The potential of lignin as a maritime biofuel

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ABSTRACT

In the 1940s, efforts towards lignin valorisation were triggered by high oil prices, but today, the motives are much more varied. The movement towards a greener future to combat climate change and the expected introduction of an emission-based fee have all surged interest towards renewable fuels – a topic that has been at the core of this entire study.

This research project delves into different pathways that currently exist of utilising lignin as a maritime biofuel. In particular, lignin extracted from the Kraft pulping process, with a gross heating value measured at 27 MJ kg^{-1} and a potential worldwide production capacity estimated at 78 million tonnes per year, is considered to be the source that could make the biggest difference on the fuel market as of now. The challenge lies in both the isolation of the lignin from its feedstock and producing a viable fuel from it – one that can be cost-competitive with the marine fossil fuels currently in use.

Several experiments (e.g., bomb calorimetry and elemental analysis) were carried out at a laboratory of Åbo Akademi University, and various approaches to create a lignin fuel were trialed in accordance with the equipment available. The results provided a ground for parameters used in a sensitivity analysis, where variables such as production costs and raw material prices were evaluated against a possible introduction of the EU emissions trading system, or an equivalent, also in the marine sector. While the production methods found need to be further assessed to provide a deeper understanding of the chemistry and the techno-economics behind them, the results obtained indicate that the cost of an emissions allowance unit would have to be 160 to 190 euros per CO_2 equivalent for a lignin-methanol fuel produced to be directly competitive with the widely used marine fuel IFO 380.

Keywords: lignin, biofuels, Kraft process, marine diesel engine

ABBREVATIONS

admt	Air-dried metric ton
ECA	Emissions Control Area
EJ	Exajoule, 10^{18} Joule, unit of energy
ETS	Emissions Trading System
EUA	EU Allowance, emission credits used in the EU Emissions Trading System
FAME	Fatty acid methyl esters
HFO	Heavy fuel oil
HHV	Higher heating value
HLB	Hydrophilic-lipophilic balance
HWE	Hot water extraction
IFO	Intermediate fuel oil
IMO	International Maritime Organization
ISO	International Organization of Standardization
kDa	Kilodalton, unit of mass
LHV	Lower heating value
LNG	Liquified natural gas
LSMGO	Low-sulphur marine gas oil
MDO	Marine diesel oil
MGO	Marine gas oil
MSDS	Material safety data sheet
M_w	Molecular weight
PDI	Polydispersity index
RED	Relative energy difference
ULSFO	Ultra-low-sulphur fuel oil
VLSFO	Very-low-sulphur fuel oil

Types of technical lignins

AFEX	Ammonia fibre expansion lignin
HL	Hydrolysis lignin
KL	Kraft lignin
LS	Lignosulphonates
OL	Organosolv lignin
SEL	Steam-explosion lignin
SL	Soda lignin

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1 INTRODUCTION

Due to the ongoing changes in our climate, largely caused by humans, more and more actions are being taken to prevent the constantly increasing temperatures on our planet, referred to as *global warming*. A large part of this change can be traced back to the greenhouse gas (GHG) emissions, which end up in the atmosphere, capturing a significant portion of the heat that is radiated off the earth. Since an extension of the Kyoto Protocol failed to receive enough support by the state parties, the Paris Agreement is now the primary tool of the United Nations in this mission. The 196 parties who have signed it are legally bound to transform their economic and social behaviour in order to limit the global warming to "well below 2, preferably to 1.5 degrees Celsius" compared to pre-industrial levels (United Nations Framework Convention on Climate Change, 2015).

In support of this mission, the International Maritime Organization, IMO, is pushing for a reduction in emissions on the seas. In their *MARPOL Annex VI*, they are limiting emissions of SO_x, NO_x and particulate matter on a global level, and in certain areas (called Emission Control Areas), particularly strict regulations are in place. However, these actions by the IMO are not putting enough emphasis on the actual maritime GHG emissions, mainly CO_2 emissions, which for the year 2012 were estimated at 938 million tonnes in the *3rd IMO GHG study*, with a potential growth of 50 % to 250 % before year 2050 (International Maritime Organization, 2015). This has triggered the EU to take actions, and many expect that an emissions trading system, like the ETS governed by the EU, is on the cards. Many shipowners and associated parties, such as Elomatic Oy and Auramarine Oy, are now looking for ways to mitigate this possible blow to the fuel economics, mainly by replacing parts of or all the fossil fuels commonly used to run ships. This brings us onto the use of biomass as a fuel, which is considered to be carbon neutral by the European Commission (2003/87/EC).

While there are many different methods to utilise the large amounts of energy stored in biomass, deriving it into a viable product for the shipping industry (preferably a liquid fuel) comes at a cost which is easily outcompeted by the relatively low-priced fossil fuels. This is what brings the interest onto lignin, which is one of the world's most abundant polymers found in all lignocellulosic plants. The lignin content of lignocellulosic biomass amounts to up to 30 % of the mass, and in many different processes this fraction is considered a waste product. Especially in the Kraft pulping process, most of the lignin is currently being combusted in an on-site boiler to generate energy and electricity for the mill's own demands. In most cases, there is an excess of lignin, meaning energy can be sold onwards – and occasionally, the lignin surplus even causes a bottleneck for the entire mill.

Carbon neutral energy can be generated from a wide range of sources ashore, such as nuclear reactions, as well as water or solar energy, different limitations are in place on ships. In the marine sector, any space needed for both equipment and fuel storage reduce the valuable cargo capacity, which makes the energy density of the fuels a top priority, second only to the aviation sector. The high heating value of lignin, together with the possibility to increase it even further through deoxygenation processes, makes a lignin-based fuel a good alternative to the energy-rich fossil fuels. Because of this, utilisation of Kraft lignin has been the focal point of this thesis, with an estimated annual potential of 78 million tonnes (Dessbesell et al., 2020), equalling over 2 EJ of energy; about a fifth of the fossil fuel demand of the shipping industry.

In addition to Kraft lignin, other types of technical lignin have also been investigated, with their fuel-related properties being a prime focus. Based on previous literature and empirical research, this work outlines some of the different technologies capable of producing a liquid marine fuel from lignin. The most promising candidates have been further investigated, and their potential as a competitive fuel alternative evaluated based on a number of techno-economical scenarios.

2 BACKGROUND

The purpose of this chapter is to give the reader an insight into several possible lignin sources, some attributes specific to each lignin type, and finally a look into the current fuel situation in the maritime sector. Included are by no means all details and all methods, but a mere overview of characteristics relevant to this study.

2.1 Pulping processes

Ever since papermaking was first introduced over 2.000 years ago in China, many different raw materials and methods of extracting their fibres to produce paper pulp have been used. At the beginning, inner bark fibres of mulberry and other plants, called *bast fibres* were used. In the 14th century, when papermaking had expanded in Europe, hemp, linen, and later cotton were the primary source of pulp, and it was not until 1844 that wood became an option. Behind this was the development of the *Fourdrinier machine* which enabled continuous production of paper on a roll, together with the first process for making modern paper out of wood, developed by Charles Fenerty and Friedrich Gottlob Keller (Clapperton, 1967).

Today, the majority of the pulping industry is using wood-based raw materials. The main reason is the massive supply of wood in the forests, with the global forest area estimated to be 4,06 billion ha in 2020, equal to 31 percent of the total land area. Despite a net deforestation area of 178 million ha in the last 30 years, the reduction has firmly declined, with only 10 million ha of forest area being eliminated in the years 2015 to 2020. While the rest of the world has started counteracting the negative development, South America and Africa have now become the main culprits of the global deforestation (FAO, 2020). The solution is of course simple, with more and more companies, forest owners, as well as governments, setting strict plantation quotas – meaning for every tree that is cut down, at least one new will be planted in its place. Not only does this ensure a future supply of wood, but in a world battling with continuously increasing carbon dioxide levels in the atmosphere causing global warming – every tree helps by using carbon dioxide in its growth process called the *photosynthesis*.

The tree types used in the pulp-making process is naturally a geographical matter, where the options are limited to which trees can be cultivated in a certain climate zone. The option of importing or transporting the raw materials to the pulp mill is there, but in a competitive industry like pulping and papermaking, it is not feasible to transport wood lengthy distances across the world.

Out of the different wood types, coniferous trees (softwood) are usually preferred in the paper-making process due to their longer cellulose fibres, which improve both the quality and durability of the paper. The ratio between cellulose, lignin, and hemicellulose of the feedstock determines the different yields of the process; a higher cellulose content improves the yield of chemical pulp, a larger fraction of lignin raises the heating value of the spent cooking liquor, and the hemicellulose and other extractives determine the yield of by-products, such as rosin, tall oil and turpentine. On average, hardwoods have a cellulose content of 45 % compared to 42 % in softwoods, a lignin content of 20 % compared to 28 %, and hemicelluloses taking up 30 % versus 27 % in softwoods (Young, Kundrot & Tillman, 2003).

2.1.1 Kraft process

The sulphate process, mainly called the *Kraft process* or *Kraft pulping*, stems from the German word for strength – 'kraft'. When invented by Carl F. Dahl in 1879, the paper produced with this process was considered exceptionally strong compared to the product of other papermaking processes at the time.

In Kraft pulping, debarked wood is first chopped into chips of the size 12–25 mm (length) x 2–10 mm (thickness). Before entering the digesters, the wood chips normally enter a pre-steaming step, where a part of the air trapped in cavities of the wood is expanded and expelled. The chips are then impregnated with the so-called *white liquor* at a temperature below 100 °C to ensure homogenous cooking, and then transferred into pressurised digesters.

The white liquor is a strongly alkaline solution, with a pH around 13–14 according to Biermann (1996). Predominantly sodium hydroxide (NaOH), commonly referred to as *lye*, and sodium sulphide (Na_2S) are the main ingredients of the cooking liquor. Other chemicals that can be found, which are largely considered inert in the process are: sodium sulphate, sodium and calcium carbonates, sodium chloride, sodium thiosulphate and other inorganic salts accumulated from various reactions. The main function of the cooking liquor is to break down ether bonds between lignin and cellulose, which is a slow process taking place at a temperature of 170–176 °C for at least 1½ h (Murzin, 2015). During the process, also the hemicellulose (i.e., polysaccharides) degrades and dissolves in the cooking liquid. After the cooking, pulp can be filtered out, washed, and further processed depending on the desired paper quality. The focus lies mainly on removing remaining lignin fractions from the brown-coloured pulp, most commonly through bleaching with the Elemental Chlorine-Free (ECF) technique. The pulp is then either sold as an intermediate good, or in most cases used to produce paper products by feeding it into a paper machine, which presses and dries the water and cooking liquor from the pulp. However, in this study it is the leftover cooking liquor containing lignin, now called *black liquor*, which is of interest.

What can be pinpointed as the sole reason why Kraft pulping has become the paramount process in the pulping industry, was when the American industrial manufacturer company Babcock & Wilcox (now: Babcock & Wilcox Enterprises Inc.) built the first recovery boiler in 1929. Continuous development and optimisation of the process parameters have resulted in a procedure where most of the chemicals can be reused, while simultaneously supplying the mill with all the energy it consumes, plus excess energy that can be used in a turbine or to distribute process steam. The overall process can be seen in Figure 2.1.

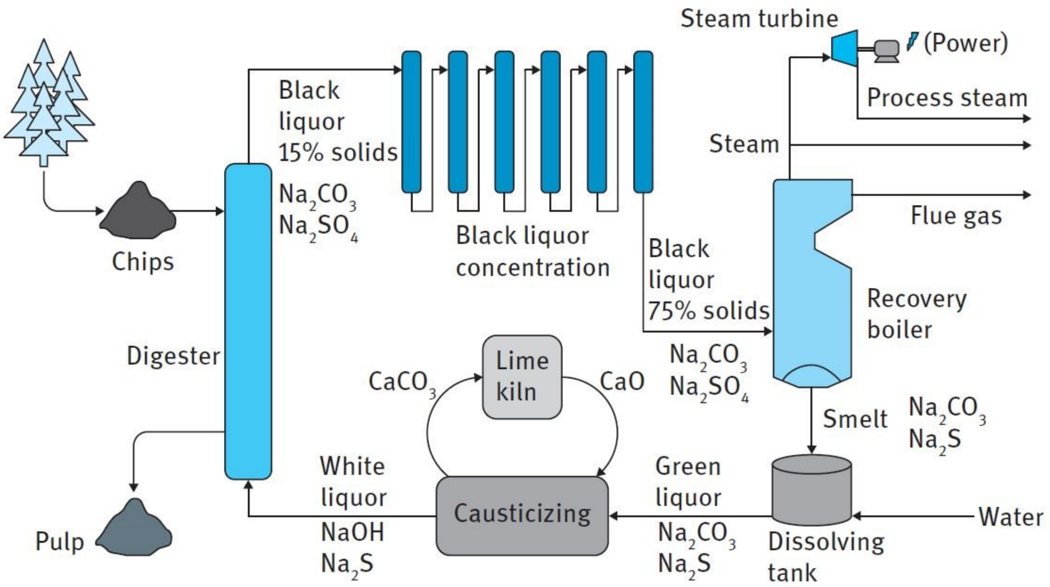


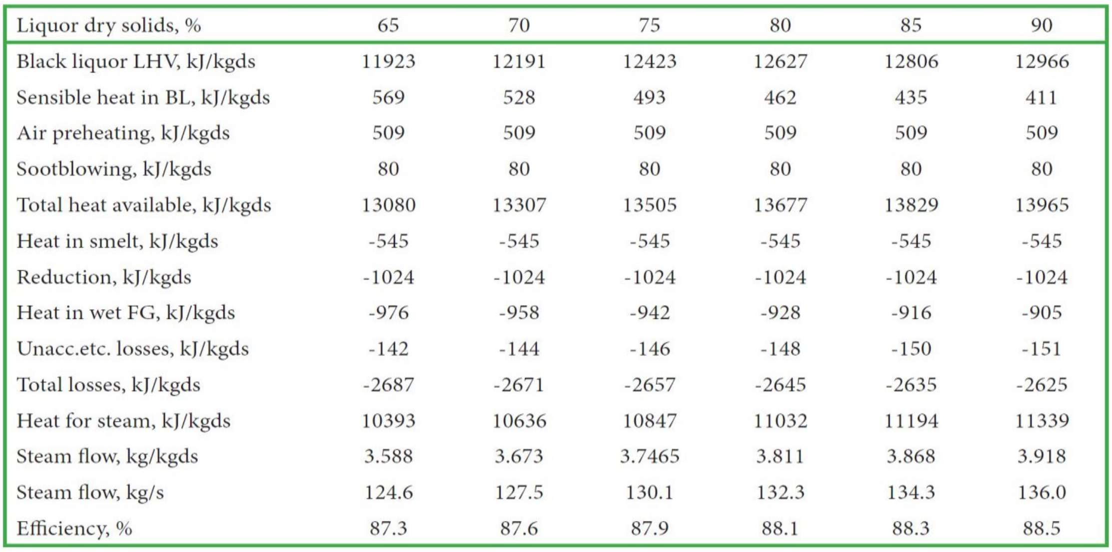
Figure 2.1. *Simplified overview of the Kraft process and the circulation of chemicals (Murzin, 2015).*

The recovery boiler

The black liquor coming from the digesters has a dry solids content of about 15 %, which means liquid needs to be evaporated in order to increase the heating value before the combustion in the recovery boiler. Several by-products can be obtained from the *multiple-effect evaporator*, which consists of a series of evaporators using hot steam from the recovery boiler. At a solids concentration of 20–30 %, rosin soap can be skimmed off and further processed to produce tall oil. Up to 30–50 kg of tall oil can be collected per ton of pulp produced, which not only creates a side-stream of income, but also enhances the subsequent evaporation.

When the levels of dry substance exceed 65 % the liquor is called *strong black liquor*, or 'heavy' black liquor. As predicted, the lower heating value (LHV) increases with the ratio of dry solids going up from 65 % to 90 %, which can be seen in the energy balance of Vakkilainen's (2005) example boiler seen in Table 2.1. The data presented in this table is for a recovery boiler with a capacity to handle 3.000 tonnes of dry substance per day. More surprising is perhaps the fact that the boiler net efficiency only improves by 1.4 % when burning black liquor with a 10 % moisture content, compared to 35 %. This is mainly due to the increase in steam flow required to evaporate the remaining liquid in the black liquor and higher pressure losses in the superheater. While the efficiency might increase, there are also limitations to how concentrated the liquor can be. Its viscosity has to be low enough for it to flow through pipes and eventually be sprayed into the boiler, and furthermore, issues with precipitation of solid particles might occur if too much moisture is removed.

Table 2.1. *Energy balance for an example boiler (Vakkilainen, 2005).*



Liquor dry solids, %	65	70	75	80	85	90
Black liquor LHV, kJ/kgds	11923	12191	12423	12627	12806	12966
Sensible heat in BL, kJ/kgds	569	528	493	462	435	411
Air preheating, kJ/kgds	509	509	509	509	509	509
Sootblowing, kJ/kgds	80	80	80	80	80	80
Total heat available, kJ/kgds	13080	13307	13505	13677	13829	13965
Heat in smelt, kJ/kgds	-545	-545	-545	-545	-545	-545
Reduction, kJ/kgds	-1024	-1024	-1024	-1024	-1024	-1024
Heat in wet FG, kJ/kgds	-976	-958	-942	-928	-916	-905
Unacc.etc. losses, kJ/kgds	-142	-144	-146	-148	-150	-151
Total losses, kJ/kgds	-2687	-2671	-2657	-2645	-2635	-2625
Heat for steam, kJ/kgds	10393	10636	10847	11032	11194	11339
Steam flow, kg/kgds	3.588	3.673	3.7465	3.811	3.868	3.918
Steam flow, kg/s	124.6	127.5	130.1	132.3	134.3	136.0
Efficiency, %	87.3	87.6	87.9	88.1	88.3	88.5

In the boiler, combustion of mainly lignin and hemicellulose is what releases energy, but there are also a wide range of chemical reactions taking place. The chemical recovery process focuses on recovering the sodium in the black liquor, amounting to around 20 percent of the liquor that is fed into the boiler. The conditions in the furnace, especially the temperature, can be controlled and optimised to facilitate the reduction of sodium sulphate with char through reactions 2-1 and 2-2 (Vakkilainen, 2005).

$$\mathrm{Na_2SO_4} + 2\mathrm{C} \rightarrow \mathrm{Na_2S} + 2\mathrm{CO_2} \tag{2-1}$$

$$\mathrm{Na_2SO_4} + 4\mathrm{C} \rightarrow \mathrm{Na_2S} + 4\mathrm{CO} \tag{2-2}$$

Causticisation

The *smelt*, i.e., the mixture of inorganic salts; primarily sodium carbonate and the sodium sulphide produced, is removed from the bottom of the furnace. It is dissolved in process water, and the solution, now called *green liquor*, enters the causticisation process. Here, sodium hydroxide is formed when the sodium carbonate reacts with added calcium hydroxide (2-3), and the calcium carbonate produced is precipitated from the solution, leaving behind the white liquor needed in the pulping process.

$$\mathrm{Na_2CO_3} + \mathrm{Ca(OH)_2} \rightleftharpoons 2\mathrm{NaOH} + \mathrm{CaCO_3} \tag{2-3}$$

To achieve a closed chemical cycle, the calcium carbonate is heated in a lime kiln where carbon dioxide is removed (2-4), and the remaining calcium oxide can be reused in reaction 2-3 by adding water (2-5).

$$\mathrm{CaCO_3} \rightarrow \mathrm{CaO} + \mathrm{CO_2} \tag{2-4}$$

$$\mathrm{CaO} + \mathrm{H_2O} \rightarrow \mathrm{Ca(OH)_2} \tag{2-5}$$

Summary

There are several reasons why the Kraft process is the most common pulping method in the world, with around 90 % of all pulp mills using this technology (Azadi et al., 2013). According to Tran & Vakkilainen (2008), some of the reasons for this are:

i) A wide range of raw materials (including most species of hardwood and softwood) can be utilised in the pulping process, which makes the Kraft process an attractive option almost anywhere in the world.

ii) The resistance to tearing and the high tensile strength of Kraft paper are some of the properties making it superior to other paper qualities, partly due to the high sulphidity maintained in the paper.

iii) The favourable economics behind the recoverability of about 97 % of the chemicals used in the process and the self-sufficiency when it comes to energy usage is another monumental advantage.

