fractionation: A Fundamental Platform for the Future Biorefinery. ChemSusChem, 9(13), pp. 1544-1558.

Garcia, G., Aparicio, S., Ullah, R. & Atilhan, M. 2015. Deep Eutectic Solvents: Physicochemical Properties and Gas Separation Applications. *Energy & Fuels, 29*(4), pp. 2616-2644. doi:10.1021/ef5028873

George, A., Brandt, A., Tran, K., Zahari, S. M. S. N. S., Klein-Marcuschamer, D., Sun, N., . . . Hallett, J. P. 2015. Design of low-cost ionic liquids for lignocellulosic biomass pretreatment. Green Chemistry, 17(3), pp. 1728-1734. doi:10.1039/c4gc01208a

Gillet, S., Aguedo, M., Petitjean, L., Morais, A. R. C., Da Costa Lopes, A. M., Ukasik, R. M. & Anastas, P. T. 2017. Lignin transformations for high value applications: Towards targeted modifications using green chemistry. Green Chemistry, 19(18), pp. 4200 – 4233.

Harmsen, P., Huijgen, W.J., Bermudez, L.G., & Bakker, R.R. (2010). Literature review of physical and chemical pretreatment processes for lignocellulosic biomass. [cited 17-02-2020]. Available: [https://www.semanticscholar.org/paper/Literature-review-of-physical-and-chemical-for-Harmsen-Huijgen/aaab2afd9f4da70759c4667474b292f63dd53fd8]

Hayyan, M., Hashim, M., Hayyan, A., Al-Saadi, M., Alnashef, I., Mirghani, M. & Saheed, O. 2013. Are deep eutectic solvents benign or toxic? Chemosphere, 90(7), pp. 2193-2195.

Helen (Electricity Product) [cited 24-03-2020]. Available: https://www.helen.fi/en/companies/electricity-for-companies/electricity-products-for-smes-and-associations2

Herbert, S. & Gabriele, S. 2009. A NEW GENERATION KRAFT PROCESS: Lenzinger Berichte 87 (2009) 26–37 [cited 10-06-2020]. Available: [https://www.academia.edu/28812539/A_NEW_GENERATION_KRAFT_PROCESS]

Hocking, M. B. (1997). Vanillin: Synthetic flavoring from spent sulfite liquor. Journal of Chemical Education, 74(9), 1055-1059. Retrieved from https://ezproxy.cc.lut.fi/docview/211891414?accountid=27292

Holladay, J. E., White, J. F., Bozell J. J., Johnson, D., 2007. Top Value-Added Chemicals from Biomass - Volume II, Results of Screening for Potential Candidates from Biorefinery Lignin.

Hou, X., Feng, G., Ye, M., Huang, C. & Zhang, Y. 2017. Significantly enhanced enzymatic hydrolysis of rice straw via a high-performance two-stage deep eutectic solvents synergistic pretreatment. Bioresource Technology, 238, pp. 139-146.

Hou, Q., Ju, M., Li, W., Liu, L., Chen, Y. & Yang, Q. 2017. Pretreatment of Lignocellulosic Biomass with Ionic Liquids and Ionic Liquid-Based Solvent Systems. *Molecules, 22*(3), . doi:10.3390/molecules22030490

Hou, Y., Gu, Y., Zhang, S., Yang, F., Ding, H. & Shan, Y. 2008. Novel binary eutectic mixtures based on imidazole. Journal of Molecular Liquids, 143(2-3), pp. 154-159. doi:10.1016/j.molliq.2008.07.009

Humphreys, K. & Engush, L. 1993. Project and Cost Engineers' Handbook. European Journal of Engineering Education, 18(2), p. 218. doi:10.1080/03043799308928353

HSY (Helsingin seudun ympäristöpalvelut), Water Service Price list, (2020). [cited 23-03-2020]. Available: https://julkaisu.hsy.fi/the-pricelist-and-service-fee-price-list-for-hsy-water-services-2020.html

HSY[b] (Helsingin seudun ympäristöpalvelut), Water Service Price list, (2020). [cited 23-03-2020]. Available: https://www.hsy.fi/en/residents/sorting/sorttistations/Pages/default.aspx

Isikgor, F. & Becer, C. 2015. Lignocellulosic biomass: A sustainable platform for the production of bio-based chemicals and polymers. *Polymer Chemistry, 6*(25), pp. 4497-4559. doi:10.1039/C5PY00263J