Due to the considerably large investments needed for evaporators, the recovery boiler and the lime kiln, as well as contrasting market prices for energy, various alternatives have been investigated. Alternative methods for recovering the process chemicals, such as *direct alkali recovery* and *autocausticisation* have been proposed, but most of them have been abandoned due to economic reasons (Vakkilainen, 2005). In some places with access to an external source of low-priced fuel, like Russian natural gas, the combustion of the black liquor, or parts of it, are unlikely to be financially viable. In these cases, as well as instances where the calorific capacity of the recovery boilers has been exceeded, precipitation of lignin from the excess black liquor is an option. Between 5 to 20 percent of the total lignin could be extracted without affecting the mill's own energy demand according to VanCaeseele (2018). A more conservative estimate is given by Berlin & Balakshin (2014), where they state that about 6–7 % of the spent liquor "could be used for lignin extraction". To exemplify this, they have used Domtar's targeted rate of over 27.000 tons of lignin annually produced at their new lignin separation plant in Plymouth, US (Domtar, 2013).

Some extracting processes and ways to utilise this technical Kraft lignin (KL), as well as its properties, will be further explained in Chapter 2.2.

2.1.2 Sulphite process

The sulphite pulping process has got its name from the various sulphite ($SO^{2-}{}_3$) or bisulphite ($HSO^{-}{}_3$) salts that can be used to prepare the cooking liquor. The counterions of the salts include sodium (Na^+), ammonium ($NH^{-}{}_4$), calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+). In the chemical part of the process, lignin bonds are cleaved and the depolymerisation leads to the formation of sulphonate groups, resulting in the technical lignin type commonly called *lignosulphonates*.

Treatment of wood with sulphurous acid was first done by Julius Roth in 1857, while ten years later, Benjamin Tilghman used calcium bisulphite ($Ca(HSO_3)_2$) in the first patented version of this pulping method. In 1874, the first commercial mill was constructed in Sweden, using the magnesium cation based on a discovery by chemical engineer Carl D. Ekman. Eventually, the sulphite process became the leading pulping method in the world for several decades until the recovery boiler was introduced as a part of the Kraft pulping process, reversing the trend in favour of the Kraft process. Today, less than 10 percent of the world's pulp mills use this process, despite some recent developments in production and an increased demand for by-products from the process.

One of the benefits of the process is that it can be carried out at a wide range of pH, limited between 2 and 12 depending on the cationic counterions used (Luo & Abu-Omar, 2017). Calcium or magnesium ions are used to achieve acidic conditions, while the more rarely used sodium, potassium or ammonium ions are used to achieve alkaline process conditions. The process itself is very slow, with the required cooking time being between 4 and 14 hours according to Luo & Abu-Omar (2017). The pulping, i.e., the treatment of the wood chips is operated at temperatures of approximately 120 to 150 °C and pressures ranging from 500 to 700 kPa (Biermann, 1996).

The cooking liquor is normally prepared at the site by first burning sulphur at 1000°C in order to form SO_2 through oxidation. By dissolving the product in water, sulphurous acid is obtained, which is then treated with either hydroxide or carbonate salts of the cations used in the process (Biermann, 1996). Examples of this procedure for magnesium carbonate and sodium hydroxide can be seen in reactions 2-6 through 2-10 below.

$$\mathrm{S} + \mathrm{O_2} \rightarrow \mathrm{SO_2} \tag{2-6}$$

$$\mathrm{SO_2} + \mathrm{H_2O} \rightarrow \mathrm{H_2SO_3} \tag{2-7}$$

For magnesium:

$$\mathrm{H_2SO_3} + \mathrm{MgCO_3} \rightarrow \mathrm{MgSO_3} + \mathrm{H_2O} \tag{2-8}$$

or for sodium:

$$\mathrm{H_2SO_3} + \mathrm{NaOH} \rightarrow \mathrm{NaHSO_3} + \mathrm{H_2O} \tag{2-9}$$

$$\mathrm{NaHSO_3} + \mathrm{NaOH} \rightarrow \mathrm{Na_2SO_3} + \mathrm{H_2O} \qquad \text{(2-10).}$$

Similar to the Kraft pulping process, which also takes place in one or several digesters, the temperature is initially only raised moderately to ensure complete liquor penetration into the wood chips. Without this process being conducted slowly at a lower temperature, SO_2 could become volatile and enter the wood chips separate from the cations, causing char formation. This is the main reason why the cooking time is so long for the sulphite process. After the impregnation, the temperature is quickly increased to the optimal temperature depending on the chemicals used, and the reaction pressure is more than halved in order to preserve the fibre strength. According to Biermann (1996), this sudden decompression during the blowing step "effectively separates the wood fibres", and the pulp can be separated from the spent cooking liquor – in the sulphite process called *brown liquor*.

Differences between the various bases and their processes

There are numerous differences between the bases that can be used in the process and the reasoning behind them. The choice of chemicals can be subject to availability or their price, or simply their potential to be recovered or reused. The solubility of the base is further dependant on the desired pH, with product-specific requirements such as the end product of the pulp, or by-products, such as lignosulphonates, also being decisive.

The divalent cations Ca^{2+} and Mg^{2+} are initially added as carbonates, and apart from the reactions being carried out at lower pH, this is where the similarities end. While calcium carbonate (*limestone*) is relatively inexpensive, it is not recoverable in the process. Due to the precipitation of calcium sulphite at higher pH, the cooking liquor is kept highly acidic with excess SO_2. Despite the lack of chemical recovery, the pulping is reasonably fast and with limestone being relatively inexpensive, calcium has remained one of the most popular bases in the sulphite process. Magnesium, on the other hand, is a comparatively expensive metal, which has led to the recovery operation being thoroughly developed and optimised. Two alternative processes exist, one using magnesium sulphite and the other one magnesium bisulphite, also called *the magnefite process*. The magnefite process is particularly interesting, since the magnesium bisulphate can be recovered by scrubbing sulphur from the flue gases of the recovery boiler (reactions 2-11 and 2-12).

$$\mathrm{MgO + H_2O \rightarrow Mg(OH)_2} \quad (2\text{-}11)$$

$$\mathrm{Mg(OH)_2 + 2\,SO_2 \rightarrow Mg(HSO_3)_2} \quad (2\text{-}12)$$

After a few purification steps, the liquor is ready to be reused in the cooking process, which usually takes place at a pH of around 4.5. The magnesium sulphite process, called *acid sulphite*, requires a higher acidity due to the lower solubility of sulphite, and the pH can be as low as below 2.

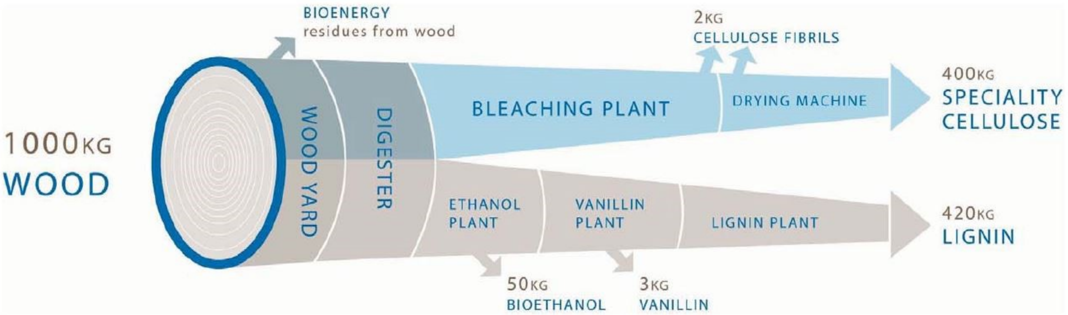
The use of ammonium has two big advantages: i) sulphite pulping with ammonium requires the shortest cooking time, and ii) usage of ammonium hydroxide allows recovery of the sulphur. However, the ammonium is lost in the recovery boiler, since ammonia and its salts oxidise to nitrogen or nitrogen oxides during combustion. The liquor needs to be kept below a pH of 9, since the acid dissociation equilibrium for ammonia is 9.24 at 25 °C, meaning half of the ammonium will be present as free ammonia in more alkaline conditions (Biermann, 1996).

$$\mathrm{NH_4^+ \rightleftharpoons H^+ + NH_3}, \quad \mathrm{pK_a = 9.24\ at\ 25\ ^\circ C} \quad (2\text{-}13)$$

Apart from using potassium as the sulphite base, which is a relatively novel technology and has the advantage of the spent liquor being a useful fertiliser, sodium is a base that can be used in both acidic and alkaline conditions. This means that both NaOH (see reactions 2-9 and 2-10) as well as Na_2CO_3 can be used to produce the cooking liquor.

Summary

Despite the many shortcomings of this process compared to the Kraft process, including a weaker pulp, much longer cooking cycles and various issues with the chemicals used and the recovery of them, it still has some benefits. As can be seen in Figure 2.2, Borregaard is able to utilise almost 90 % of the wood-based raw material in their Sarpsborg biorefinery. In addition to the utilisation rate, the refining of the products into higher value ones is also of importance. Besides the traditionally produced cellulose pulp, lignosulphonates obtained from the cooking liquor has a growing market demand and e.g., bioethanol or other chemicals can be produced through fermentation of sugars found in the hemicellulose. A fraction of synthetic biovanillin can also be produced with copper-catalysed oxidation, of which Borregaard are the biggest producer in the world (Fache et al., 2016).



SPECIALTY CELLULOSE	LIGNIN	VANILLIN	BIOETHANOL	CELLULOSE FIBRILS
Construction materials	Concrete additives	Food	Pharmaceutical industry	Adhesives
Filters	Animal feed	Perfumes	Biofuel	Coatings
Inks and coatings	Agrochemicals	Pharmaceuticals	Paint/varnish	Agricultural chemicals
Casings	Batteries		Car care	Personal care
Food/Pharma/Personal care	Briquetting			Home care
Textiles	Soil conditioning			Construction

Figure 2.2. *Range of products from the Borregaard biorefinery in Sarpsborg, Norway, using the sulphite process in the pulping step (Borregaard, 2017).*

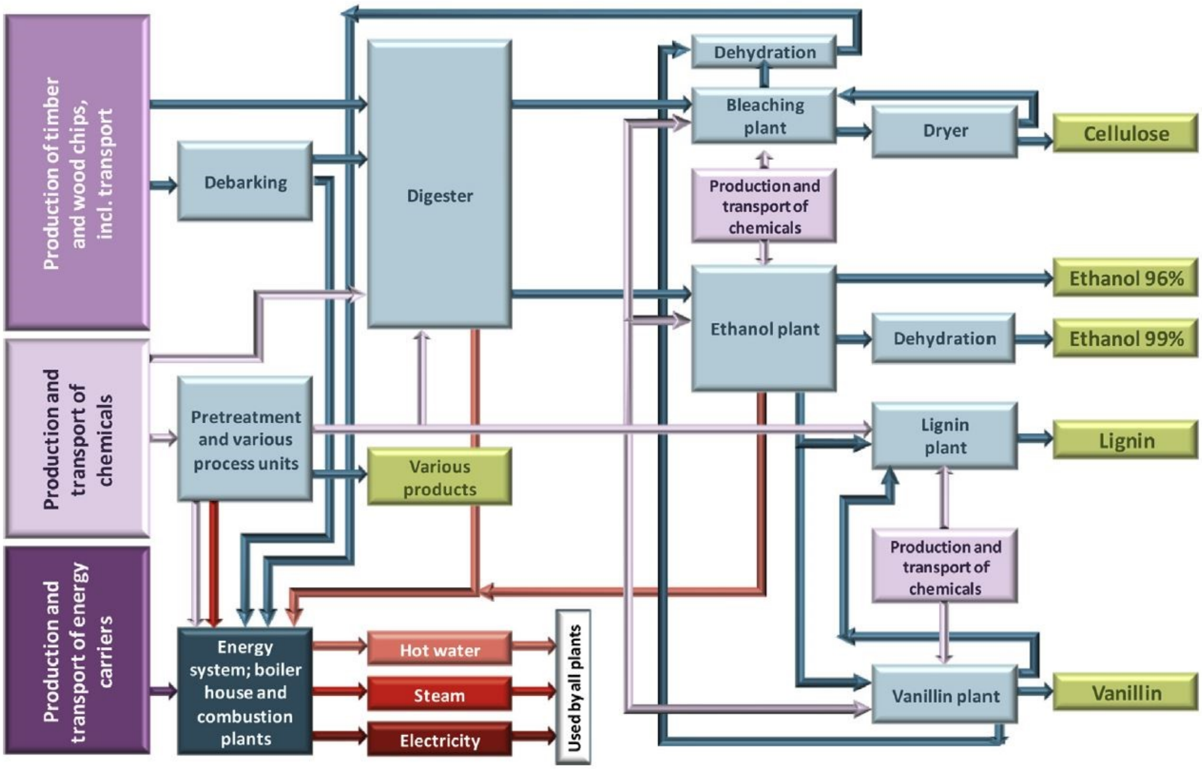


Figure 2.3. *Principal overview of the Borregaard biorefinery in Sarpsborg, Norway (Modahl et al., 2015).*

The investment costs of the various process steps will, however, need to be accounted for, with the somewhat complex scheme of processes illustrated in Figure 2.3. When it comes down to the rivalry with the Kraft process, either recovery of cooking chemicals or an adequate source of the non-recoverable bases at a reasonable price is paramount.

2.1.3 Mechanical pulping

Mechanical pulping, from which modern-day papermaking originates, only uses water and steam in addition to the lignocellulosic feedstock. This means no additional chemicals are needed, which is the primary reason why this pulping method has remained a relevant alternative to the chemical processes almost 200 years after it was first invented.

The incredibly high yields of up to 98 % of the wood input is something that characterises mechanical pulping. The pulp produced is of lower quality, largely due to the wood logs either being ground to pieces by grindstones or attrition of wood chips by disc refiners, leaving all the lignin in the pulp. This causes yellowing of paper when exposed to air and light, making it more suitable for newspapers, cardboard, or books (Biermann, 1996). Bleaching is possible to some extent, but the lignin will still remain in the pulp. Due to the relatively poor quality of the paper produced through mechanical pulping, together with a somewhat high energy demand, this method is not used for producing high value products, but is more suitable for processes utilising recycled paper as an alternative feedstock.

To date, a number of different mechanical pulping processes have been developed: Pressurised groundwood pulping (PGW), Refiner mechanical pulping (RMP), Thermomechanical pulping (TMP), and Chemi-mechanical pulping (CMP), to mention a few (Biermann, 1996). However, due to the lignin remaining in the pulp and being unavailable as a fuel feedstock, the mechanical pulping methods are not of interest in this thesis, and thus the processes will not be further elaborated on in this work.

2.1.4 Soda process

The soda process, also called *soda pulping*, is quite similar to Kraft pulping. The major difference is the absence of sulphur compounds, meaning the majority of the cooking liquor consists of NaOH – hence hydroxide being the active reagent. According to Windeisen & Wegener (2012), the method "causes hydrolytic cleavage of the native lignin into smaller fragments that are soluble in the strongly alkaline cooking liquor". The soda process is carried out at the same process conditions as Kraft pulping, at a pH around 13–14 and at a maximum temperature of 155–175 °C. The yield can be up to 70 % for hardwood, but it comes at a cost of almost double the cooking time of the Kraft process (Sjöström, 1993).

The sulphide used in the Kraft process can partly be replaced by addition of an organic compound called *anthraquinone* as catalyst. Anthraquinone volumes lower than 0.5 % of the feedstock mass is added to the digestion step of the pulping, accelerating the delignification process as well as decreasing degradation of carbohydrates through stabilisation of polysaccharides (Sjöström, 1993; Biermann, 1996). In wood pulping, about 0.1 mass-% of anthraquinone can increase the yield with 1–3 %, and therefore this additive has also been trialed in the Kraft process (Biermann, 1996).

Correspondingly to the chemical recovery of the Kraft process, sodium is recycled through combustion of the used cooking liquor. The sodium carbonate, obtained as a product of the combustion, is recovered and together with added Na_2CO_3 to make up for chemical losses, causticised to form NaOH for the fresh cooking liquor (Sjöström, 1993). Despite the simplicity of the process, the soda process is today mainly used for easily pulped materials such as bagasse, wheat straw and residue from other agricultural crops.

2.1.5 Organosolv process

Organosolv is the combined name for pulping methods using organic solvents to dissolve lignin and hemicelluloses. Ethanol, methanol and acetone are the most common solvents used, but also other organic solvents have been trialed in laboratory environments recently, together with a wide range of typically acid or chloride catalysts (de la Torre et al., 2013). Despite the method being invented and patented by Theodor Kleinert already in 1968 (Kleinert, 1971), the implementation of larger-sized production units have been discarded for various reasons up until recently. However, with the recent transition towards more environmentally friendly processes, the interest towards biorefineries has surged. In biorefineries the cellulose is often used to produce ethanol, which can then partly be used as a raw material for the process.

Some processes currently in use are:

i) *Alcell®*, which uses aqueous 50 % ethanol solution to pulp hardwood or annual plants at 190 °C and 28 bar (Azadi et al., 2013),

ii) *Organocell*, which is isolating the components of softwoods, hardwoods or annual plants with a mixture of methanol, water, sodium hydroxide and anthraquinone (Windeisen & Wegener, 2012), and

iii) *Formico®*, a method patented by the Finnish company Chempolis Oy, which uses formic acid to pretreat the biomass feedstock. Through very selective fractionation, a wide range of chemicals can be obtained and further refined to produce high-end products by e.g. enzymatic hydrolysis and fermentation of glucose to produce ethanol (Chempolis Oy, 2012).

The key benefits of the organosolv process are that the solvents in most cases can be recycled through evaporation and distillation, and that the lignin and hemicellulose obtained from the process has some desired properties, such as low ash and insignificant sulphur content. It is also easily scalable, meaning smaller production units can be economically viable which could be a great option for farms with large agricultural waste streams, such as rice husk, wheat straws and corn stalks as well as bagasse.

2.1.6 Other processes

As the transitioning towards a more sustainable future intensifies, scientists are striving to utilise more and more of the side streams from pulping processes, previously considered as waste or low-value products. While most novel methods are yet to be considered as being economically competitive with the production methods currently in commercial use, finding a way to replace the fossil-based feedstock by recovering and upgrading components of cellulose, lignin and hemicellulose is what drives this evolution.

Especially since the demand for paper is continuously decreasing, new applications and uses for the cellulose are also needed. Lately, there has been a growth in development of various methods of producing ethanol from biomass, which can be further upgraded to value-added chemicals. *Steam explosion* is a pretreatment method on the rise, where pressurised hot steam (around 200 °C) is used to treat the biomass for a short time, usually around 5 minutes. Additional pre-impregnation with $\mathrm{SO_2}$ could also be used to improve the fractionation efficiency. The alkaline extractable lignin can easily be removed with acidification and filtration, with yields up to 86 % of the original lignin found in wood. The steam explosion treatment is commonly used to facilitate acid or enzymatic hydrolysis and the subsequent fermentation in ethanol production, but is not considered to be economically viable without utilisation of the lignin stream (Li, Gellerstedt & Toven, 2009).