ISPT (Institute for Sustainable Process Technology) (n.d). DEEP EUTECTIC SOLVENTS, The green alternative for lignocellulose fractionation. [cited 20-01-2020]. Available: https://ispt.eu/clusters/deep-eutectic-solvents

Jain, S., Triantis, K. P. & Liu, S. 2011. Manufacturing performance measurement and target setting: A data envelopment analysis approach. *European Journal of Operational Research, 214*(3), pp. 616-626. doi:10.1016/j.ejor.2011.05.028

Jablonský, M., Škulcová, A. & Šima, J. 2019. Use of deep eutectic solvents in polymer chemistry–a review. Molecules, 24(21),. doi:10.3390/molecules24213978

Jablonský, M., Skulcova, A., Majova, V. & Sima, J. 2018. Swelling properties of pulp treated with deep eutectic solvents. Drewno, 61(202), pp. 153-164.

Jablonský, M., Škulcová, A., Kamenská, L., Vrška, M. & Šíma, J. 2015. Deep Eutectic Solvents: Fractionation of Wheat Straw. BioResources, 10(4), pp. 8039-8047.

Kalhor, P. & Ghandi, K. 2019. Deep Eutectic Solvents for Pretreatment, Extraction, and Catalysis of Biomass and Food Waste. Molecules, 24(22).

Kangas, P., Kaijaluoto, S. & Maattanen, M. 2014. Evaluation of future pulp mill concepts - Reference model of a modern Nordic kraft pulp mill. Nordic Pulp &

Paper Research Journal, 29(4), pp. 620-634. doi:10.3183/npprj-2014-29-04-p620-634

Kouisni, L., Gagne, A., Maki, K., Holt-Hindle, P. & Paleologou, M. 2016. LignoForce System for the Recovery of Lignin from Black Liquor: Feedstock Options, Odor Profile, and Product Characterization. Acs Sustainable Chemistry & Engineering, 4(10), pp. 5152-5159. doi:10.1021/acssuschemeng.6b00907

KnowPulp_Learning Environmnet for Chemicl pulping Automation, 2020. [cited 26-01-2020]. Available: http://www.knowpulp.com/www_demo_version/english/pulping/general/2_cooking/frame.htm

Lalman, J., Seth, R., Ray, S., Biswas, N., Saadat, G. B. F. 2017. Using deep eutectic solvents (DESs) to extract lignin from black liquor. [Cited 05.1.2020]. Available: https://www.aiche.org/conferences/aiche-annual-meeting/2017/proceeding/paper/597d-using-deep-eutectic-solvents-dess-extract-lignin-black-liquor.

Lan, W., Liu, C. & Sun, R. 2011. Fractionation of bagasse into cellulose, hemicelluloses, and lignin with ionic liquid treatment followed by alkaline extraction. Journal of agricultural and food chemistry, 59(16), p. 8691. doi:10.1021/jf201508g

Li, A., Hou, X., Lin, K., Zhang, X. & Fu, M. 2018. Rice straw pretreatment using deep eutectic solvents with different constituents' molar ratios: Biomass fractionation, polysaccharides enzymatic digestion and solvent reuse. Journal of Bioscience and Bioengineering, 126(3), pp. 346-354.

Li, C., Tanjore, D., He, W., Wong, J., Gardner, J., Thompson, V., . . . Singh, S. 2015. Scale-Up of Ionic Liquid-Based Fractionation of Single and Mixed Feedstocks. BioEnergy Research, 8(3), pp. 982-991. doi:10.1007/s12155-015-9587-0

Li, P., Sirviö, J. A., Asante, B. & Liimatainen, H. 2018. Recyclable deep eutectic solvent for the production of cationic nanocelluloses. *Carbohydrate Polymers, 199*, pp. 219-227. doi:10.1016/j.carbpol.2018.07.024

Liang, L., Yan, J., He, Q., Luong, T., Pray, T. R., Simmons, B. A. & Sun, N. 2019. Scale-up of biomass conversion using 1-ethyl-3-methylimidazolium acetate as the solvent. Green Energy & Environment, 4(4), pp. 432-438. doi:10.1016/j.gee.2018.07.002