Hot water extraction, or pressurised hot water extraction, are two other methods used to extract the different fractions from biomass. The hot water can cause degradation of the material into toxic compounds, e.g., sugars forming furfural. The Finnish biotech company CH-Bioforce Oy have solved some of these problems by removing most of the oxygen from the reactor before treating the biomass with hot water at a sub-atmospheric pressure. Through some additional separation processes, they are able to extract hemicellulose, cellulose and lignin using very small amounts of chemicals and external water (von Schoultz, 2020).

Other pretreatment or fractionation methods mentioned in the literature include ammonia fibre expansion and aldehyde-assisted fractionation, as well as methods using protic ionic liquids or deep eutectic solvents to extract lignin from biomass. These are all relatively new technologies, with a very long way to go before they could produce lignin at volumes enough to make a dent on the current marine fuel demand.

2.2 Lignin types and their recovery

Recovered lignin polymers are called technical lignins due to the chemical modifications caused on them by their respective extraction method. It is yet unknown what the three-dimensional, amorphous lignin molecules look like in their **native form** because of their inaccessible position together with cellulose particularly in the cell walls of lignocellulosic plants. The appearance of native lignin is considered to be colourless or pale yellow, but changes to brown or dark brown when reacting to acid in the isolation process.

According to Berlin and Balakshin (2014), it is important to understand the chemical properties of lignin with its very complex structure in order to target the chemical modifications needed to achieve desired products through depolymerisation. What makes this challenging is the fact that all technical lignins differ from each other, influenced by both the raw material used and the processes through which it has been extracted and isolated. This means comparison between different processes and research results is difficult, and methods will have to be modified to suit the feedstock and process conditions used.

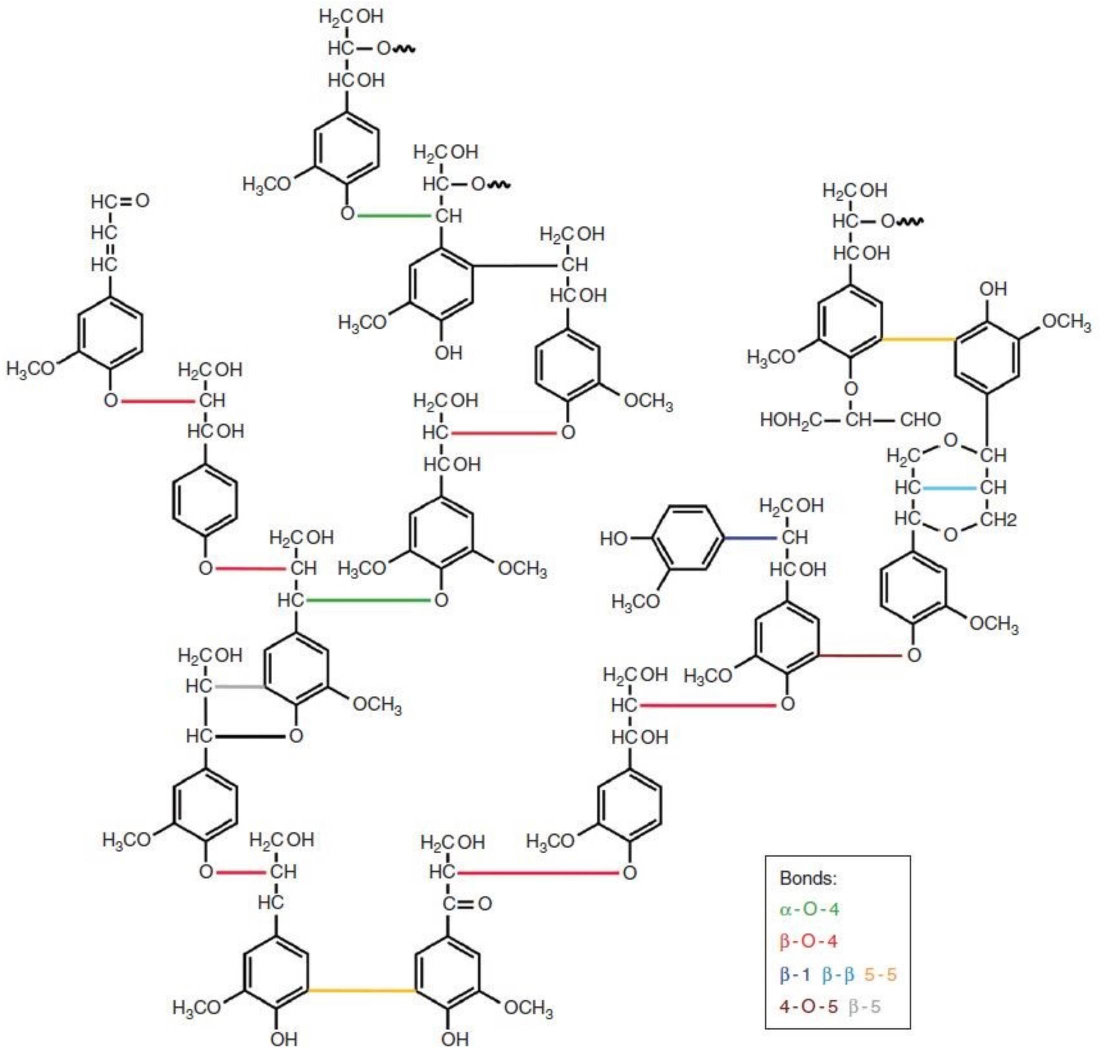


Figure 2.4. *Section of softwood lignin with the most characteristic linkages. (Windeisen & Wegener, 2012).*

To demonstrate the complexity of the lignin molecule, a small segment of a softwood lignin molecule is illustrated in Figure 2.4. The three most abundant monomers in lignin, (i.e., building blocks), are the following alcohols: i) p-coumaryl, ii) coniferyl, and iii) sinapyl, depicted in Figure 2.5. There are, however, large contrasts in the proportions of these. As reported by Azadi (2013), hardwood lignins contain an equal 50 %:50 % share of coniferyl and sinapyl, while the sinapyl fraction of softwood lignins are as low as 5 %, with coniferyl making up the rest. Neither of these two wood types contain p-coumaryl, contrary to grass lignins which contain about 5 % p-coumaryl in addition to the 75 % coniferyl, with sinapyl making up for the last 20 %.

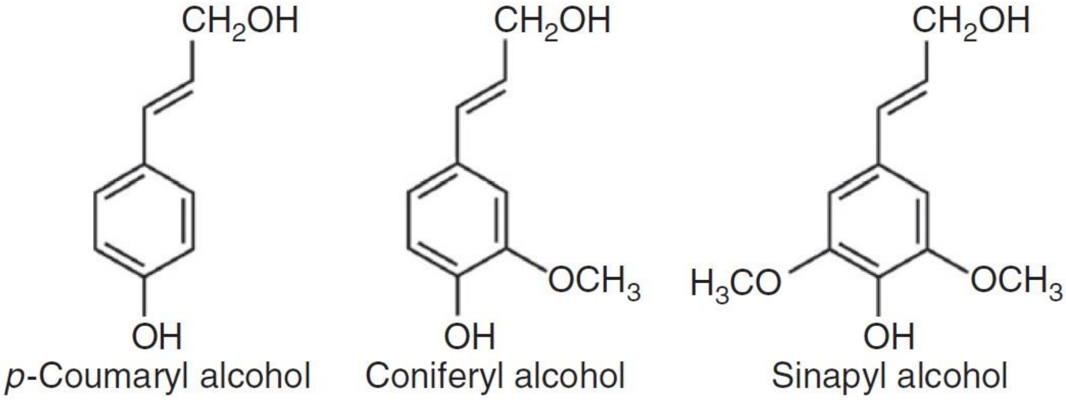


Figure 2.5. *The three most common building blocks of lignin molecules p-coumaryl, coniferyl, and sinapyl. (Azadi, 2013).*

Out of all the bonds holding the monomers together, the β–O–4 linkages are by far the most abundant, with a share of 46 % in softwoods and 60 % in hardwoods. Alongside them, the proportions of the rest of the dominant bonds have been estimated in Table 2.1 (Azadi, 2013).

Table 2.1. *Proportion of linkages: comparison between wood types (Azadi, 2013).*

Wood type	**β–O–4**	**α–O–4**	**4–O–5**	**β–5**	**β–1**	**β–β**	**5–5**
Hardwood	60 %	6–8 %	6.5 %	6 %	7 %	3 %	4.5 %
Softwood	46 %	6–8 %	3.5–4 %	9–12 %	7 %	2 %	9.5–11 %

In this subchapter, different characteristics of the most common technical lignin types will be summarised based on findings in the literature. More specifically, the effect of each extraction process and isolation method is considered to carry implications for further valorisation of the lignin, especially since research shows that considerable degradation and condensation occurs during the pulping process (Constant et al., 2016). Lastly, a quick overview of the lignin market situation will be presented, including the adaptations which would have to be made by lignin producers, with an emphasis on pulp mills.

2.2.1 Kraft lignin

As previously mentioned, the Kraft process is by far the most common pulping method worldwide, meaning the capacity of lignin supply of this type is the most interesting from a mass-production point of view. Previously mentioned capacities for lignin extraction vary between a conservative estimate of 5 % up to 37 % suggested by Tomani et al. of the total lignin content in the black liquor (Tomani et al., 2011; Berlin & Balakshin, 2014; VanCaeseele et al., 2018).

A characteristic specific to Kraft lignin is the relatively high levels of sulphur it contains, measured at 1.7 % in softwood Indulin Kraft lignin in a study by Constant et al. (2016). Constant et al. (2016) also measured the ash content at 2.6 % (which can be compared to the almost non-existent levels in organosolv lignins), an average molecular weight (M_w) and a polydispersity index (PDI) of 4,290 g mol^{-1} and 8.1, respectively. A clear correlation between both the extraction process and the feedstock used was proven by, for instance, the sulphur that was detected as a result of the Na_2S used in the cooking process.

Up to now, valorisation of Kraft lignin has been a challenging topic, and little incentive has existed for pulp mills to invest in the process steps required to extract lignin from the black liquor. A few methods have emerged commercially in the recent decade or so, of which three processes currently available on the market will be further described below: *LignoBoost*™ by Valmet Oyj, the *LignoForce System*™ developed by the Canadian company FPInnovations, and the ANDRITZ Lignin Recovery process called "*A-Recovery+*". Additionally, a lignin isolation method used by SunCarbon is briefly discussed based on details available to the public.

LignoBoost™

LignoBoost™, a two-step method for separating lignin from black liquor, was first invented by a group of Swedish researchers in the early 2000s, and the original patent application was filed in 2005 (Öhman et al., 2006). The patent has since then been approved and its current assignee is Valmet Power AB (Öhman et al., 2013).

The overall process is described in points 1–6 below, and a process scheme can be seen in Figure 2.6 (Öhman et al., 2013).

1. Black liquor with a dry lignin content of around 30 % is taken from the evaporation plant.
2. pH is lowered with CO_2 and gas from the second step of the process until the lignin precipitates.
3. The precipitated lignin is separated from the liquid and dewatered with a filter press.

4. In a "reslurry tank", the separated lignin is then redissolved in a mixture of spent wash water and concentrated H_2SO_4 to overcome typical filtering issues and problems with sodium separation.
5. The slurry is again filtrated with a filter press and washed with acidic wash water, after which lignin with a dry content of around 70 % is produced.
6. The leftover cooking liquor is recycled to the pulping stages of the process.

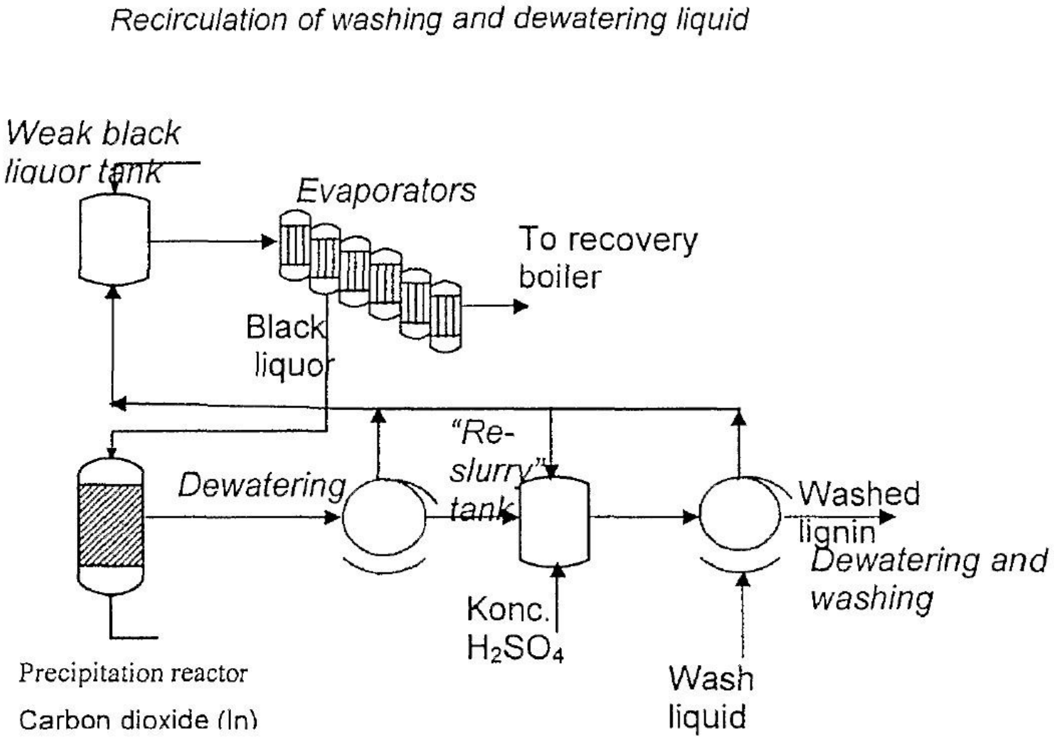


Figure 2.6. *Simple scheme of the LignoBoost™ process (Öhman et al., 2013).*

LignoForce System™

FPInnovations' method for separating lignin from black liquor is quite similar to the conventional process of lignin precipitation through acidification and filtering with either belt filters or filter presses. As a step towards reducing problems during filtration, their method is suggesting an oxidation step after the evaporation (Kouisni & Paleologou, 2011; Kouisni et al., 2012). While the oxidation step will require additional investment costs, it has been shown that the lignin slurry filtration rate can be increased vastly without affecting the lignin structure in a substantial way. It also showed a reduction in acid volumes needed during the acidification steps, and the Total Reduced Sulphur emissions were reduced in all processing steps, making the surrounding environment less hazardous. The reason for the improved filtration rate is, however, the agglomeration of lignin particles that the oxidation is causing. This could potentially be a problem during further treatment of the lignin, e.g., during depolymerisation processes (Kouisni et al., 2012; Kouisni et al., 2016). A comparison of lignin characteristics between oxidised and unoxidised black liquor can be seen in Table 2.2.

Table 2.2. *Properties of an unoxidised lignin vs oxidation with the LignoForce™ System (Compiled from Kouisni et al., 2012).*

Characteristic	Without black liquor oxidation	With black liquor oxidation
Filtration rate (kg lignin / h^{-1} m^{-2})	0–80	100–200
Total solids (%)	30–58	60–62
Ash content (%)	0.2–15	0.1–0.7
Lignin particle size (µm)	0.2–1	5–10

A-Recovery+

The foundations of the A-Recovery+ process was invented by Lars Stigsson and Curt Lindström, and is nowadays licenced to ANDRITZ Oy, who have commercialised it (Stigsson & Lindstöm, 2012). This process also follows the same overall principles of lignin removal from black liquor and is designed for black liquor which has been evaporated to reach a 35–45 % solids content at a pH around 12–13. As seen in Figure 2.7, carbon dioxide is used for the acidification also in the A-Recovery+ process, but the subsequent filtering is done with a membrane filter press. After filtration, sulfuric acid is used to leach impurities from the lignin, and a counter-current displacement wash using hot pressurised water from the black liquor cooling unit is used to remove any possible sodium sulphate formed. The slurry is dewatered with a secondary membrane filter press, and lastly, dried through a flash dryer utilising excess heat from the recovery boiler or the lime kiln. The moisture content decreases from about 40 % down to 5 % during the drying stage (ANDRITZ, 2017).

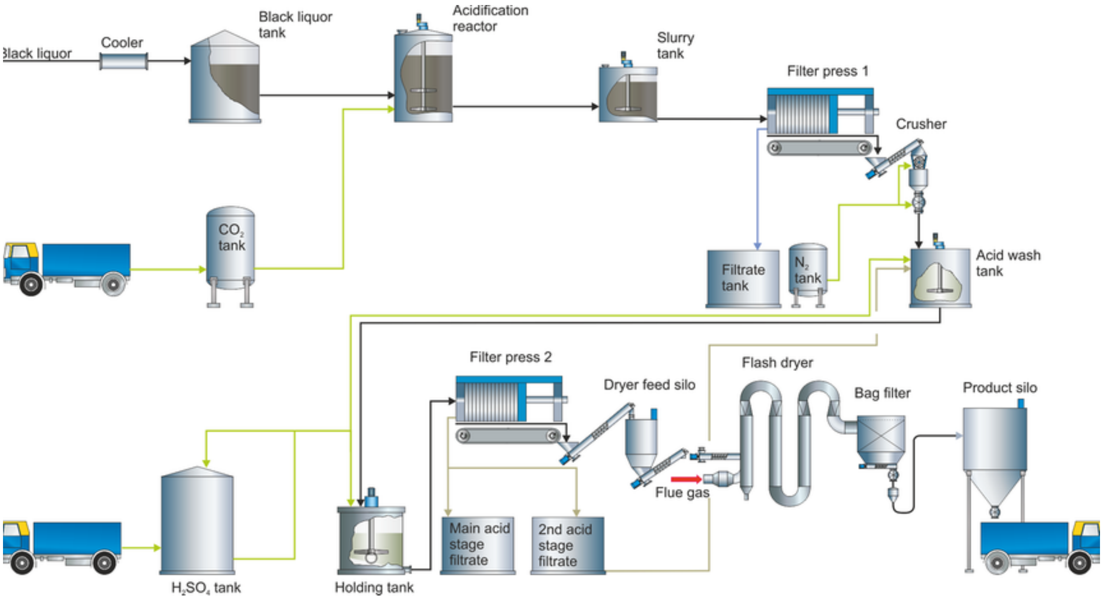


Figure 2.7. *The ANDRITZ Lignin Recovery process, called A-Recovery+ (ANDRITZ, 2017).*

SunCarbon membrane separation

Another interesting method already in use by SunCarbon Ab in Sweden, is separation of lignin and hemicelluloses from the black liquor through a membrane separation step. Without too many technological details about the process being public, the summary below is based on Jafri et al. (2020) and a description of the process by SunCarbon themselves:

The alkali-rich permeate stream obtained from the separation can be recycled to the chemical cycle, while the lignin-rich retentate stream is treated in a thermal catalytic cracker with indirect steam heating, breaking down the organic compounds catalysed by an alkalic compound internal to the pulp mill. Following these steps are the usual lignin isolation steps including precipitation through carbon dioxide treatment and acidic washing to remove impurities like ash and other residues. Ultimately, after a finalising desalting step, a lignin oil containing depolymerised lignin is obtained (Jafri et al., 2020; SunCarbon Ab, 2021).

Other methods

Ultrafiltration is a more costly option for isolation of lignin, but it allows separation of lignin fractions by their molecular weight. In a study by Toledano et al. (2010) ultrafiltration membranes were used to separate alkali lignin with the cut-off sizes 5, 10 and 15 kDa. As a result, the M_w went down from 5,654 to 1,806 g mol^{-1}.