Linna, M., Häkkinen, U. & Magnussen, J. 2006. Comparing hospital cost efficiency between Norway and Finland. *Health policy, 77*(3), pp. 268-278. doi:10.1016/j.healthpol.2005.07.019

Liu, J. S., Lu, L. Y., Lu, W. & Lin, B. J. 2013. Data envelopment analysis 1978–2010: A citation-based literature survey. *Omega, 41*(1), pp. 3-15. doi:10.1016/j.omega.2010.12.006

Loow, Y., Wu, T. Y., Yang, G. H., Ang, L. Y., New, E. K., Siow, L. F., . . . Teoh, W. H. 2018. Deep eutectic solvent and inorganic salt pretreatment of lignocellulosic biomass for improving xylose recovery. Bioresource Technology, 249, pp. 818-825.

Ma, C., Laaksonen, A., Liu, C., Lu, X. & Ji, X. 2018. The peculiar effect of water on ionic liquids and deep eutectic solvents. Chemical Society Reviews, 47(23), pp. 8685-8720. doi:10.1039/c8cs00325d

Ma, J., Chen, H. H., Song, L. & Li, Y. 2016. Residential Load Scheduling in Smart Grid: A Cost Efficiency Perspective. IEEE Transactions on Smart Grid, 7(2), pp. 771-784. doi:10.1109/TSG.2015.2419818

Mamilla, J. L., Novak, U., Grilc, M. & Likozar, B. 2019. Natural deep eutectic solvents (DES) for fractionation of waste lignocellulosic biomass and its cascade conversion to value-added bio-based chemicals. Biomass and Bioenergy, 120, pp. 417-425. doi:10.1016/j.biombioe.2018.12.002

Marcus, Y. k., 2019. Deep Eutectic Solvents. 1st ed. 2019. Cham: Springer International Publishing.

Menon, V. & Rao, M. 2012. Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. Progress in Energy and Combustion Science, 38(4), pp. 522-550. doi:10.1016/j.pecs.2012.02.002

Mohtar, S. S., Tengku Malim Busu, T. N. Z., Md Noor, A. M., Shaari, N. & Mat, H. 2017. An ionic liquid treatment and fractionation of cellulose, hemicellulose and lignin from oil palm empty fruit bunch. Carbohydrate Polymers, 166, pp. 291-299. doi:10.1016/j.carbpol.2017.02.102

Moya, J. A. & Pavel C. C. (2018), Energy efficiency and GHG emissions: Prospective scenarios for the pulp and paper industry, pp 8–10. [Cited 15.03.2020]. Available:[https://publications.jrc.ec.europa.eu/repository/bitstream/JRC111652/k jna29280enn_jrc111652_online_revised_by_ipo.pdf].

Mussatto, S. I. & . 2016. Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery, pp 369 – 370.

Muhammad, N., Man, Z. & Bustam Khalil, M. 2012. Ionic liquid—a future solvent for the enhanced uses of wood biomass. *European Journal of Wood and Wood Products, 70*(1), pp. 125-133. doi:10.1007/s00107-011-0526-2

Nataraja, N. R. & Johnson, A. L. 2011. Guidelines for using variable selection techniques in data envelopment analysis. European Journal of Operational Research, 215(3), pp. 662-669.

NORAM LignoForce Process a Breakthrough for Canada [cited 11-06-2020]. Available: [http://www.noram-eng.com/lignoforce-process-a-breakthrough-for-canada/]

Oleskowicz-Popiel, P., Klein-Marcuschamer, D., Simmons, B. A. & Blanch, H. W. 2014. Lignocellulosic ethanol production without enzymes--technoeconomic analysis of ionic liquid pretreatment followed by acidolysis. Bioresource technology, 158, p. 294. doi:10.1016/j.biortech.2014.02.016

Oliveira, F. S., Pereiro, A. B., Rebelo, L. P. N. & Marrucho, I. M. 2013. Deep eutectic solvents as extraction media for azeotropic mixtures. *Green Chemistry, 15*(5), pp. 1326-1330. doi:10.1039/c3gc37030e

Paiva, A., Craveiro, R., Aroso, I., Martins, M., Reis, R. & Duarte, A. 2014. Natural Deep Eutectic Solvents - Solvents for the 21st Century. Acs Sustainable Chemistry & Engineering, 2(5), pp. 1063-1071. doi:10.1021/sc500096j

Pan, M., Zhao, G., Ding, C., Wu, B., Lian, Z. & Lian, H. 2017a. Physicochemical transformation of rice straw after pretreatment with a deep eutectic solvent of choline chloride/urea. Carbohydrate Polymers, 176, pp. 307-314.