Guimmarella et al. (2016) compared ultrafiltrated KL that had been filtrated with a 5 kDa cut-off size, with KL from the LignoBoost process – and a significant improvement in the solubility of low-molecular weight lignin in many solvents was reported. However, as estimated by Jönsson, Nordin & Wallberg (2008), ultrafiltration of evaporated black liquor could cost as much as 33 EUR per tonne of lignin for a unit capable of handling a feed volume of 200 m^3 h^{-1}.

There are of course other variations of extracting KL from the black liquor, but because of Kraft lignin's dissolution in alkaline conditions, the acidification step is naturally essential. The various washing steps and the optional drying can be modified to suit the quality and properties of the desired end product.

2.2.2 Lignosulphonates

Lignosulphonates, also called sulphite lignin, or lignin sulphonates, are usually isolated from the spent liquor of the sulphite process described earlier. The main reactions of *sulphonation* are sulphonic acid groups locating themselves in alkyl side chains of lignin, mainly at the α-position of propane chains, at the conjugated α-hydroxyl groups, and at carbonyl groups. It is the sulphonate groups that give lignosulphonates their high solubility in aqueous solutions. Also *sulphometylated Kraft lignins* exist on the market, but their chemical properties differ from lignosulphonates, and are therefore used for different purposes.

An important detail to keep in mind is that the lignosulphonate composition naturally varies depending on the counter ion used in the pulping process. As previously mentioned, these are: Na^+, NH^-_4, Ca^{2+}, Mg^{2+}, and K^+, and traces of them are expected to be found in the chemical structure of the lignosulphonate molecule.

Extraction of the lignosulphonates from the spent sulphite liquor brings on a few different challenges. The major difference compared to isolation of Kraft lignin is the **water-solubility** of lignosulphonates, meaning precipitation by acidification is impossible. Instead, there are a handful other methods of separating the lignin, mainly different types of ultrafiltration and membrane filtration. Isolating the lignin from the other solid components is however difficult, due to e.g., hemicellulose having similar molecule weight as lignosulphonates. Other factors determining which separation method should be used range from membrane life-length and production costs and rate, to desired lignosulphonate purity etc.

Additional methods studied, some of which are already used commercially, are the *Howard method* (used for extracting calcium lignosulphonates), the *Pekilo process*, electrolysis, reverse osmosis, dialysis, and ion-exchange resins (Aro & Fatehi, 2017).

Depending on the intended use, the production method and thus, the chemical structure and properties of the lignosulphonates can be altered to a certain degree.

2.2.3 Soda lignin

Soda pulping is a relatively mild process when it comes to changing the chemical structure of the lignin, at least compared to some other pulping methods. This improves its purity and is also the reason the lignin has a lower M_w of around 800–3,000 kg mol^{-1} and an ash content around 2–4 %, making purification less likely to be needed (Luo & Abu-Omar, 2017). Both the feedstock used, and whether anthraquinone has been used as catalyst, have a big impact on the M_w, with Azadi et al. (2013) listing several types of biomass species used, ranging from 1,300 kg mol^{-1} for long fibre plants to 10,400 kg mol^{-1} for Alfa grass. As a comparison, straw and grass P1000 soda lignin was tested by Constant et al. (2016), which showed an ash content of 2.5 % and an M_w of 3,270 g mol^{-1}.

In soda pulping, sodium hydroxide breaks down the native lignin molecules into smaller fractions by hydrolytic cleavage, which makes it soluble in alkaline solutions. A significant difference compared to Kraft lignin and lignosulphonates is the lack of sulphur used in the pulping process, which makes the lignin sulphur-free. This is of importance when searching for ways to utilise the lignin for instance, in catalytical processes which cannot tolerate sulphur being present, or combustion in areas where sulphur emissions are regulated (see ECAs, chapter 2.3.1).

The isolation of the soda lignin, mostly stemming from lignocellulosic agricultural waste or annual plants, is commonly done with the *Granit process*, precipitating the lignin by acidification with typically mineral acids (Windeisen & Wegener, 2012).

2.2.4 Organosolv lignin

Organosolv lignin (OL) contains more hydroxyl and carbonyl groups due to the alcohols used in the delignification process. The lack of sulphur used in the process is another detail that characterises OL, while some other properties which stand out, mentioned by de la Torre et al. (2013), are the lower glassy transition temperature enhancing thermal processing, and the increased fluidity making it easier to pump in liquid solutions. As mentioned previously, the ash content is also considerably lower in the OL, which is a considerable factor especially if the lignin is combusted as a fuel.

Because of the wide range of components in the spent liquor, including lignin, hemicelluloses and the solvent, various methods exist for separating these and isolating the lignin. In the Alcell® process the solvent, i.e., ethanol, is evaporated in a flash drum. A clarifier is used, and the precipitating lignin can be removed with a centrifuge. Another method imposes precipitation of lignin with the help of phosphoric acid until a pH around 4 is reached.

The Alcell lignin is highly soluble in alcohols such as acetone and Tetrahydrofuran, but insoluble in water. Azadi et al. (2013) reports an M_w for hardwood of 3.3 kDa and a PDI of 3.7, while Constant et al. (2016) measured values of 2,580 g mol^{-1} for M_w and a PDI of 4.3. For other organosolv lignins, stemming from wheat straw, poplar and spruce, average molecular weights of 1,960, 2,180, and 2,030 g mol^{-1} were measured, with PDI values of 4.4, 3.8, and 4.9, respectively. The ash content for all four of Constant et al.'s organosolv lignins were less than 0.1 %.

Organocell lignin is deemed to have low prospects of being turned into high-value products, but could provide for a viable production of syngas through gasification (Azadi et al., 2013).

2.2.5 Other lignin types

Most other types of technical lignins are considered to be structurally quite mildly affected by their respective extraction processes, especially compared to lignin from the sulphate and sulphite processes. Other process conditions might nonetheless affect the lignin, such as the temperature of a process exceeding the melting temperature of lignin. For hydrothermal pretreatments like steam explosion, this can cause agglomeration and condensation, resulting in a M_w of up to 40.000 g mol^{-1} (Nielsen, 2016).

Hydrolysis lignin (HL) is another lignin on the rise, and most commonly produced as a by-product from cellulosic ethanol plants. The purity of the lignin is reported to be as low as 60 % and a M_w of over 20.000 g mol^{-1}, making it insoluble in common organic solvents (Mahmood et al., 2015).

Many other types of lignin exist, with Calvo-Flores et al. (2015) describing over 25 different types. Most of these have only been produced in laboratories and are unlikely to have a future in terms of being commercially produced at a larger scale.

2.2.6 Summary and market outlook

While there are a multitude of emerging processes on the market with lignin as a potential side stream, there is still a long way to go before any of them will produce substantial amounts of lignin for the comparatively massive marine fuel market. The financial viability of the processes is moreover largely dependent on attainable optimisation that could reduce the production costs. Additionally, the outlooks are largely affected by the demand and price developments of the products or chemicals that lignin could be valorised to.

As of now, lignosulphonates are dominating the market of produced lignin with a 79 % market share in 2018, amounting to 1,315 kt y^{-1} out of its estimated potential of 3,000 kt y^{-1}. KL is the type with a far superior potential of about 78,000 kt y^{-1} available to be extracted without affecting the internal energy balance of the sulphate pulp mills (Dessbesell et al., 2020). The very few commercial-scale plants in the world that produce cellulosic ethanol were set to add 1.6 million tonnes of sulphur-free lignin to market in 2018 – an output expected to increase every year as the biorefinery boom continues (Obydenkova et al., 2017).

Table 2.3. *Classification of lignins (Berlin & Balakshin, 2014).*

Lignin type	Scale	Chemistry	Sulphur content	Purity
KL	Industrial	Alkaline	Moderate	Moderate
SL	Industrial	Alkaline	Free	Moderate-low
LS	Industrial	Acid	High	Low
OL	Pilot/demo	Acid	Free	High
HL	Industrial/pilot	Acid	Low-free	Moderate-low
SE	Demo/pilot	Acid	Low-free	Moderate-low
AFEX	Pilot	Alkaline	Free	Moderate-low

Table 2.3 shows the prominent lignin types including some important factors when it comes down to whether they are suitable as a marine fuel feedstock. Lignosulphonates already have a large portfolio of industrial applications. The uses range from plasticiser and additive in the production of concrete and cement, to dispersant, flocculant, dust suppressant, or it can be utilised as a part of composites

and ion-exchange resins (Aro & Fatehi, 2017). These other applications not only decrease the potential supply of LS as a fuel feedstock, but also increase the market price to levels that rule out its feasibility as a marine fuel, which is close to the bottom of the value pyramid of potential lignin utilisation. Abbati de Assis et al. (2018) cited a lignosulphonate price of 300 USD per tonne, while an industry contact indicated that the market price in 2020 was as high as 500 USD per tonne.

Precipitation of KL has been on the rise, with production volumes having almost tripled since 2015, spearheaded by North American mills (Dessbesell et al., 2020). So far, phenol replacement in resins seems to be the only notable use for KL in industrial applications (Castro Garcia, Cheng & Cross, 2020).

In a very advanced and comprehensive study, Culbertson (2017) has evaluated the potential commercialisation of lignin extraction with the LignoBoost process, and found that profitability would be dependent on lignin versus electricity price, and the cost of CO_2 used in the precipitation of lignin (79 USD per tonne used in the study). He also found that pulp production would have to be maximised in accordance with the full capacity of the recovery boiler in order for the investment to be justifiable. In the case where lignin was sold as a biofuel product, it was assumed to have been pelletised with a market value of 245 USD per admt. The overwhelming cash costs of 374 USD per admt produced was much higher, but included international freight costs of 98 USD per admt and packaging-related costs of 32 USD per admt. Without these, the lignin could be produced for 244 USD per admt. Furthermore, it was determined that for a lignin price of 20 USD per MWh, "lignin separation and sale as a biofuel could be more cost advantaged than a recovery boiler upgrade". Also worth mentioning is that the value of the extracted lignin combusted in the on-site lime kiln, in lieu of natural gas, was estimated to give a fuel credit of 110 USD per admt (Culbertson, 2017).

It is clear that both the production rates and the demand will have to keep increasing substantially in order to drive the market prices for KL down. For biorefinery lignins, the future market situation is uncertain, but the sulphur-free lignin types have a wider range of high-value products they could be valorised to. On the other hand, the lack of sulphur also means a possible lignin fuel could be compared to low-sulphur marine fuels like ULSFO and VLSFO instead of residual oils.

2.3 Marine fuel industry

Just like its counterparts, the marine industry is heavily regulated. Since shipping is an international matter, the regulations for the whole maritime sector are controlled by the International Maritime Organization, IMO. As a subdepartment of the UN, the IMO is in charge of governing safety, security and emissions on the seas. To ensure fuel users, producers, and engine manufacturers alike are all on the same page, regulations for the fuel characteristics also exist – guaranteeing a more sustainable market situation. In order to adapt to the continuous change in legislation worldwide, the maritime regulations must also be kept up to date to ensure compliance.

2.3.1 Regulations and guidelines

The most immense change in the regulations in recent times is known as "*IMO 2020*". It originates from an amendment to the *MARPOL Annex VI* (regulation 14) which limits the sulphur in the fuel oil on board ships to 0.5 mass-% outside of, and to 0.1 mass-% inside so called ECAs, Emission Control Areas. The four ECAs currently in use are: a) the Baltic Sea area, b) the North Sea area, c) the North American area, covering the coasts of the United States and Canada, and d) the United States Caribbean Sea. Suggestions have been made that more waters should be instated as ECAs, such as the Mediterranean Sea, the Arctic waters, and the coastal areas of Japan, Australia, Norway and Mexico.

The options for compliance with the new IMO 2020 regulations are quite limited for ships previously run with heavy fuel oils. Either a) low-sulphurous fuels have to be used, increasing the fuel costs, b) a scrubber system must be used to clean the exhaust gases, or c) retrofitting of equipment in order to enable the use of a new type of fuel.

To help with the process of identifying which fuels to use, and where, the different types have been standardised by industry-specific requirements. First released in 1987, ***ISO 8217*** is a standard specifically for marine fuels managed by the International Organization for Standardization. In order to keep up with recent technological advancements, it is reviewed every five years, and its sixth and newest edition was released in 2017. It provides shipowners, operators, marine fuel suppliers and producers, national as well as international regulating bodies etc. with guidelines to ensure smooth and safe operations for everyone involved in the maritime fuel industry (ISO, 2017).

2.3.2 Current fuel alternatives

Distillate and residual fuels

The vast majority of fuels used in the marine sector can be classified in two types: i) distillate and ii) residual fuels. All fuel types following the ISO guidelines are generally named with a three-letter code, consisting of D or R (for distillate or residual) as the first letter, M, as in marine, and a letter between A and Z that is interrelated to a specific set of fuel specifications.

From the two typical petroleum distillate fuel sources, Marine Gas Oil (MGO) and Marine Diesel Oil (MDO), three distinct grades, DMA, DMZ, and DMB are the most common. While DMB is considered a diesel made from lighter distillate fractions, with an aromatic content around 25 % and a sulphur content between 0.3 and 2.0 mass percent, DMA and DMZ are light gas oils with an aromatics content of 60 % and contain a lower sulphur percentage. Normal MGO has a sulphur content between <0.10 and 1.50 %, while there are also methods of reducing the sulphur content to under 0.1 %, sold as LSMGO (Hsieh & Felby, 2017).

Table 2.4. *Characteristic guidelines for distillate marine fuels (ISO, 2017).*

Characteristics	**Unit**	**Limit**	**Fuel type**		
			DMA	**DMB**	**DMZ**
Kinematic viscosity (40 °C)	cSt	Max.	6.000	11.00	6.000
		Min.	2.000	2.000	3.000
Density (15 °C)	kg m^{-3}	Max.	890.0	900.0	890.0
Cetane number		Min.	40	35	40
Sulphur content	mass-%	Max.	1.00	1.50	1.00
Flash point	°C	Min.	60.0	60.0	60.0
Oxidation stability	g m^{-3}	Max.	25	25	25
Pour point, summer	°C	Max.	0	6	0
Pour point, winter	°C	Max.	-6	0	-6
Water content	vol-%	Max.	-	0.30	-
Ash content	mass-%	Max.	0.010	0.010	0.010
Lubricity	µm	Max.	520	520	520

As seen in Table 2.4, the requirements for DMA and DMZ are relatively similar, except for the minimum viscosity limit. DMB has some differing limits, partly due to the fact that it might be stored and delivered by the same equipment and pipelines as residual fuels. This might also cause some discolouring, meaning hot filtration and water tests should be done on samples that are not considered 'clear and bright' to verify its correct fuel grade (ISO, 2017).

The other type of fuel has got its name from its origin – residual fuels, produced from the residue from oil refineries. Naturally, this also means it is one of the more low-priced fuels available. However, it comes at a cost, usually in the form of unfavourable properties requiring additional processing steps. The most eminent one is the high viscosity of the fuel, requiring heating before it meets the desired characteristics of marine engines and boilers.

As explained above, residual fuels are usually graded with a three-letter code, starting with RM for "residual marine", with the third letter determining its grade. Letters A to D are used for different grades of light fuel oil, while letters E through K are used for heavy fuel oils. An additional number is commonly used at the end to characterise what the maximum viscosity at 50 °C is. For instance, RMG 180 and RMG 380, which are two of the most common fuels for large vessels and container ships, being residual marine fuels of grade G with a viscosity less than 180 and 380 cSt, respectively, at 50 °C. When it comes to requirements for the two different grades, it is only the kinematic viscosity that separates them, as illustrated in Table 2.5 together with RMB 30, a light fuel oil used in the experimental part of this study.

IFOs, or intermediate fuel oils, are another class of fuels used in the marine sector. They are blends of both residual fuels and distillate marine gas oils, giving the fuel better ignition characteristics that are more suitable for low speed two-stroke engines. Correspondingly to RMG, also IFO is generally sold at viscosity limits of 180 and 380 cSt (Hsieh & Felby, 2017).

Table 2.5. *Characteristic guidelines for residual marine fuels (ISO, 2017).*

Characteristics	**Unit**	**Limit**	**RMB 30**	**RMG 180**	**RMG 380**
Kinematic viscosity (50 °C)	cSt	Max.	30.00	180.0	380.0
Density (15 °C)	kg m^{-3}	Max.	960.0	991.0	
Sulphur content	mass-%	Max.	3.5 %, or SECA requirements[a]		
Flash point	°C	Min.	60.0	60.0	
Carbon residue	mass-%	Max.	10.00	18.00	
Pour point, summer	°C	Max.	6	30	
Pour point, winter	°C	Max.	0	30	
Water content	vol-%	Max.	0.50	0.50	
Ash content	mass-%	Max.	0.070	0.100	

[a] *SECA = Sulphur Emission Control Area, more commonly called ECA.*

Other fuels

Currently, no other fuels can compete with fossil-based fuels on a cost per energy equivalent basis, especially in ships already equipped for a certain fuel, since retrofitting entails its own set of investments. Recent developments in efficiency, safety, and cost-effectiveness as well as availability of fuels, have gotten shipowners to turn their attention towards new, upcoming technologies. In preparation for possible stricter regulations and price developments, more and more newbuilds are fitted with a capability of solely running on a new type of fuel or with a readiness to change between different types (e.g., dual- or multi-fuel engines).

Liquified natural gas, LNG, is the most used among the gaseous fuels, but other gases, like hydrogen, compressed natural gas, liquified petroleum gas, and ammonia have received more attention lately. In spark-ignition engines, gasoline, in addition to methanol, ethanol and butanol are all valid options, also as drop-in fuels. In addition to the fuels mentioned above, environmentally friendlier versions of several of them, so called *biofuels*, also exist. Biogas, biodiesels like FAME (Fatty acid methyl esters), vegetable oils, bioethanol and biomethanol are all produced from renewable sources – but all of them come with their own specific properties and characteristics that need to be adjusted to fit the current fuel and engine systems. Bioethanol and biodiesel have for example mostly been used in the road transport sector due to their favourable miscibility with the traditional fuels used there, in addition to other fuel-specific characteristics.

2.3.3 Future of marine fuels

With the deadline for compliance with the IMO 2020 already passed, most ships will already have found a way to deal with the new emission requirements. This does not stop shipowners and regulators alike from planning for the future. Now that the majority of SO_x emissions have been dealt with and reduced, the large CO_2 emissions that are caused by the marine shipping industry are expected to be next in line – with regulations of CO_2 emissions expected to be introduced "in the short to medium term" (Hsieh & Felby, 2017).

In an extensive report made for the Finnish Government, Solakivi et al. (2020) have mapped the expected impacts that a possible emissions cap on CO_2 would have on the marine sector. The main pathways are suggested to be either entering the EU ETS, that handles the trading of emission rights for aircrafts and onshore installations with a net heat excess of 20 MW in the EU countries (2003/87/EC), or introducing a separate international commission governed by the IMO. Simply put, the EU ETS is based on units of European Union Allowances (EUAs), with each unit entitling the owner of said unit to emit 1 tonne of CO_2, or an equivalent amount of two other greenhouse gases; nitrous oxide (N_2O) and perfluorocarbons. While the unit price for an EUA has been moderately low for most of the 2010s, Figure 2.8 shows how the prices have climbed substantially since 2018, with new highs being reached on a weekly basis. The highest price so far of 56.90 euros per EUA was reached on May 14th, 2021, up almost 1,000 % from the average price between 2012–2017.