Pan, X. & Zhu, J. 2011. An update on Sulfite Pretreatment (SPORL) of lignocellulosic biomass for effective production of cellulose ethanol.

Peters, M. & Timmerhaus, K. 1991. Plant design and economics for chemical engineers. *Engineering Economist, 4*th ed, pp. 33–36.

Peters, M. S., Timmerhaus K. D., and Wrest, R. E. 2003. Plant Design and Economics for Chemical Engineers, McGraw Hill, New York, 5th edn, 2003.

Phaechamud, T., Tuntarawongsa, S. & Charoensuksai, P. 2016. Evaporation Behavior and Characterization of Eutectic Solvent and Ibuprofen Eutectic Solution. AAPS PharmSciTech, 17(5), pp. 1213-1220. doi:10.1208/s12249-015-0459-x

Prado, R., Erdocia, X. & Labidi, J. 2014. IONIC LIQUID APPLICATION FOR LIGNIN EXTRACTION AND DEPOLYMERIZATION. International Journal of Cognitive Linguistics, 13(4), pp. 263-280.

Prado, R., Erdocia, X. & Labidi, J. 2016. Study of the influence of reutilization ionic liquid on lignin extraction. Journal of Cleaner Production, 111(PA), pp. 125-132. doi:10.1016/j.jclepro.2015.04.003

Rastogi, M. & Shrivastava, S. 2017. Recent advances in second generation bioethanol production: An insight to pretreatment, saccharification and

fermentation processes. Renewable and Sustainable Energy Reviews, 80, pp. 330-340.

RENFUEL Lignin BIO Oils [cited 21-04-2020]. Available: [https://renfuel.se/preem-och-renfuel-skapar-varldens-forsta-ligninanlaggning-for-biodrivmedel/?lang=en]
[https://www.lesprom.com/en/news/Rottneros_to_build_new_lignin_plant_for_biofuels_at_its_pulp_mill_in_Vallvik_Sweden_83290/]

Rodrigues, A. E. k., Pinto, P. C. d. O. R. k., Barreiro, M. F. k., Esteves da Costa, C. A. k., Ferreira da Mota, M. I. k. & Fernandes, I. k. 2018. *An Integrated Approach for Added-Value Products from Lignocellulosic Biorefineries: Vanillin, Syringaldehyde, Polyphenols and Polyurethane.* Cham: Springer International Publishing.

Rogge, N. & De Jaeger, S. 2013. Measuring and explaining the cost efficiency of municipal solid waste collection and processing services. Omega, 41(4), pp. 653-664.

Sarmad, S., Xie, Y., Mikkola, J. & Ji, X. 2016. Screening of deep eutectic solvents (DESs) as green CO_2 sorbents: From solubility to viscosity. *New Journal of Chemistry, 41*(1), pp. 290-301. doi:10.1039/c6nj03140d

Satlewal, A., Agrawal, R., Bhagia, S., Sangoro, J. & Ragauskas, A. J. 2018. Natural deep eutectic solvents for lignocellulosic biomass pretreatment: Recent developments, challenges and novel opportunities. Biotechnology Advances, 36(8), pp. 2032-2050. doi: 10.1016/j.biotechadv.2018.08.009

SCITECH EUROPA (2019). Paving the way for green chemistry: the role of deep eutectic solvents [cited 24-01-2020]. Available: https://www.scitecheuropa.eu/deep-eutectic-solvents/91989/

Schuur, B., Brouwer, T., Smink, D. & Sprakel, L. M. 2019. Green solvents for sustainable separation processes. *Current Opinion in Green and Sustainable Chemistry, 18*, pp. 57-65. doi:10.1016/j.cogsc.2018.12.009

Singh, S., Cheng, G., Sathitsuksanoh, N., Wu, D., Varanasi, P., George, A., . . . Simmons, B. 2015. Comparison of different biomass pretreatment techniques and their impact on chemistry and structure. Frontiers in Energy Research, 2.

Sirviö, J. A., Visanko, M., Liimatainen, H. 2015. Deep eutectic solvent system based on choline chloride-urea as a pre-treatment for nanofibrillation of wood cellulose. Green Chemistry, 17(6), pp. 3401-3406. doi:10.1039/c5gc00398a

Sirviö, J. A., Visanko, M., Liimatainen, H. 2016. Acidic Deep Eutectic Solvents As Hydrolytic Media for Cellulose Nanocrystal Production. *Biomacromolecules, 17*(9), p. 3025. doi:10.1021/acs.biomac.6b00910

Smink, D., Juan, A., Schuur, B. & Kersten, S. 2019. Understanding the Role of Choline Chloride in Deep Eutectic Solvents Used for Biomass Delignification. *Industrial & Engineering Chemistry Research, 58*(36), pp. 16348-16357. doi:10.1021/acs.iecr.9b03588

Smith, E., Abbott, A. & Ryder, K. 2014. Deep Eutectic Solvents (DESs) and Their Applications. Chemical Reviews, 114(21), pp. 11060-11082.

SpringerLink (Online service), Akpan, E. I. t. & Adeosun, S. O. t. 2019. Sustainable Lignin for Carbon Fibers: Principles, Techniques, and Applications. 1st ed. 2019. Cham: Springer International Publishing. Pp. 403-420

Stora Enso annual capacity [cited 21-04-2020]. Available: [https://www.storaenso.com/en/about-stora-enso/stora-enso-locations/sunila-mill]

Škulcová, A., Haščičova, Z., Hrdlička, L., Sima, J. & Jablonsky, M. 2018. Green solvents based on choline chloride for the extraction of spruce bark (Picea abies). Cellulose Chemistry and Technology, 52(3-4), pp. 171-179.

Škulcová, A., Majová, V., Šima, J. & Jablonskỳ, M. 2017. Mechanical properties of pulp delignified by deep eutectic solvents. BioResources, 12(4), pp. 7479-7486.

Tan, S. S. Y., Macfarlane, D. R., Upfal, J., Edye, L. A., Doherty, W. O. S., Patti, A. F., . . . Scott, J. L. 2009. Extraction of lignin from lignocellulose at atmospheric

pressure using alkylbenzenesulfonate ionic liquid. *Green Chemistry, 11*(3), pp. 339-345. doi:10.1039/b815310h

Tan, Y. T., Chua, A. S. M. & Ngoh, G. C. 2020. Deep eutectic solvent for lignocellulosic biomass fractionation and the subsequent conversion to bio-based products – A review. Bioresource Technology, 297, . doi:10.1016/j.biortech.2019.122522

Tang, X., Zuo, M., Li, Z., Liu, H., Xiong, C., Zeng, X., . . . Lin, L. 2017. Green Processing of Lignocellulosic Biomass and Its Derivatives in Deep Eutectic Solvents. Chemsuschem, 10(13), pp. 2696-2706. doi:10.1002/cssc.201700457

Tomé, L., Baião, V., da Silva, W. & Brett, C. 2018. Deep eutectic solvents for the production and application of new materials. Applied Materials Today, 10, pp. 30-50. doi:10.1016/j.apmt.2017.11.005

UPM, shop. upmbiochemical [cited 21-04-2020]. Available: [https://shop.upmbiochemicals.com/categories/13ee4132-9b84-4e7c-8547-53c20a3ea731]

UPM Annual Report 2019. [cited 27-05-2020]. Available: https://www.upm.com/siteassets/asset/investors/2019/upm-annual-report-2019.pdf

UPM Financial Results 2019. [cited 27-05-2020]. Available: https://www.upm.com/siteassets/asset/investors/2019/upm-results-2019-en.pdf

Valmet forward technologies, service and Automation 2020 [cited 14-04-2020]. Available:[https://www.valmet.com/media/news/press-releases/2020/valmet-to-deliver-key-pulp-mill-technology-and-automation-for-lenzings-and-duratexs-joint-pulp-mill-project-in-brazil/]

Valmet.com LignoBoost process [cited 11-06-2020]. Available: [https://www.valmet.com/pulp/other-value-adding-processes/lignin-separation/]

Van Osch, D. J. G. P., Kollau, L. J. B. M., Van Den Bruinhorst, A., Asikainen, S., Rocha, M. A. A. & Kroon, M. C. 2017. Ionic liquids and deep eutectic solvents for

lignocellulosic biomass fractionation. Physical Chemistry Chemical Physics, 19(4), pp. 2636-2665. doi:10.1039/c6cp07499e

Veronika, F., 2015. Properties and Applications of Deep Eutectic Solvents and Low-Melting Mixtures Available: [https://epub.uni-regensburg.de/31832/1/Doktorarbeit_Veronika_Fischer_04_05_15.pdf]

Virkola, N., Pusa, R. & Kettunen, J. 1981. NEUTRAL SULFITE AQ PULPING AS AN ALTERNATIVE TO KRAFT PULPING. Tappi, 64(5), pp. 103-107.