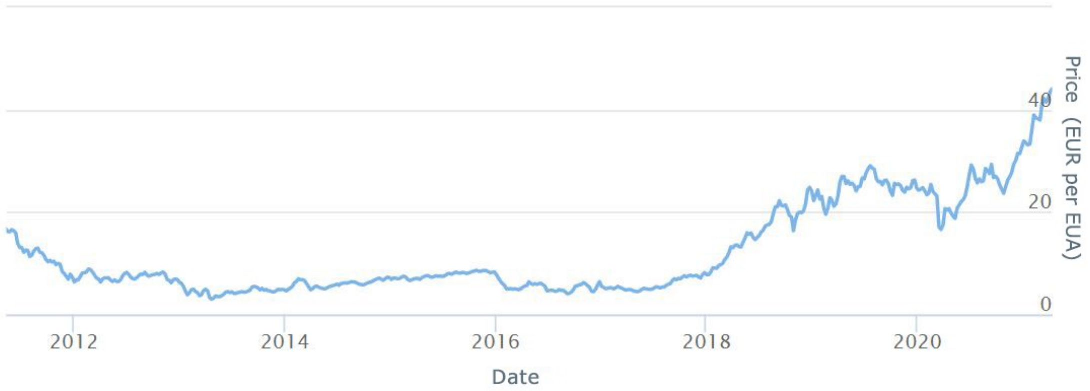


Figure 2.8. *The evolution of EUA prices dating 10 years back from April 16th, 2021. (EMBER, 2021).*

With emissions of 3.114 tonnes CO_2 per tonne HFO, 3.206 tonnes CO_2 per tonne MGO and 2.75 tonnes CO_2 per tonne LNG (International Maritime Organization, 2015), the premium paid for the EUAs would be as high as 137 to 160 EUR per tonne of fuel with an EUA unit price of 50 EUR. Solakivi et al. (2020), however, points out that the blow might be mitigated with handing out free emission quotas to start with. Through investments into replacing the high-emission fuels with more sustainable ones, the shipping companies could then auction out their EUAs. This is expected to lead to a conservative estimate of over 1 billion euros being put into emission-lowering technology over the next decade, where biofuels will play a big role (Solakivi et al., 2020). Another incitement that will certainly influence the transition towards biofuels is the taxation of fossil fuels (i.e., energy tax), that governments can control to steer the development in order to reach emission targets (2003/96/EC).

The marine sector has limited knowledge and readiness for biofuels and their characteristics, and regulations alike will have to be updated to adapt to the fuels of the future. What is clear is that renewable fuels will play a key role in the upcoming efforts towards reducing GHG emissions worldwide.

3 LIGNIN FUEL PRODUCTION PROCESSES

This chapter delves into several different methods of turning lignin into a fuel that is potentially suitable for marine diesel engines, both found in literature and based on empirical research. While lignin is usually utilised through valorisation of lignocellulosic biomass, this work focuses mainly on lignin already separated from its biomass source, e.g., a residual stream from a pulping process or a biorefinery. The most promising technologies found have been included in this study, however, this chapter will not put too much weight on their techno-economic feasibility, as this will be assessed in Chapter 6.

In order to utilise the current fuel infrastructure and ensure suitability with the diesel engines currently in use, the lignin fuel would naturally have to be in a liquid state. This also reduces the additional investments needed to start using a new type of fuel. In the case of marine fuels, biobased supplements to the fossil fuels currently in use (i.e., bio-hydrocarbon mixtures) are mostly referred to as *drop-in* biofuels. For a fuel to fulfil the definitions of a drop-in fuel, it needs to meet certain requirements – namely favourable miscibility with petroleum fuels, good storability and transportability, as well as compatibility with the existing fuel systems and engines (Hsieh & Felby, 2017).

The common perception is, simply put, that depolymerisation of lignin is required to produce a liquid lignin fuel. Cleavage of ether bonds is the preferred way to do this since they have a lower bond energy than C–C linkages. Furthermore, an additional oxygen removal step (e.g., hydrodeoxygenation or decarboxylation) is usually required to attain desirable fuel properties, such as increased solubility in solvents, higher energy density, lower viscosity, and better stability (Nielsen, 2016). An ideal drop-in biofuel would also need to have "non-corrosive, non-reactive and non-hydrophilic properties" to ensure the possibility of full utilisation of the current fuel pipelines and equipment (Karatzos, McMillan & Saddler, 2014).

Due to the diesel engines in the marine sector not being as sensitive to lower quality fuels as road and air transport engines, there is still hope that expensive secondary refining processes like (typically catalytic) hydrotreatment could be avoided. Most catalysts are also very sensitive to and get severely damaged by sulphur, which means sulphurous KL would have to go through an additional desulphurisation process before further catalytical processing.

A possible solution to problems with stability and miscibility between drop-in fuels and petroleum fuels could be the utilisation of external chemicals. These chemicals fall under the category of surfactants, which are chemicals aiding the miscibility of the involved substances through surface chemistry. There are, for instance, many cases where diesel-bioethanol or diesel-biooil emulsions aided by non-ionic surfactants have been studied (Martin, Mullen & Boateng, 2014; Nandakumar & Malayalamurthi, 2015; Farooq et al., 2019). The possible utilisation of surfactants or other chemicals will be further discussed where relevant.

3.1 Solvolysis

The solubility of lignin can be numerically predicted based on solubility parameters calculated from the fractions of different monomers present in the lignin molecules, especially guaiacyl, syringyl and p-hydroxyphenyl phenylpropane. The two prominent parameters are called *Hildebrand's solubility parameter* and *Hansen's partial solubility parameter*. For the Hildebrand parameter, a similar value for both the solvent and lignin is preferred for a better solubility. An estimated value for lignin of around 14 was reported by Guimmarella et al. (2016) and can be compared to a few potential solvents with similar values listed in Table 3.1. Included in the table is also the *Hansen Relative Energy Difference* (RED) parameter, which must be around 1 or below for a solvent to ensure high affinity between the solvent and the lignin.

Table 3.1. *Compilation of solubility parameters for selected solvents (Guimmarella et al., 2016).*

Solvent	**Hildebrand parameter (cal cm^3)$^{-½}$**	**Hansen's RED number**
Water	23.27	2.07
Methanol	14.42	1.08
Ethylene glycol	13.63	1.00
Furfuryl alcohol	12.49	0.82
Ethanol (96 vol-%)	12.10	0.99
Butanol	11.33	1.06
Furfural	11.32	0.87

These two parameters can be of considerable help when selecting a solvent for the solvolysis process. Other factors, like availability and price, or even process parameters, are of course also important factors, but according to Guimmarella et al. (2016) and Kouris et al. (2020) it is the higher polarity and hydrogen-bonding ability of the solvents that play a crucial role in lignin dissolution.

When producing a marine fuel that can be cost-competitive with regular fossil-based fuels, it is necessary to design a production process that is both optimised in every way and takes crucial parameters into account. For instance, in a second generation (2G) biorefinery that produces both ethanol and lignin, the ratio of lignin to ethanol produced is somewhere between 0.5 to 0.3 according to Kouris et al. (2019). This means in order to achieve a continuous, optimal process without the need for an external ethanol supply, lignin would have to make up for almost half of the produced lignin oil.

In a more recent study, Kouris et al. (2020) experimentally tested a range of polar organic solvents for lignin solvolysis and concluded that the optimum process conditions for a batch process would be a temperature of 200 °C, a reaction time of 30 minutes, and a pressure high enough to keep the solvent below its boiling point. For a lignin type named *Protobind soda lignin,* and with a lignin-to-solvent weight/volume ratio of 1:5, methanol was deemed to be the best solvent, with the other tested solvents listed in Table 3.2.

Table 3.2. *Solubilisation degree of Protobind soda lignin in solvents after a mild solvolysis reaction (Kouris et al., 2020).*

Solvent	Solubilisation degree (wt-%)
Methanol	61
Ethanol	57
1–propanol	53
1–butanol	51
1–octanol	38

In terms of the yields relating to the solvolysis process, three different degradation products can be identified: lignin oil, char, and gas. Usually, the gas fraction can be neglected, but for the purpose of producing a fluid fuel that meets the standards, the char together with undissolved lignin must be removed. This is usually accomplished through a filtration step, where it is important to take into consideration the relatively large amount of unconverted lignin and char that could clog the filters if the process is poorly designed. Experiments carried out by Kouris et al. (2019) resulted in a conversion ratio of 40 % for KL in methanol, and 67 % for enzymatic lignin in ethanol, leaving residue of 60 % and 33 %, respectively, of the added lignin left to be removed through filtration. The residue stream that consists of about half unconverted lignin, and half collected char, contains a large amount of energy. This energy could be fed back into the energy cycle of the mill through combustion in a boiler or lime kiln. For further optimisation of the process, Azadi et al. (2013) suggests that the solid residue could be sent to a gasifier to produce the hydrogen required for the fuel upgrading instead of combusting it on-site to produce energy.

The low conversion rates, in addition to the low volumes of lignin that can be added to avoid issues related to mixing, result in a low lignin content in the solution after filtration. To increase the lignin ratio, the solvent could be partially removed through distillation or evaporation, which also enables most of the solvent to be recycled. Kouris et al. (2019) are claiming that a heavy crude lignin oil consisting of up to 80 w-% lignin can be produced with this method, with only small amounts of solvent (5–7 %) lost due to condensation issues in the distillation process. According to Kouris et al. (2019), the obtained crude lignin oil is stable and storable, and they are suggesting that methanol should be the preferred solvent used in the production of marine fuels. While they claim that the lignin oil is usable in this state, it is unclear if they refer to it being directly usable in a marine diesel engine, and if it fulfils all the fuel requirements listed in the *ISO 8217* standard.

Since solvolysis is one of the most researched depolymerisation methods for lignin, many other examples can be given. However, Castro Garcia, Cheng & Cross (2020) claim that research usually focuses too exclusively on just one of the three controlling factors of lignin solvolysis; i) lignin-catalyst interaction, where the catalysts used in solvolysis would promote the hydrogenation process, ii) reactions between catalysts and the reaction media (i.e., the solvent), which can prevent char formation through hydrogen donation, and iii) lignin solubility at different temperatures and the simultaneous reactions that could occur.

Castro Garcia, Cheng & Cross (2020) suggest that some alcohols together with catalysts used in the solvolysis could provide good yields of biooil as long as "the solvent provides a source of hydrogen and prevents the formation of char". They also recommend that the solvent used for depolymerisation of KL should be carefully considered. The economic feasibility relies heavily on both the feedstock costs, and a factor that is rarely considered in studies – the durability and possible regeneration of the expensive catalysts that might be needed in the process (Castro Garcia, Cheng & Cross, 2020).

Additionally, as Guimmeralla et al. (2016) and Kouris et al. (2020) both point out, the differences between lignin types and their characteristics, especially the molecular weight and number of functional hydroxyl groups of the lignin, significantly affect the yields. This is partly shown by Kouris et al. (2020) and their solvolysis of the previously mentioned Protobind soda lignin with an average M_w of 2,465 g mol^{-1}. The fractions soluble in methanol and ethanol had an average M_w of 1,417 and 1,273 g mol^{-1}, respectively, while the M_w of the insoluble fractions were as dense as 3,984 and 51,547 g mol^{-1}, respectively. This shows that lignins with a lower M_w have a better solubility in these two media, but also that methanol is more proficient in dissolving lignin molecules with a higher M_w.

3.2 Pyrolysis

Pyrolysis is the term used for thermal depolymerisation of a material at an elevated temperature and in an inert atmosphere. It is commonly used to process organic materials, resulting in three roughly equal parts of non-condensable gases, liquid oil, and solids. The method is one of the most prominent methods for decomposing lignin in biomass in order to produce biofuels. Pyrolysis is usually used to treat biomass, resulting in biogas, biooil and char – but several studies have been made on pyrolysis of pre-extracted lignin stemming from various processes (Brebu & Vasile, 2010). Depending on the process parameters, mainly temperature, pressure and residence time, pyrolysis can be divided into six different categories: fast pyrolysis, slow pyrolysis, intermediate pyrolysis, flash pyrolysis, vacuum pyrolysis, and ablative pyrolysis (Luo & Abu-Omar, 2017). Fast pyrolysis is the most frequently used method for producing biooils, having a residence time of only around 2 seconds and temperatures of around 500 °C (Obydenkova et al., 2017).

Depending on the type, lignin starts degrading at a temperature of around 150 °C, and continues gradually until about 1,000 °C, as seen in Figure 3.1. In comparison, during pyrolysis of biomass, the other two components, hemicellulose and cellulose, have pyrolysis windows between 210–300 °C and 300–380 °C, respectively.

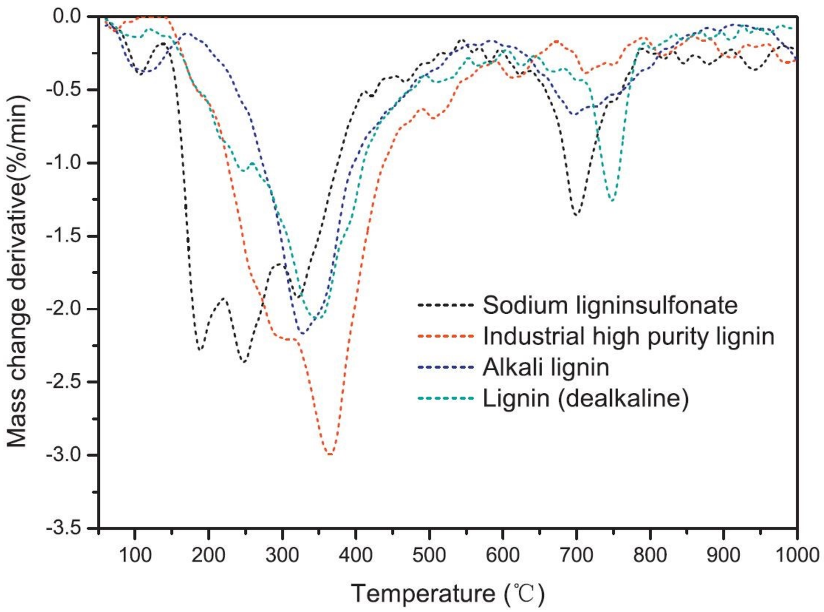


Figure 3.1. *Derivative thermogravimetric curves of different lignin types during pyrolysis at a gradual temperature increase of 10 °C min^{-1} (Zhou et al., 2013).*

The complexity of both the composition and the structure of the lignin molecules makes in particular, the selectivity of the desired fraction, and also quality management of the pyrolysis products, difficult. Factors such as moisture content, extraction process, reaction temperature and residence time all affect the yields and product quality of the pyrolysis process, and addition of catalysts may well be the key to making the hydrocarbon extraction from lignin more controllable and economically feasible (Luo & Abu-Omar, 2017). The challenging part is trying to model the decomposition of lignin, which involves activation energies for each reaction, controlling temperature-dependent subsequent reactions, as well as heat and mass transfer rates during the process. For instance, kinetic studies of Kraft and Alcell (organosolv) lignins showed that a higher heating rate of 15 °C min^{-1} increased the conversion rate to 65 and 57 %, respectively (Brebu & Vasile, 2010). For added context, Obydenkova et al. (2017) refer to several studies where the highest oil yields were 43–45 % on a dry basis, all of which were produced with pyrolysis at temperatures between 500 and 600 °C. Temperatures below 500 °C have shown to produce a more unstable biooil, with a tendency of re-polymerisation of the compounds, while temperatures higher than 550 °C accelerates unwanted secondary reactions that increase the gas yield (Obydenkova et al., 2017).

An important difference when comparing pyrolysis of lignin with the corresponding treatment of biomass, is that the biooil yields in general are lower for lignin. In addition, impurities like sugars and ashes found in lignin originating from an extraction process will also affect the yields and mixture of compounds obtained (Obydenkova et al., 2017).

Figure 3.2 shows a possible flow scheme for a fast pyrolysis plant using biomass as feedstock. The process flow is very similar to the setup needed for lignin pyrolysis, where the pre-treatment steps of chopping and grinding the biomass could be disregarded. In the scheme, hydrotreatment of the pyrolysis oil is also included, since it is assumed to be necessary to fulfil the requirements of a drop-in biofuel (Brown et al., 2013).

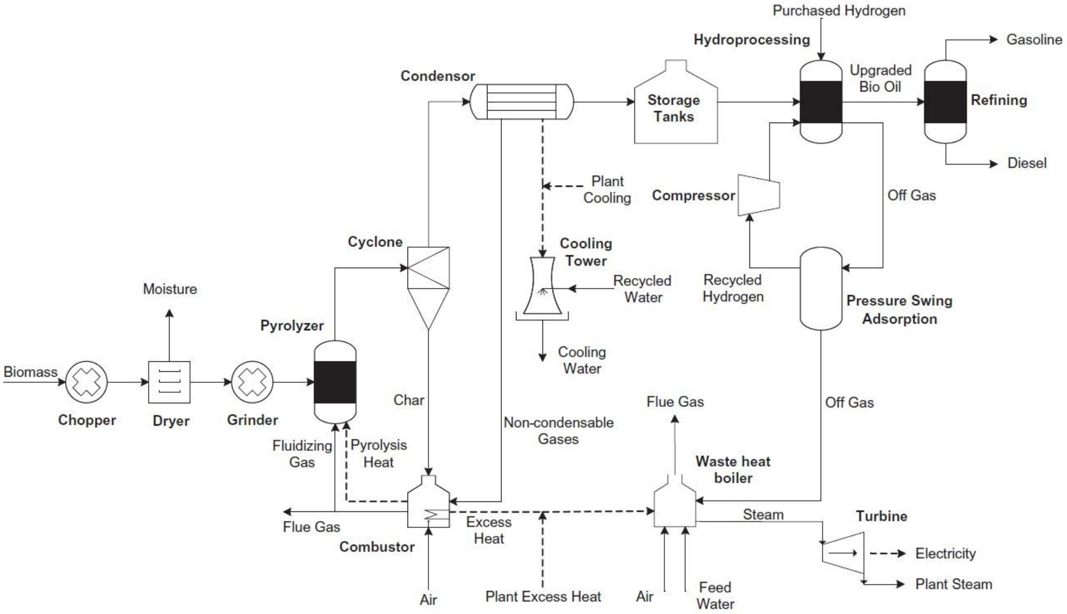


Figure 3.2. *Process scheme of biomass pyrolysis with hydroprocessing of the resulting biooil included (Brown et al., 2013).*

As Brebu & Vasile (2010), Kawamoto (2017) and Obydenkova et al. (2017) agree and conclude their studies with – the key to making a pyrolytic lignin fuel viable is the production costs associated with it. Since the relatively low-value fuel is meant to compete with and replace fossil fuels, separation of the compounds needs to be carried out cost-efficiently. In order to achieve this, the complex reactions that occur during pyrolysis need to be further studied and understood. While the raw biooil from lignin pyrolysis does have a somewhat high gravimetric heating value of 29.7 MJ kg^{-1} (Obydenkova et al., 2017), the oil is corrosive due to its oxygen content. Hsieh & Felby (2017) are suggesting that a catalytic upgrading step (e.g., hydrogenation) is necessary for the pyrolysis oil to meet the requirements of a drop-in fuel and to improve its stability.

Producing an emulsion with pyrolysis oil and diesel is also an option, which would not only increase the stability of the fuel, but also act as a particle reducer in the exhaust gases and increase its thermal efficiency. In addition, the surfactants needed to enable the emulsification could also be used to customise the viscosity of the resulting fuel (Hsieh & Felby, 2017). The relatively high costs of surfactants as well as the catalytic hydrogenation at, for instance, a petroleum refinery, will to a high degree increase the production costs of the fuel.

A recent study by Liu et al. (2020) shows that there are ways to circumvent the conventional catalytic hydrodeoxygenation which usually requires high temperatures and pressures up to ten times the atmospheric pressure. The multiphase hydrodeoxygenation method can be performed at temperatures below 100 °C, preventing tar and char formation on the catalyst, and a hydrogen pressure lower than 1 atm. The method resulted in an efficient oxygen-reduction while also increasing the hydrogen content of the bio-oils with the aid of platinum-on-carbon (Pt/C) catalysts (Liu et al., 2020). Despite the somewhat costly catalysts needed, the milder process conditions alone show that there is still room for improvement in terms of cost-cutting optimisation.