VWR Chemical catalogue 2017-2019. [cited 23-03-2020]. Available: https://fi.cmd.vwr.com/bin/public/idoccdownload/10139416/VWR%20-%20Chemical%20Catalogue_NORDIC%20Pdf?s=1074983:1&sort=4&iframe=1&hide_header=1&type=10001&category=10038&manufacturer=10019&act=search&show=0002

VWR[b] Chemical catalogue 2017-2019. [cited 26-03-2020]. Available: https://fi.vwr.com/store/cart/cart.jsp

VTT research center [cited 26-03-2020]. Available: [https://www.vttresearch.com/sites/default/files/julkaisut/muut/2013/VTT-R-07962-13.pdf] pp. 21–23

Wagle, D., Zhao, H. & Baker, G. 2014. Deep Eutectic Solvents: Sustainable Media for Nanoscale and Functional Materials. Accounts Of Chemical Research, 47(8), pp. 2299-2308.

Xie, Y., Björkmalm, J., Ma, C., Willquist, K., Yngvesson, J., Wallberg, O. & Ji, X. 2018. Techno-economic evaluation of biogas upgrading using ionic liquids in comparison with industrially used technology in Scandinavian anaerobic digestion plants. Applied Energy, 227, pp. 742-750. doi:10.1016/j.apenergy.2017.07.067

Xu, P., Zheng, G., Zong, M., Li, N. & Lou, W. 2017. Recent progress on deep eutectic solvents in biocatalysis. Bioresources and Bioprocessing, 4(1), pp. 1-18.

Yan, P., Xu, Z., Zhang, C., Liu, X., Xu, W. & Zhang, Z. C. 2015. Fractionation of lignin from eucalyptus bark using amine-sulfonate functionalized ionic liquids. Green Chemistry, 17(11), pp. 4913-4920. doi:10.1039/c5gc01035g

Yiin, C. L., Quitain, A. T., Yusup, S., Sasaki, M., Uemura, Y. & Kida, T. 2016. Characterization of natural low transition temperature mixtures (LTTMs): Green solvents for biomass delignification. Bioresource Technology, 199, pp. 258-264. doi: 10.1016/j.biortech.2015.07.103

Yu, Q., Zhang, A., Wang, W., Chen, L., Bai, R., Zhuang, X., . . . Yuan, Z. 2018. Deep eutectic solvents from hemicellulose-derived acids for the cellulosic ethanol refining of Akebia' herbal residues. Bioresource Technology, 247, pp. 705-710.

Zhang, C., Xia, S. & Ma, P. 2016. Facile pretreatment of lignocellulosic biomass using deep eutectic solvents. *Bioresource Technology, 219*, pp. 1-5.

Zhang, Q., De Oliveira Vigier, K., Royer, S. & Jrme, F. 2012. Deep eutectic solvents: Syntheses, properties and applications. Chemical Society Reviews, 41(21), pp. 7108-7146. doi:10.1039/c2cs35178a

Zhang, W., Cheng, S., Zhai, X., Sun, J., Hu, X., Pei, H., & Chen, G. (2020). Green and Efficient Extraction of Polysaccharides From Poria cocos F.A. Wolf by Deep Eutectic Solvent. Natural Product Communications. https://doi.org/10.1177/1934578X19900708

Zhang, Y. P., Ding, S., Mielenz, J. R., Cui, J., Elander, R. T., Laser, M., . . . Lynd, L. R. 2007. Fractionating recalcitrant lignocellulose at modest reaction conditions. Biotechnology and Bioengineering, 97(2), pp. 214-223. doi:10.1002/bit.21386

Zhu, J., Pan, X., Wang, G. & Gleisner, R. 2009. Sulfite pretreatment (SPORL) for robust enzymatic saccharification of spruce and red pine. Bioresource Technology, 100(8), pp. 2411-2418. doi:10.1016/j.biortech.2008.10.057