3.3 Gasification

The third process to be discussed in this study is gasification of organic materials at an elevated temperature. Relatively little emphasis has been put on gasification of isolated lignin, in comparison to the multiple studies that have been conducted on both gasification of pure, concentrated black liquor (BLG, a method developed by Chemrec AB), and gasification of a mixture of black liquor and up to 25 % pyrolysis oil (Jafri et al., 2020). The gasification product, syngas, consists of mainly carbon monoxide, hydrogen and carbon dioxide, with small traces of methane, hydrogen sulphide and ash being present in the syngas produced through gasification of lignin (Azadi et al., 2013).

The three different types of gasification methods for lignin valorisation that have been reported by Azadi et al. (2013) are:

i) Conventional gasification of black liquor with oxygen or steam present, resulting in a syngas with fractions of, for example, 33.6 % CO_2, 28.5 %

CO, 34.8 % H_2, 1.4 % CH_4, and 1.7 % H_2S obtained from a pilot process operating at 1,000 °C and 30 bar (Wiinikka et al., 2010).

ii) Capture of gas, mainly H_2 and CH_4, formed in high-temperature pyrolysis reactions at up to 900 °C, leaving behind a large fraction of solid residue. This method favours OL over KL, and the yields can be significantly improved with the aid of catalysts (Azadi et al., 2013).

iii) Supercritical water gasification that takes place at lower temperatures between 350–500 °C, but higher pressures of up to 250 bar to keep the water in its supercritical state. Due to water being used as the reaction medium, no drying is needed, which together with some differences in chemical properties benefits gasification of biomass over pre-extracted lignin. Catalysts also have a significant effect on the gas yields in this process, especially in terms of hydrogen production (Azadi et al., 2013).

The syngas produced from gasification needs scrubbing and sulphur-reduction before it can be used to produce crude methanol by addition of hydrogen. By distilling the crude methanol, stabilised methanol is obtained, from which petrol and liquid petroleum gas can be produced through the methanol-to-gasoline (MTG) process (Jafri et al., 2020). In addition to methanol, syngas can be valorised to a wide range of products, such as hydrogen, ammonia, and dimethyl ether, which could theoretically also be used as marine fuels, but with larger modifications needed to the existing engines.

According to Nielsen (2016), gasification is disadvantageous due to the high temperatures required and the resulting low yields of the process. The long chain of processing steps required to get from lignin or black liquor all the way to a usable fuel also require unreasonably large investments for the generated value of the end product. Also, the cost of catalyst for the syngas upgrading needs to be considered, with a price estimated at 11 EUR per ton methanol produced (Jafri et al., 2020).

3.4 Dispersion of ground lignin

Inspired by Orimulsion, a bitumen-in-water emulsified fuel, and coal-in-water slurries, both of which were previously common fuels used for combustion in different types of boilers. Their usage has declined mostly because of the pollution they cause, but there are also various issues relating to the solid particles in the fuels, such as wear and tear of the nozzles, which are an integral part of marine diesel engines.

The original Orimulsion mixture, Orimulsion 100, consisted of 70 % Orinoco bitumen, 29.6 % water and 0.2 % each of magnesium nitrate and nonyl-phenol ethoxylate. The purpose of the magnesium nitrate is to promote the stability of the emulsion and to prevent corrosion, while the non-phenol ethoxylate serves as a surfactant. When the new Orimulsion 400 mixture was introduced in 1998, the chemical additives were replaced with 0.13% tridecylalcohol ethoxylate, and 0.03% monoethanolamine as surfactant (Miller & Srivastava, 2000). Similarly, coal-in-water slurries are using a surfactant and a stabilising agent to form a liquid fuel out of pulverised coal and water. In the latter case, the coal particle diameters were generally around 100 µm, which makes it unusable in a marine diesel engine with fuel filter pores much smaller than that (Williams, 1990). The idea behind these fuels is to produce a dispersion that stays stable with the help of stabilising chemicals and surfactants, something that technically should be possible with lignin particles as well.

The first step of the process is size-reduction of the lignin particles, which can be achieved with several methods. For softwood KL isolated with the LignoForce System™, wet ball-milling was reported as the most efficient compared to two other industrially applicable methods: grinding and homogenisation. In addition, a smaller-sized medium and utilisation of a lignin that had never been dried before the milling also improved the efficiency. Despite an effective milling setup, the required milling time to bring the particle sizes down to well below 10 µm can be several hours – and even longer if dry ball-milling is used (Miao & Hamad, 2017).

Secondly, the right chemical additives for the dispersion must be selected. The milled lignin particles need to be kept from re-agglomerating, and later kept from precipitating in the medium used. Potential issues with flocculation, coagulation, creaming, and Ostwald ripening also need to be addressed in order to produce a stable dispersion. Conveniently, several types of lignosulphonates and oxidised, sulphomethylated hardwood KL have been suggested as potential dispersants in coal-water slurries and other dispersions (Konduri & Fatehi, 2018), which could decrease the number of chemical additives needed in the lignin dispersion.

3.5 Lignin separation-hydrotreatment

There is one more process in particular that deserves attention in this work. The method uses lignin extracted with the SunCarbon membrane separation process explained previously, and is currently in use in Sweden. There is, however, a distinct lack of technical information about the process available to the public, but the purified and isolated lignin is reported to be mixed half-and-half with vacuum gas oil in a mixture that is stabilised with the aid of an organic solvent. The mixture is transported to a traditional oil refinery where it is treated in an iso-cracker. The intermediate oil is first hydrotreated in the presence of a catalyst to remove oxygen and sulphur. The hydrodeoxygenation brings the oxygen content down below 5 %, which is a requirement for the subsequent cracking and isomerisation process that generates smaller hydrocarbon components in the diesel or petroleum range, that can eventually be used as a drop-in fuel (Jafri et al., 2020).

Because of the lack of essential details about the process, it is hard to estimate its feasibility. Currently, the vacuum gas oil is acquired from the oil refinery and transported back and forth to the Kraft pulp mill. The energy balances for a model mill by Jafri et al. (2020) shows that the biodiesel yield would be around 80 % of the lignin input, while also requiring as much hydrogen for the hydrotreatment process, of which over 80 % can be reused in the refinery as a natural gas substitute.

4 MATERIALS AND METHODS

The materials used in this study were limited to what was accessible through industry contacts and through regular chemical suppliers of the university. Both the materials and the methods used were therefore adapted according to the materials obtained.

4.1 Materials

4.1.1 Technical lignins

Various types of technical lignins were previously described on a deeper level in Chapter 2.2. Samples of five different lignin types (numbered 1 to 5 below) were acquired and are listed in order by acquisition date together with their respective material properties provided by the producer.

1. *Domsjö Lignin DA30*

This sample of lignosulphonates was provided by the producers themselves, Domsjö Fabriker Ab from Sweden. The alternative chemical name for their product is *Sodium Lignosulphonate* and can be identified with the CAS-No 8061-51-6. According to their MSDS, the concentration is over 95 % (Domsjö Fabriker Ab, 2019), and a few other relevant basic chemical properties provided can be seen in Table 4.1. In this study, the sample of Domsjö Lignin DA30 (seen in Figure 4.1), will be referred to as **DA30**.

Table 4.1. *Basic properties of Domsjö Lignin DA30 (Domsjö Fabriker Ab, 2019).*

Specification	Typical value
Lignin type:	Lignosulphonate
Appearance:	Brown, fine powder
Odour:	Mild
pH:	7.5–9.1, in a 10 % aqueous solution
Bulk density:	~600–700 kg/m^3

Figure 4.1. *Oven-dried (105 °C) sample of Domsjö Lignin DA30.*

2. *UPM BioPiva™ 100*

This sample of "purified, Kraft softwood lignin" originates from a sulphate pulp mill in the US, and was provided by UPM Biochemicals, Finland. The BioPiva™ 100 lignin will hereafter be referred to as **BP100**. Some relevant material data and properties of the lignin together with a picture can be seen in Table 4.2 and Figure 4.2, respectively.

Table 4.2. *Basic properties of UPM BioPiva™ 100 (UPM Biochemicals, 2020a).*

Specification	**Typical value**
Lignin type	Kraft lignin
Appearance	Dark brown powder
Solid content (105 °C)	65 %
Molecular weight, M_w	5.000 g/mol
Ash content (700 °C)	< 2 %
Storage stability (20 °C)	3–6 months

Figure 4.2. *Oven-dried (105 °C) sample of UPM BioPiva™ 100.*

3. UPM BioPiva™ 300

This sample of "purified, Kraft softwood lignin" is from a European mill, and was also provided by UPM Biochemicals, Finland. From this point onwards, the BioPiva™ 300 lignin will be referred to as **BP300**. Some relevant material data and properties of the lignin and an image to illustrate it can be seen in Table 4.3 and Figure 4.3, respectively.

Table 4.3. *Basic properties of UPM BioPiva™ 300 (UPM Biochemicals, 2020b).*

Specification	**Typical value**
Lignin type	Kraft lignin
Appearance	Dark brown powder
Solid content (105 °C)	63 %
Molecular weight, M_w	6.000 g/mol
Ash content (700 °C)	< 2 %
Storage stability (20 °C)	3–6 months

Figure 4.3. *Oven-dried sample of UPM BioPiva™ 300.*

4. BLN lignin

This lignin, seen in Figure 4.4, has been extracted from a novel pressurised hot water extraction (PHWE) process called **BLN**, invented by CH-Bioforce Oy, Finland. The lignin samples of this type will also carry the name of the process in this study. Since the lignin extraction process is yet to be standardised, no detailed specifications could be provided for this particular sample. The only details provided by the company are that birch was used as the raw material for this specific batch and that it is an *alkali lignin*.

Figure 4.4. *Oven-dried (105 °C) sample of BLN birch lignin.*

5. *Enzymatic hydrolysis lignin*

Lignin from an unnamed biorefinery was obtained through another project at Åbo Akademi. The product is yet to be sold on the market, and therefore very few technical details are known about the lignin. The biorefinery is producing mainly bioethanol from sawdust, with lignin as a waste stream. Enzymes are used in the hydrolysis step of the process to remove the lignin from the raw material, and the lignin samples (Figure 4.5) will accordingly be referred to as **EHL**, short for enzymatic hydrolysis lignin.

Figure 4.5. *Oven-dried (105 °C) sample of EHL.*

4.1.2 Marine fuels

The fuel samples listed in Table 4.4 were provided by Neste Oyj. All three are currently used in marine diesel engines and are all part of the Neste Marine™ 0.1 product group of marine fuels with a sulphur content less than 0.1 %. They also meet the requirements specified in the ISO 8217:2017 standard for marine fuels (ISO, 2017) and are free from FAME (Neste Oyj, 2017a).

In Figure 4.6 the difference in appearance can be seen, which is mainly caused by the different levels of residual oils they contain. DMA must, by definition, be free from residual fuel traces. Some traces are allowed in DMB – usually contamination from using the same means of supply as residual fuels. RMB, classed as a non-distillate, is of course affected by its large residual oil content, which also largely affects its viscosity at room temperature.

Table 4.4. *Low-sulphur marine fuels with notable product specifications compiled from details provided by Neste Oyj (2017; 2019a; 2019b; 2019c).*

Product grade	**Neste DMA**	**Neste DMB**	**Neste RMB**
Product type	MGO	MDO	Residual bunker oil
Viscosity at 40 °C (mm^2/s)	2–6	2–11	-
Viscosity at 50 °C (mm^2/s)	-	3.20–8.30 (calc.)	8–12 (Max. 30)
Density (15 °C) (kg/m^3)	820–890	Max. 900	Max. 960
Cloud point (winter/summer)	-5 °C/0 °C	-	-
Pour point (winter/summer)	-	6 °C/9 °C	Max. 30 °C
Storage temperature		20 °C	40 °C
Flash point	≥ 60 °C	≥ 60 °C	≥ 60 °

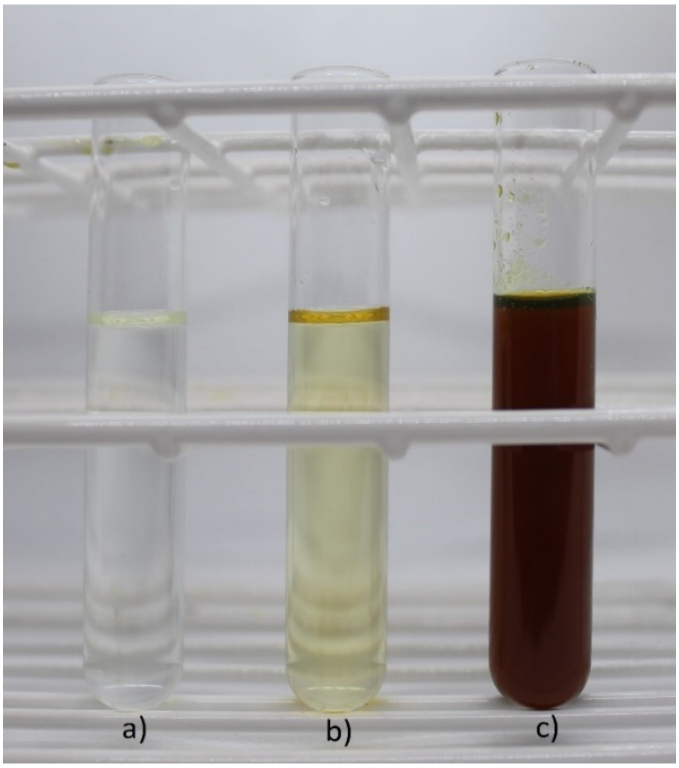


Figure 4.6. *The three marine fuels used for mixing fuel blends in this study: a) Neste DMA, b) Neste DMB, and c) Neste RMB.*

4.1.3 Solvents

The two solvents used in the solvolysis experiments were a technical grade (96 v-%) ethanol named ETAX B, produced by Altia Oyj, and a >99.8 % pure 'BAKER ANALYZED' methanol supplied by J.T.Baker, with a maximal H_2O content of 0.01 %.

4.1.4 Surfactants

The nonionic surfactant Span® 80 (CAS 1338-43-8) and nonionic detergent TWEEN® 60 (CAS 9005-67-8), both of which are trademarks of Croda International PLC, were chosen for emulsifying experiments based on diesel-ethanol emulsions reported in literature. Both were purchased from and delivered by Sigma-Aldrich, and some of their relevant properties have been compiled in Table 4.5.

Table 4.5. *Properties of Span® 80 and TWEEN® 60.*

Commercial name	**Span® 80**	**TWEEN® 60**
Chemical name	Sorbitan monooleate	Polyethylene glycol sorbitan monostearate
Molecular weight	428.62 g/mol	1309 g/mol (estimated)
HLB	4.3	14.9
Density (25 °C)	Not stated	1.044 g/mL

4.2 Methods

For the experimental part of the study, the two processes which were estimated to require the lowest production costs were pursued: 1) solvolysis of lignin, and 2) grinding or milling of lignin powder for dispersion into diesel oil.

First, the chemical properties and heating values of the lignins were assessed, to give an indication of which are the most suitable as a fuel raw material. Based on these results, it was decided that an emphasis should be placed on investigating the Kraft lignins – with additional limitations to the study, such as time and limited access to equipment, further steering the path of this project.

4.2.1 Elemental analysis

The elemental analyses in this work were purchased through a service internal to the Åbo Akademi University. Pre-dried (105 °C) lignin samples were measured at around 2 mg and analysed with a PerkinElmer Optima 5300 DV Optical Emission

Spectrometer (PerkinElmer, Inc., Waltham, MA, USA). As per common practise, the fractions of carbon, hydrogen, nitrogen, and sulphur were measured, while the oxygen content was assumed to make up for the rest and calculated by difference.

4.2.2 Bomb calorimetry

All gross calorific heating values, or higher heating values (HHVs), were measured using a Parr 1341 Oxygen Bomb Calorimeter combined with a Parr 1672 Thermometer (Parr Instrument Company, Moline, IL, USA). Samples of the lignin powders, both in the moist state they were delivered as well as dry, were pelletised with a Parr 2811 Pellet Press (Parr Instrument Company, Moline, IL, USA). Pellets of approximately 1 g were weighed and inserted into the bomb calorimeter at ambient temperature. The temperature difference caused by the combustion of the sample was measured and the calorimeter returned a figure with four decimals for the gross heating value.

The drying of the samples was carried out in an oven, with a temperature of 105 °C for 12 hours, after which most of the water was deemed to have evaporated.

4.2.3 Mixing and grinding

For the mixing of lignin into the various solvents, an IKA® T18 basic ULTRA-TURRAX high-shear mixer was used (IKA®-Werke GmbH & Co. KG, Staufen, Germany). The lignin was measured with a scale and slowly added to the beaker containing the continuously stirred mixture to avoid any clumping of lignin or clogging of the stirrer.

The same mixer was also used in the attempted production of a dispersion, where the lignin first had to be ground. The same methodology was used for the grinding, but even higher mixer speeds were used, requiring a larger beaker.

4.2.4 Filtration

Filtrations were carried out through vacuum filtration, using a filtering flask, a Büchner funnel, and Whatman filter papers, purchased from Sigma-Aldrich. With the filters in marine engine fuel systems usually being around 10 µm, a filter pore size of 8 µm was deemed as sufficient and Whatman filters of grade 40 with a diameter of 110 mm and a pore size of 8 µm, were used.

When all the lignin oil had visibly passed through the filter, the filter paper and all lignin residue around the funnel was carefully placed in a ceramic crucible and oven-dried for 12 hours at 105 °C until all the moisture and remaining solvent had evaporated. The weight of the remaining lignin and char was then weighed to calculate the estimated lignin content of the produced lignin oil.

4.2.5 Particle size measurements and ultrasonication

The equipment used for all particle size measurements was a Mastersizer 3000 (Malvern Panalytical Ltd, Malvern, Worcestershire, UK). A small sample of the dispersed lignin blend was added to the continuously stirred medium, in this case distilled water, until the obscuration reached the required range, in this case around 15 %. For the ultrasound treatment, the in-built ultrasonic probe was used. The maximum effect of the probe was 40 W and it was used at full capacity during all the tests.

4.2.6 Emulsification with surfactants

The effect of surfactants on emulsification of produced lignin oil with the marine fuels was carried out by first mixing the two surfactants in different ratios to achieve various HLB values. Both surfactants were first measured and mixed in 60 °C, after which the lignin oil was added, and the mixture was stirred for 5 minutes. After this, DMA was added to the mixture and stirred for another 10 minutes with the high-shear mixer. The emulsion was then left untouched and the stability of it was examined visually.

5 RESULTS AND DISCUSSION

The following results have been compiled from the findings of the experiments carried out as a part of this study. Some results were directly measured, and others were results of calculations explained where applicable.

5.1 Bomb calorimetry

The gross heating values of the different lignin types measured with a bomb calorimeter can be seen in Table 5.1. The lower heating values, i.e., the net calorific heating values, have been calculated with the help of formulas 5-1 and 5-2, using the results for hydrogen content from the elemental analysis listed in Table 5.3.

$$m_c = 9 \cdot m_{dm} \cdot x_H, \tag{5-1}$$

where:

m_c = mass of condensate (kg)

m_{dm} = mass of dry matter (kg)

x_H = hydrogen fraction of a matter (% dry matter)

$$LHV = HHV - (m_w + m_C) \cdot \Delta H_{vap,w}, \tag{5-2}$$

where:

LHV = lower heating value (MJ kg^{-1})

HHV = higher heating value (MJ kg^{-1})

m_w = mass of water (kg)

m_c = mass of condensate (kg)

$\Delta H_{vap,w}$ = enthalpy of vaporisation (2,453.6 kJ kg^{-1} water at 20 °C).