9 APPENDICES

Table A 9—1. Key process parameters data for Kraft pulp from Finnish pulp industry based on the pulp wood (Kangas et al. 2014)

Key process	Parameter	Data	Unit
Pulp	Capacity	620000	adt /y
	Type of pulp	Market pulp; integrated	
	Fibre line	Single line operation	
Digester (continuous)	Digester yield	48	%
	Cooking kappa	28	
	Temperature (Pretreatment)	165	ºC
	Alkali charge (NAOH)	20	%
	Alkali charge	4	t/ adt
	Active alkali concentration (NaOH)	145	g/L
	Sulfidity	42	%
Oxygen delignification	Alkali charge (NaOH)	18	kg/ adt
	Oxygen charge (O_2)	15	kg/ adt
	Kappa after O2-delignification	14	
	Temperature	85-95	ºC
	Dilution factor (unbleached)	2	m^3/ adt
Bleaching type (ECF)	Temperature	70-80	ºC
	ClO_2	47	kg a-Cl/ adt
	NaOH charge	11	kg/ adt
	H_2O_2 charge	7	kg/ adt
	Water consumption in bleaching	14	m^3/ adt
Evaporation	Evaporation (of solids dry)	75-85	%
	Tail-oil recovery	42	kg/ adt
Recovery boiler	Recovery boiler	3600	t ds/day
	Steam temperature	505	ºC
	Steam pressure	10.2	MPa
	Heating value in black liquor	14	MJ/kg ds
	Air Combustion pre-heating	190	ºC
	Feed water pre-heating	150	ºC
	Bark	Gasification (lime kiln)	

Re-causticizing and lime kiln	Re-causticizing and lime kiln		m³/day
	Causticizing efficiency	80	%
	Lime kiln fuel	Gasified bark	
Turbine	Pressure levels	0.45–10.2	MPa
	Condensing turbine		yes
Energy balance	Steam generation	19	GJ/ adt
	Steam consumption	12	GJ/ adt
	Electricity consumption	610	kWh/ adt
	Electricity production	1000	kWh/ adt

Table A 9—2. The breakdown of share cost investment in Kraft pulp processing, the original data retrieved from Kangas et al. (2014).

Processing stages	Shares of investments cost (%)
Wood handling	7
Delignification	15
Bleaching	7
Pulp drying processing	16
Evaporation stage	7
Recovery boiler	22
Re-causticizing and lime kiln	7
Turbine plant	8
Water treatment section	4
Infrastructure	9

Table A 9—3. Wood price and Unit consumption (Price taken from FOEX)

Type	Quantity (consumption) m³/ adt	Price (€/m³)
Pulpwood	5.7	16.96

Table A 9—4. The breakdown of Electricity consumption in Kraft pulp processing data retrieved from (Alex & Simons) report on energy used in Kraft pulp industry.

Area	Quantity (consumption) kWh/ adt
Wood room	65
Pulp mill	96
Pulp dryer	110
Recovery boiler	74
Water treatment	42
Effluent treatment	40
Cleaning and chemical preparation	137
Bleach plant	14
Boiler power	41
Evaporation	79
Re-causticizing	14
Other services	14
Total	726

Table A 9—5. The Chemical prices and the volume consumption during the Kraft pulp process.

The Chemical prices and unit consumptions in fibre line processing		
Type	Quantity Consumption (kg/adt)	Price (€/kg)
ClO_2*	39	1.3
NaOH*	19.8	0.6
O_2***	29.3	
$MgSO_4$*	3.8	0.5
H_2O_2*	7.4	0.3
The Chemical prices and unit consumptions in recovery processing		
Type	Quantity Consumption (kg/ adt)	Price (€/kg)
NaOH*	9.2	0.6
CaO*	5.3	0.15
H_2SO_4*	4.9	0.19

*Price obtained from Alibaba.com

Table A 9—6. Water and dispose prices with amount consumed during the processing

Type	Quantity (Consumption) (m^3/ adt)	Price ($€/m^3$)
Cooling water*	63 (m^3/ adt	1.19 ($€/m^3$)
Process water**	16.4 (m^3/ adt	1.25 ($€/m^3$)
Boiler water**	0.5 (m^3/ adt	1.5 ($€/m^3$)
Wastewater *	17.7 (m^3/ adt)	1.41 ($€/m^3$)
Ash waste dispose***	13.6 (kg/ adt)	5 ($€$/kg)
Dregs waste dispose***	1.7 (kg/ adt)	5 ($€$/kg)