Table 5.1. *Heating values of lignin types tested with a Parr 1341 Oxygen Bomb Calorimeter.*

Lignin sample	Moisture content	HHV (MJ kg^{-1})	LHV (MJ kg^{-1})[a]
DA30	2.5 %	17.1	- [b]
	0 %	17.6	- [b]
BP100	33.7 %	20.3	18.7
	0 %	26.9	25.7
BP300	36.2 %	17.9	16.3
	0 %	27.1	25.9
BLN	4.2 %	25.8	24.4
	0 %	26.5	25.3
EHL	51.2 %	13.1	11.2
	0 %	24.9	23.5

[a] *Calculated with equations 5-1 and 5-2.*

[b] *The lignosulphonates (DA30) were not tested with EA, thus no LHV could be calculated.*

Large fluctuations can naturally be noticed for the heating values of the undried samples due to the variation in moisture content. For the dried samples, the results are more converged towards an expected value around 27 MJ kg^{-1}. The values for EHL are a fraction lower, which can be explained by the higher ratio of oxygen to carbon. Lastly, the HHV of DA30 was surprisingly around 35 % lower than the Kraft lignins; impurities like hemicelluloses, and a higher sulphur content, reported by Aro & Fatehi (2017) are expected to be the reason behind this.

In addition, also the HHV of some of the fuel samples were measured and illustrated in Table 5.2. Noteworthy is that the ethanol used was an impure 96 vol-% technical ethanol (ETAX B). The hydrogen content in the fuel oils and ethanol were estimated at 13.5 % and 13.0 %, respectively, for the calculations of the LHV.

Table 5.2. *Heating values of fuels tested with a Parr 1341 Oxygen Bomb Calorimeter.*

Fuel sample	Moisture content	HHV (MJ kg^{-1})	LHV (MJ kg^{-1})[a]
Neste DMA	0 %	45.1	42.1
Neste DMB	0 %	45.4	42.4
Neste RMB	0 %	45.4	42.5
ETAX B	4 %	27.2	24.3

[a] *Calculated with equations 5-1 and 5-2.*

5.2 Elemental analysis

The mean values of three tests of each pre-dried sample have been compiled in Table 5.3. The sulphur content of the Kraft lignins BP100 and BP300 were slightly lower than expected, while the BLN and EHL lignins were proven to be sulphur-free.

Table 5.3. *Results from elemental analysis of four different lignins with mean values (μ) and standard deviations (σ).*

	C (% w/w)		**H (% w/w)**		**N (% w/w)**		**S (% w/w)**		**O (% w/w)**[a]	
Lignin sample	*μ*	*σ*	*μ*	*σ*	*μ*	*σ*	*μ*	*σ*	*μ*	*σ*
BP100	64.78	0.20	5.61	0.03	0.30	0.04	1.40	0.02	27.91	0.28
BP300	64.64	0.63	5.59	0.07	0.15	0.01	1.26	0.16	28.35	0.84
BLN	64.45	0.04	5.76	0.02	0.18	0.01	0	0	29.61	0.05
EHL	59.43	0.09	6.21	0.08	0.69	0.01	0	0	33.67	0.16

[a] *Calculated by difference.*

5.3 Solvolysis

The poor solubility of Kraft lignin in ethanol and methanol was confirmed by the experiments carried out. The lignin-to-solvent ratio had to be carefully selected to avoid clumping and agglomeration, and the upper limit of lignin to solvent was found to be approximately 10 % at the initial mixing phase.

The filtration of undissolved lignin and char also proved to be challenging when ethanol was used as the solvent. Filter clogging was a reoccurring theme due to the small pore sizes and large amounts of residue needing to be removed. To solve this, continuous filtration should be modelled, where residue is either frequently removed from the filter surface, or the filtering is carried out in subsequent steps with a decreasing pore size. Filtration was not a problem when methanol was used as the solvent, due to most of the lignin residue agglomerating into a large piece of mass, which meant that most of the filter pores were kept open.

To test the difference in the solubilisation degree of lignin in the solvents at ambient conditions, 13.5 g of BP100, containing 9.0 g dry lignin and 4.5 g water, was added to 100 g of ethanol and methanol under continuous stirring with a high-shear mixer.

The mixtures were stirred for 10 minutes, and afterwards filtrated through a Whatman filter of grade 40 with a pore size of 8 µm. The filter and all the lignin residue, including what was obtainable from the sides of the stirrer and the flask, were oven-dried for 12 hours in 105 °C to evaporate all liquids. The lignin content left in the produced lignin oils were calculated based on the weight of the residues, resulting in estimated lignin conversion rates of 48 % in ethanol and 52 % in methanol.

With a lignin content in the produced oils estimated at only around 5 %, the solvents were evaporated at a temperature above their respective boiling point. At a lignin content of around 30–35 %, the first signs of precipitating lignin became visible for both oils. At a 1:1 lignin-to-solvent ratio, seen in Figure 5.1, the oils were still fluid and easily pumpable, without much noticeable precipitate. However, soon after, the oil dried up and set at a lignin content of approximately 55 w-%, most likely because the methanol at the surface got exposed to air. This could largely be because of the small volume of oil that was left, and could possibly be avoided if the evaporation container was sealed from air and if the volume of oil was higher, making the relative change in lignin content easier to control.

The lower conversion rates or solubilisation degrees obtained, compared to the results of Kouris et al. (2019), can be explained by the difference in process temperatures, since the conversion rates have been reported to increase with higher temperatures. It was also proven that methanol has a higher solubilisation degree for Kraft lignin, even at 20 °C, and no charring is expected to occur at this low temperature.

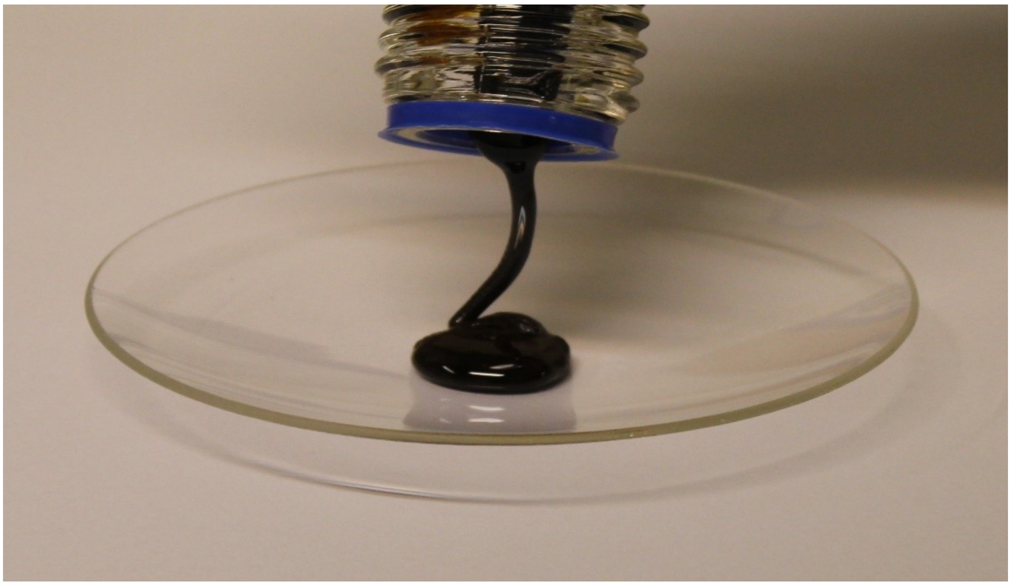


Figure 5.1. *Lignin:methanol oil with 50 % each produced through solvolysis, filtration and lastly evaporation of the solvent.*

5.4 Grinding and dispersing

Continuous high-shear mixing of the lignin was carried out in water in an attempt to grind the lignin particles smaller and to monitor the change of particle sizes in the dispersion. An example of the changes can be seen in Figure 5.2, where BP100 was mixed at a high rotation frequency for 10, 30 and 60 minutes. The results show that it is possible to grind the lignin particles with a high-shear mixer until a particle size that is viable in marine fuels is achieved. However, it took 60 minutes to accomplish a yield of 90.5 % where the particles were under the size of 10 µm. This is only an increase of 14.1 % from the yield obtained after 10 minutes of high-shear mixing, meaning the efficiency is remarkably low and requires an unreasonable amount of energy.

Ultrasonic treatment was also investigated, with the effect ultrasonic cavitation has on lignin agglomerates being of particular interest. As seen in Figure 5.3, a 5-minute ultrasonic treatment with the inbuilt 40 W ultrasound probe had a significant effect on the particle sizes, decreasing the size around 20 % across all cumulative distribution ranges. In this case, Dx 90, Dx 50 and Dx 10 are the percentiles below which a certain volume of the sample is smaller than. Despite being a costly supplementary equipment, an ultrasound probe has been proven to yield extraordinary results when it comes to disintegrating lignin agglomerates.

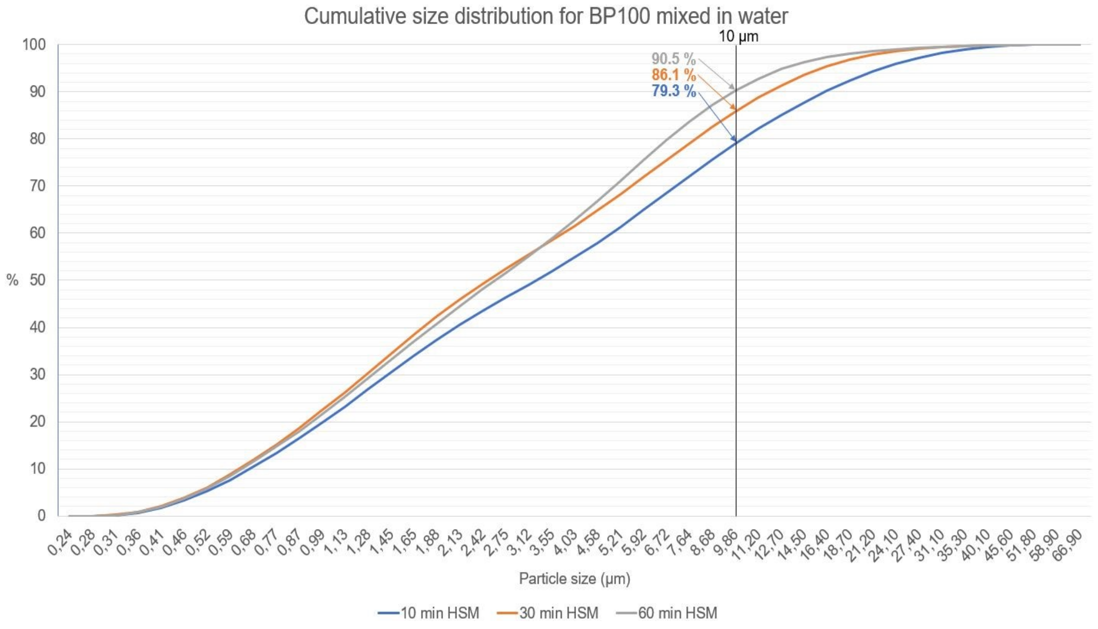


Figure 5.2. *Cumulative particle size distribution of Kraft lignin BP100 in water after different time spans of high-shear mixing.*

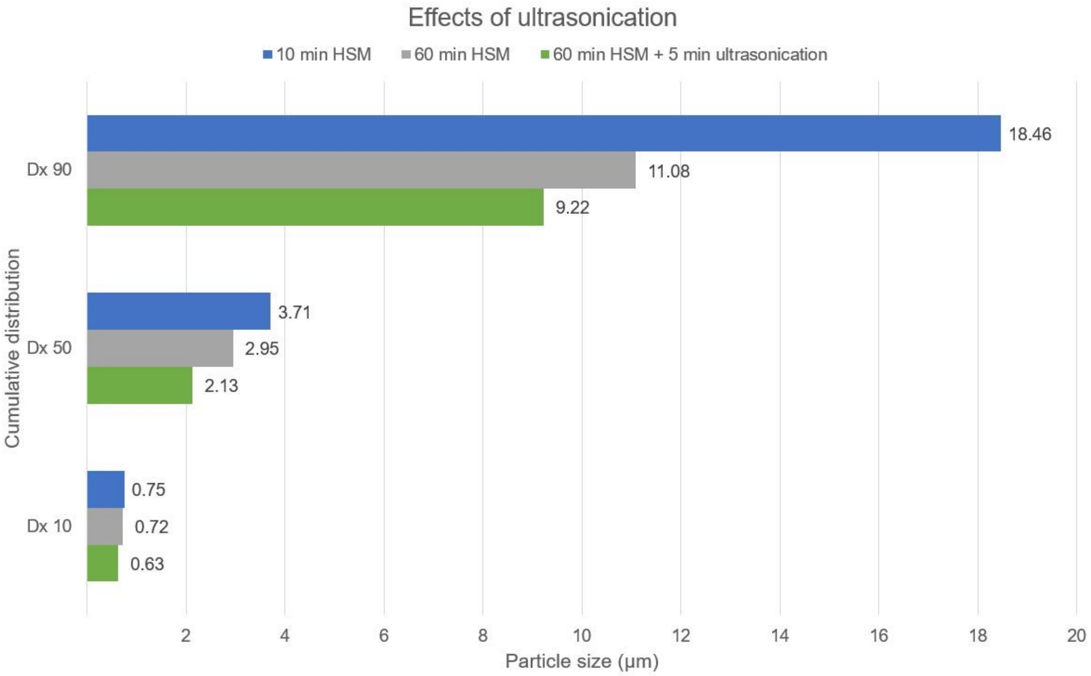


Figure 5.3. *Effects of ultrasonication on BP100 in water mixed in water.*

5.5 Emulsification tests

For the emulsification experiments, a lignin oil with 30 % lignin content and with ethanol as the solvent had been prepared through solvolysis. In the first test, using Span® 80 (HLB 4.3) in an emulsion with the lignin oil:Span® 80:Neste DMA ratios of 2.5:1:25, a seemingly stable fuel was obtained. The first signs of phase separation could be seen after 15 minutes, and as seen in Figure 5.4, all of the lignin oil had precipitated after just 24 hours.

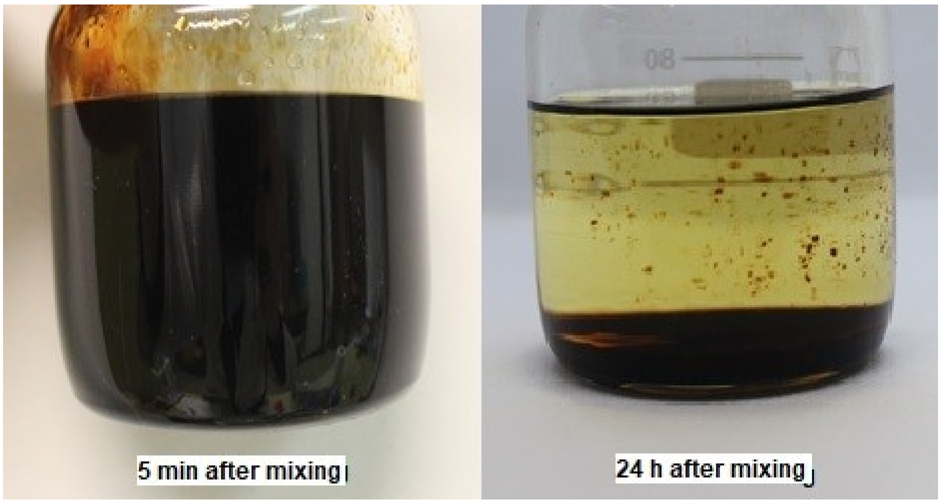


Figure 5.4. *Lignin oil-Neste DMA emulsion with Span® 80 as surfactant.*

Another test was a mixture of 3.80 g TWEEN® 60 and 10.24 g Span® 80, resulting in a HLB value of 7.2. The surfactant mixture was first mixed with 12.33 g (ethanol-based) lignin oil, after which 34.82 g of Neste DMA was added. The stability improved significantly, with the resulting emulsion after 12 hours seen in Figure 5.5. While precipitated lignin oil can be seen on the bottom of the beaker, it is visibly clear that a part of the lignin oil is still dispersed in the DMA.

From these results, it is hard to draw any conclusions whether it is the difference in HLB value or higher ratio of surfactants used that caused the improvement in stability. Since especially the small lignin particles left in the lignin oil are seen to precipitate, assumptions can be made that a different type of surfactants might be needed to stabilise the lignin in the emulsion.

Figure 5.5. *Lignin oil-Neste DMA emulsion with a mixture of surfactants TWEEN® 60 and Span® 80 (HLB 7.2) after 12 hours.*

6 SENSITIVITY ANALYSIS

Without a full-scale lignin fuel production process yet in commercial use, there is very limited information available to base investment costs, like CAPEX and OPEX, on. Therefore, this analysis will serve merely as a simplified version to illustrate proportions between different fuels and admixtures. In addition, there are also a range of variables that have a remarkable impact on the profitability of the fuel production. Some of the most prominent of these are:

a) lignin market price,
b) cost of solvent used,
c) lignin oil production costs,
d) oil price and its future development,
e) lignin-to-solvent ratio in the lignin oil, and
f) possible cost of emission allowances (or "*carbon taxes*").

A large part of the technological parameters in this analysis will be based on the solvolysis process by Kouris et al. (2019; 2020), with heating values obtained in the experimental part of this study also utilised.

6.1 Prominent variables and parameters

Lignin market price

The value of lignin is hard to estimate because of the uncertainty in future availability and demand that is largely dependent on new technologies that could utilise lignin. The isolation and production costs of around 200 EUR per tonne KL suggested by Culbertson (2017) was deemed as a realistic baseline production cost to use in these calculations. In reality, any sales price exceeding the current revenue of the energy produced from combustion of the lignin plus any costs related to the lignin extraction processes could spark an investment interest from the mills' point of view, especially if a long-term market demand can be guaranteed. On the other hand, Castro Garcia, Cheng & Cross (2020) are suggesting a lignin value as low as 50 USD per tonne for low-purity KL, which does give hope for even lower production costs, but the effects of the inferior quality would have to be further assessed.

Cost of solvent used

Methanol and ethanol are deemed to be the preferred solvents in this work due to their favourable production capacity and more adequate pricing. Methanol prevails over ethanol with both a lower and a more stable market price and a higher solubilisation degree shown by experimental research (Kouris et al, 2019). It also shows a capability to solubilise lignin molecules with a higher M_w and would therefore be usable for a wider range of technical lignins as well as lignocellulosic feedstocks (Kouris et al., 2020).

Methanol has a more controlled market situation, with the world’s largest producer Methanex Corporation publicly posting their regional contract prices that are adjusted quarterly or monthly. The average monthly price in Europe for the last decade is 339 EUR per tonne, and reached the level of 410 EUR per tonne for Q2 of 2021. The North American non-discounted reference price was 450 EUR per tonne for May 2021, while the equivalent price for the Asia Pacific region was 357 EUR per tonne (Methanex, 2021).

Ethanol, on the other hand, is a chemical with very large geographical fluctuations in price, largely dependent on factors like the size of the petroleum industry in the country, local taxation, and how well the country or region is doing economically. These factors are more of a rule of thumb, with some price examples listed in Table 6.1 showing the wide range of pricing.

Table 6.1. *Ethanol prices for selected countries on April 26th, 2021 (GlobalPetrolPrices.com, 2021).*

Country	**Ethanol price (l^{-1})**	**Ethanol price (t^{-1})**	**Ethanol price (GJ^{-1})**
USA	0.54 €	681 €	25.5 €
Thailand	0.57 €	720 €	27.0 €
Brazil	0.58 €	736 €	27.6 €
France	0.71 €	895 €	33.5 €
Sweden	1.13 €	1,433 €	53.7 €
Spain	1.50 €	1,906 €	71.4 €

While the average price for these countries, around 0.84 EUR per liter, could be used as a baseline global average, the feasibility of a lignin fuel with ethanol used as the solvent will have large geographical discrepancies. This is why methanol is preferred as a lignin oil solvent, despite some unfavourable characteristics like higher oxygen content, lower heating value and being a poisonous substance.