*The price based on current water price from HSY 2020
**The price based on Kangas et al. (2014) and current analysis
*** The price based on current waste disposal price from HSY[b] 2020

Table A 9—7. The electricity price and consumption in Kraft pulp process (price take from Helen.fi)

Type	Quantity (consumption) kWh/ adt	Price ($€$/kWh)
Electricity consumption	726	0.10419

Table A 9—8. Production cost analysis for Kraft pulping processing

Material	$€$/ adt
Pulpwood	96.67
Chemicals consumption	1489.19
Utilities	96.22
Waste	101.46
Maintenance (4% of Inv. Cost)	48
Depreciation (7.5% rate at 15 years paying back period)	136
Other costs (Fixed: assumption)	15
Logistics (fixed: assumption)	30
Labour cost (60 operators at 80 k$€$/year)	7.74

Table A 9—9. Cost and Consumption analysis for Ionic liquid Processing

Type	Quantity (consumption) kg/day	Price
1-ETHYL-3-METHYLIMIDAZOLIUM ACETATE, 97%	17kg/day**	10000* (€/kg)
HCl	2736 (1M) kg/day**	0.20 (€/kg) *
Water	3361345 (m^3)	1.19 (€/m^3)

*Price obtained online
** Oleskowicz-Popiel et al. (2014)

Table A 9—10. Cost and Consumption analysis for the DES fractionating Process

Type	Quantity (consumption) m^3/ adt	Price
Pulpwood	5.7	16.96 (€/m^3)
Chemical		
DES*	100 MT/day	
ChCl	10 MT/day	2 €/kg
LA	90 MT/day	1.2 €/kg
Acetic acid		0.5 €/kg
Ethanol		0.8 €/Kg
Sodium chlorite ($NaClO_2$)		0.5 €/kg
Potassium hydroxide (KOH)		0.19 €/kg
Malic acid		1.8 €/kg
Phenol (99 % purity)		0.9 €/kg
Oxalic acid (99.6% purity)		0.45 €/kg

Price obtained online (Alibaba.com)
*Based on the LUT experimental research

Table A 9—11. Breakdown of operating and maintenance cost for IL process based on IL 1-ETHYL-3-METHYLIMIDAZOLIUM ACETATE (Benavides et al. 2013, Chen et al. 2014, Xie et al. 2018).

Material	Description	M€/y
Pulpwood		23
Ionic Liquid		53
Chemicals (other)		2
Other costs		9
Maintenance (Mc)	3% of TFCI	2
Labour cost (LC)	100 employees with 60000 €/y	6
Supervisors (S)	15% of LC	1
Operating supplies cost	15% of MC	0.3
Laboratory cost	15 % of LC	1
Overhead cost	15% on (MC+LC+S)	5
*Depreciation	10% of TFCI	7
Utilities	3361345 m^3**	4
Electricity consumption	550000 kW/y*	0.04
Local taxes	2% on TFCI	1.4
Insurance cost	1% on TFCI	0.7
Admin Cost (AC)	20% on (LC)	1.2
Advertisement	2 % of (OC +MC)	2
Research Cost	2% of (OC+MC)	2

*Assumption based on Chen et al. 2014 with few modification
** Chen et al. 2014 updated to current value.

Table A 9—12. Breakdown of operating and maintenance cost for DES process fractionation based on LA:ChCl (9:1).

Material	Description	M€/y
Pulpwood		23
DES cost (LA)		40
Chemicals (other)		2
Other costs		7
Maintenance (Mc)	3% of TFCI	2
Labour cost (LC)	100 employees with 60000 €/y	6
Supervisors (S)	15% of LC	1
Operating supplies cost	15% of MC	0.3
Laboratory cost	15 % of LC	1
Overhead cost	15% on (MC+LC+S)	5
*Depreciation	10% of TFCI	7
Utilities	2000000 m^3	2
Electricity consumption	440000 kW/y	0.04
Local taxes	2% on TFCI	1.4
Insurance cost	1% on TFCI	0.7
Admin Cost (AC)	20% on (LC)	1.2
Advertisement	2 % of (OC +MC)	2
Research Cost	2% of (OC+MC)	2