Lignin oil production costs

Again, the production costs are hard to estimate without a production method yet in large-scale use. Using the IDEALFUEL target cost of 500 EUR per tonne for a bio-HFO produced with solvolysis using methanol as the solvent, a production cost of around 250 EUR per tonne would be adequate with the current methanol price, a lignin price of 200 EUR per tonne and an optimal lignin:solvent ratio of 70:30 (Green Car Congress, 2020).

From a price per energy equivalent perspective, this is, however, still almost twice the price of fossil fuels, mainly because of the low heating value of methanol. The energy content here is purely based on the combined value of the methanol and lignin fractions, and does not take into consideration the possible improvement that a decrease in mainly the oxygen content (e.g., through hydrodeoxygenation) could induce.

Another aspect that is important to note is that the cost of both solvent and lignin could be optimised if both were to be produced on-site in, for instance, a biorefinery.

Oil price and its development

The fuel prices used in this analysis were collected from Ship & Bunker's World Bunker Prices. The prices reported as "global average bunker price" were used, despite the largest harbours offering fuels at lower prices. While the recent development in oil prices has been heavily affected by the COVID-19 pandemic, the prices are already similar to what they were before the pandemic, despite the world economies having yet to fully recover.

The marine fuel prices as of May 5th, 2021 are listed in Table 6.2, and are selected as being a good indicator of future oil prices – despite industrial production still being in a post-pandemic recovery stage. With the new IMO 2020 regulations stepping in at the start of 2020, historical prices are also unlikely to reflect future prices, but a higher demand of low-sulphur fuels is a natural consequence that should be acknowledged.

Table 6.2. *Marine fuel prices for selected countries on May 5th, 2021 (Ship & Bunker, 2021).*

Fuel type	Sulphur content	Fuel price (t^{-1})	Fuel price (GJ^{-1})
IFO 380	< 3.5 %	354 € [a]	9.1 € [a]
MGO	< 1.5 %	517 € [a]	12.1 € [a]
VLSFO	< 0.5 %	442 € [a]	10.8 € [a]
LSMGO	< 0.1 %	447 € [b]	10.4 € [b]
ULSFO	< 0.1 %	432 € [b]	10.0 € [b]

[a] *Global average bunker price.*
[b] *Rotterdam bunker price.*

Lignin-to-solvent ratio

The lignin-to-solvent ratio will not only be dependent on the method or process used, but also for example the solubilisation degree of the solvent. For the baseline scenario, the 70:30 lignin:methanol ratio that Kouris et al. (2019) reported will be used.

For solvolysis with ethanol as the solvent, a 50 % lignin ratio was chosen as the baseline estimate. This lower ratio will of course also be heavily reflected in the competitiveness of the fuel prices.

CO_2 emissions allowances

For this simplified analysis, only the CO_2 emissions from combustion of the different fuels have been used. In reality, all emissions generated throughout the production processes as well as from transportation should also be considered in a fuel life-cycle analysis, but in this study all costs related to these have been included in the estimated production costs.

In the calculations, the amount of carbon dioxide emissions were estimated to be 3.2 tonnes CO_2 per tonne of fuel for all the fossil fuels, while 1.91 and 1.37 tonnes CO_2 per tonne were used for ethanol and methanol, respectively. In addition, all bioproducts, such as bioethanol, biomethanol, and lignins were considered to cause no emissions that would require CO_2 allowances. The cost of bioethanol and biomethanol was, however, estimated to be worth a premium of 15 % added to the cost of fossil-based equivalents. This was mainly based on the 11–12 % fee added to the cost for emissions allowances needed for combustion of the solvents.

As for the price of emissions allowances, 40 EUR per tonne CO_2 equivalent was used as a baseline scenario for if, or rather when, a possible emissions trading system will be implemented on the seas.

6.2 Analyses of different scenarios

The first analysis will use the possible implementation of emission allowances as the variable. For the baseline scenario seen in Figure 6.1, with a lignin oil production cost of 250 EUR per tonne, a lignin price of 200 EUR per tonne, and a methanol price of 410 EUR per tonne, a cost per EUA of 160 EUR is suggested to make a lignin-biomethanol oil with 70 % lignin content directly competitive with the price of IFO 380. If fossil-based methanol were to be used, the corresponding cost would be at 190 EUR per EUA due to the emissions caused from combustion of the methanol fraction. A full insight into the data used for these calculations can be seen in Appendix I.

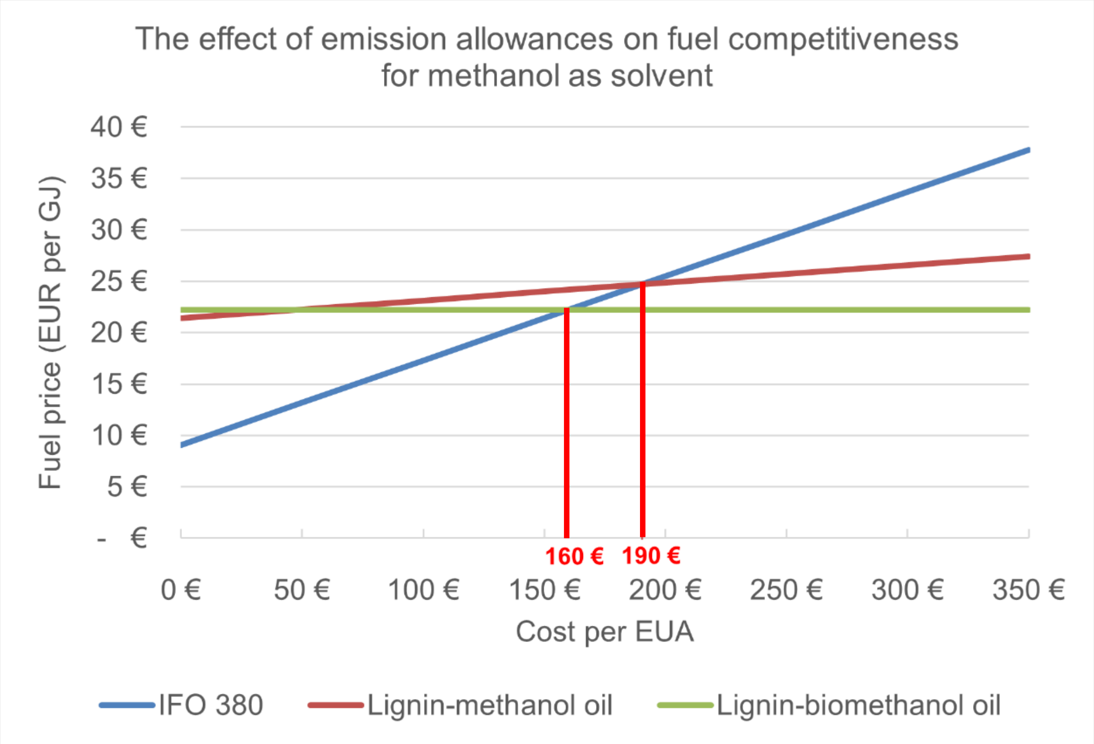


Figure 6.1. *Sensitivity analysis for BP100 solubilised in methanol and biomethanol versus IFO 380.*

To illustrate the vast differences that could be influenced by selection of solvent, Figure 6.2 shows the corresponding scenario for a lignin-ethanol oil with Sweden's ethanol price level. The only other difference is the solubilisation degree of BP100 in ethanol, estimated at 50 % in this case. The differences are remarkable, with the cost per energy equivalent being a multiple of the lignin-methanol oil cost and the cost of EUA almost needing to triple in order for the fuel to be directly competitive.

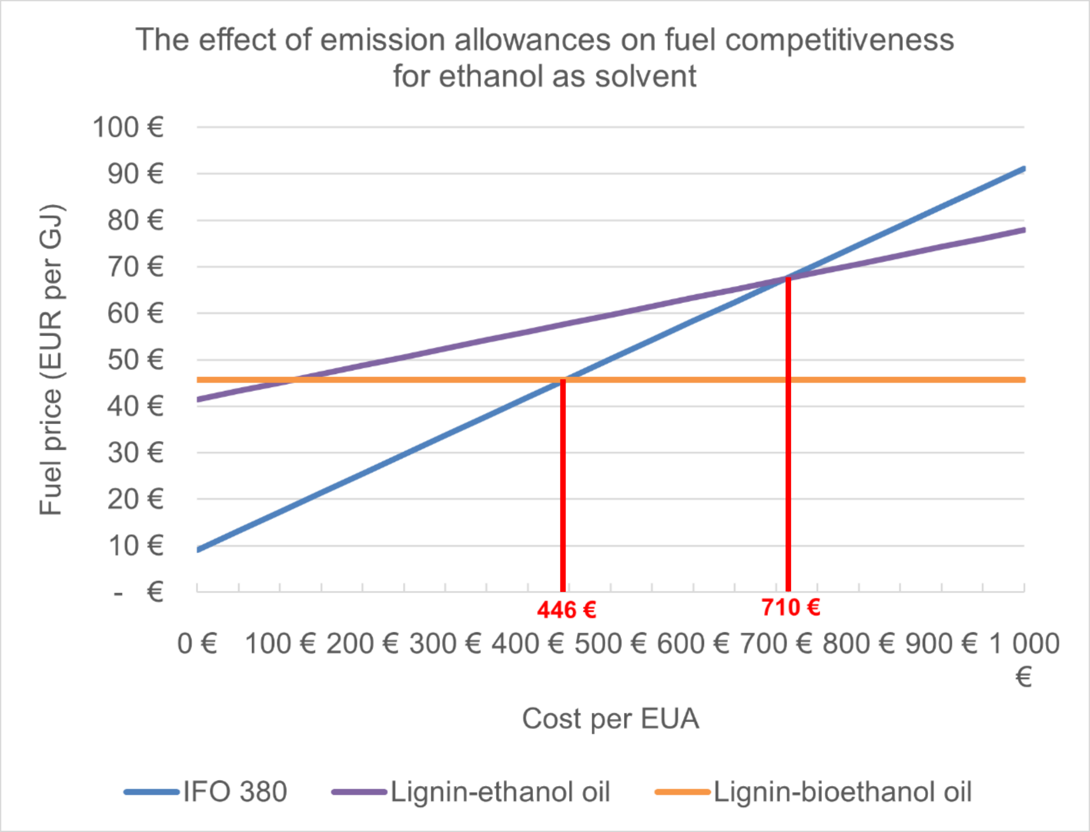


Figure 6.2. *Sensitivity analysis for BP100 solubilised in ethanol and bioethanol versus IFO 380.*

In Table 6.3 other marine fuels have been listed, with the price per unit of EUA that would be required in order for the cost to be equal to the corresponding lignin oil.

Table 6.3. *Required cost per EUA for 70 w-% lignin oils to be equal to fossil fuels.*

Fossil fuel	**Lignin-methanol**		**Lignin-biomethanol**	
	EUA unit price	**Fuel cost (GJ^{-1})**	**EUA unit price**	**Fuel cost (GJ^{-1})**
IFO 380	190 €	24.7 €	160 €	22.2 €
MGO	162 €	24.2 €	135 €	22.2 €
VLSFO	175 €	24.4 €	135 €	22.2 €
LSMGO	193 €	24.7 €	159 €	22.2 €
ULSFO	200 €	24.8 €	164 €	22.2 €

Another aspect is the potential to use the lignin oil as a drop-in fuel, and the reductions in CO_2 emissions it could lead to. Using the baseline price per EUA of 40 EUR, the results seen in Figure 6.3 show that the price increase is significant if higher reductions in CO_2 emissions are desired.

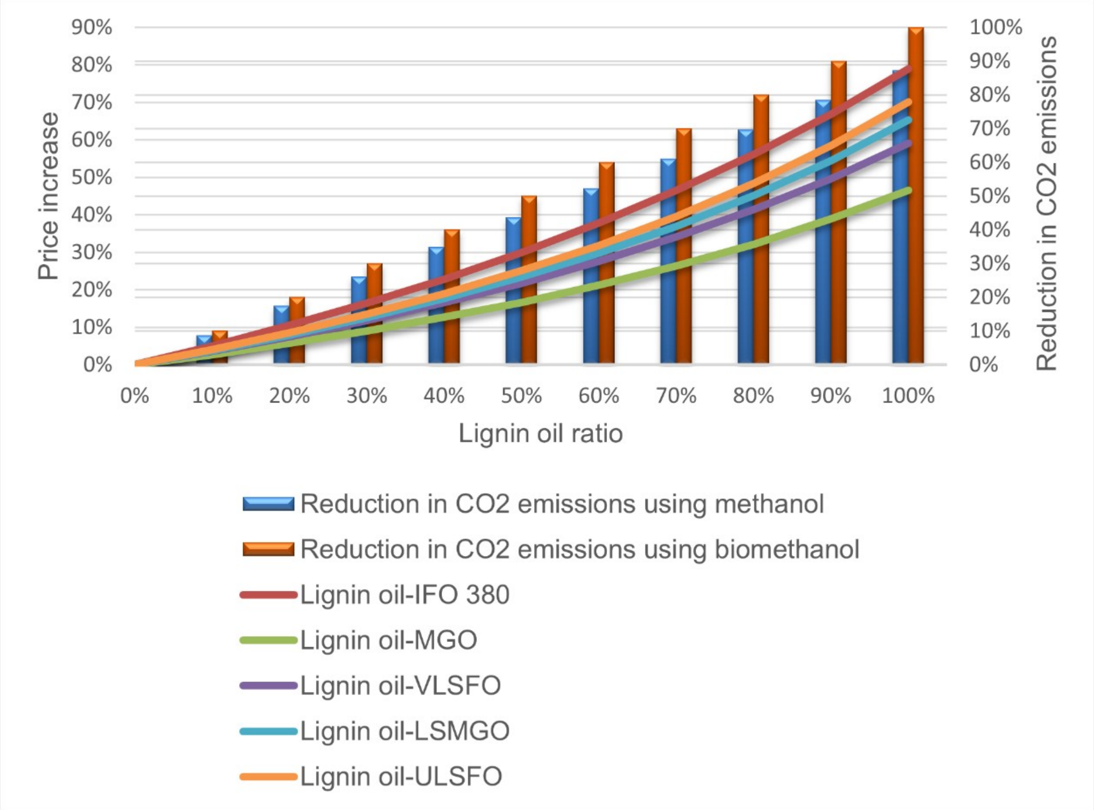


Figure 6.3. *Price increase and reductions in CO_2 emissions that the different ratios of lignin oil used as a drop-in fuel in the selected marine fossil fuels.*

From the results shown above, it is clear that an economically competitive lignin fuel cannot be produced with the baseline figures influenced by external factors used in this analysis. The obvious areas where cost-cuts can be made are the 'internal' processes of lignin extraction and the fuel production costs. For the lignin oil to become directly competitive with the current marine fuels without any emission allowances needed, the combined cost of these two posts would have to be cut down by two-thirds, i.e., down to a lignin cost of 100 EUR and a lignin oil production cost of 50 EUR. This is an unlikely scenario, with the hydrodeoxygenation process alone costing more than the total production costs allowed. Therefore, a conclusion can be made that external incentives, such as emission allowances or a "carbon tax" will be needed to even out the playing field and to make lignin fuel production an enticing alternative.

7 SAFETY

Lignin *per se* is not considered hazardous or toxic, but for instance residue from the pulping or isolation processes might contain potentially harmful chemicals and the lignin should therefore be handled with care and according to the producer's instructions (MSDSs). The biggest risk with lignin is considered to be dust explosions. Like most dry powders of organic materials, a spark or heat source could ignite the dust and cause an explosion if the levels of dust in an enclosed space get over a certain limit. In addition, oxygen would also need to be present to facilitate the combustion.

This risk is usually mitigated by handling and storing the lignin with a certain degree of moisture, as opposed to fully dried. This is why UPM are selling their BioPiva™ lignins with a moisture content of around 35 %, and why Domsjö Fabriker's DA30 lignosulphonates contain about 5 % moisture. Furthermore, UPM has set 30 g m^{-3} of dust as the upper limit in their BioPiva™ MSDSs to minimise the dust explosion risk.

With the somewhat strict ATEX regulations for explosive materials on ships and vessels (2014/34/EU), recommendations suggest that handling of lignin should be avoided onboard. The lignin fuel could instead be produced ashore before it is transferred to the ship's tanks. In this scenario, the safety of handling and storage would have to be assessed based on the solvent used and the properties of the lignin fuel.

8 CONCLUSION AND RECOMMENDATIONS

The objective of this study was to investigate what kind of methods there are for utilising lignin as a biofuel in the marine sector, and if any of them are economically viable. No processes were found to be directly competitive with fossil fuels at the current crude oil prices and with the current lack of maritime regulations for carbon dioxide emissions. However, a few methods were identified as having the potential to become more competitive in the future.

The methods investigated in this study took into account that lignin-based fuels can be separated into four different groups; solid lignin and chars, liquid fuels from depolymerisation processes and subsequent chemical modifications, hydrogen produced through lignin gasification, and synthetic alcohols like methanol produced from gasification syngas. While optimal conditions for solvolysis of lignin in a polar organic solvent only requires a temperature of around 200 °C, the more mature technologies of pyrolysis and gasification have process temperatures of 300 to 600 °C and 700 to 1,000 °C, respectively. Despite the vastly different process conditions, several of the processes are reported to be capable of producing usable lignin fuels at similar costs.

As lignin was found to have a gross calorific heating value of up to 27 MJ kg^{-1}, its price from an energy equivalent point of view, around 8 EUR GJ^{-1}, is actually lower than the one of fossil fuels. Utilisation of solid lignin in marine diesel engines would, however, require highly energy-intensive and low-efficient wet ball-milling and a mixture of surfactants, meaning that optimisation and further research into advanced surface chemistry is needed to be able to assess the feasibility of this method.

Many other processes of utilising lignin as a fuel have been previously researched, but very few have reached a stage of commercial production as of yet. Jafri et al. (2020) reports a production cost as low as 22 EUR per GJ for drop-in biofuels produced either through lignin separation followed by a two-step hydrotreatment process in a vacuum gas oil, or through gasification of black liquor with a subsequent catalytic synthesis of the produced syngas. These costs are in line with the target of below 500 EUR per tonne of fuel beyond 2030 that the EU-funded project *IDEALFUEL* have set, using a two-step process including solvolysis and hydrodeoxygenation to form a biogenic heavy fuel oil that can be used as a drop-in fuel.

The two most prominent scenarios for producing a competitive lignin fuel are suggested to be either a biorefinery that utilises lignocellulosic biomass to produce both ethanol and lignin, or lignin extraction from the black liquor of a sulphate plant, and at the same time increasing the pulp production capacity by debottlenecking the recovery boiler. While biorefineries are more of an upcoming trend for the future, implementation of a fuel production facility at the many sulphate plants across the world is something that could be done today.

To improve the properties of a lignin fuel, oxygen removal from the resulting lignin oil is essential according to most studies. This can be achieved through catalytic hydrotreatment processes like hydrodeoxygenation, or with novel technology like catalysts engaging in the solvolysis process, lowering the oxygen content as much as 50 % (Nielsen, 2016). Sulphur removal is expected to be needed for sulphurous lignins like KL, since the sulphur is described as "poison" to most catalysts. More research is suggested to be carried out in the fields of catalysts used in these processes, and alternatively, into a deeper level of surfactants that could be used to stabilise a blend of fossil fuels and biofuels. Easy access to an existing petroleum refinery with equipment already in place for hydrotreatment processes would also decrease the CAPEX needed.

A part of the problem with producing a fuel from biomass is that the hydrogen used in the commonly required hydrotreatment processes should also be renewable for the end product to be classed as a fully *green* biofuel. So called "black hydrogen" produced from fossil-based natural gas has a high GHG footprint of 87.3 g CO_2 equivalent per MJ LHV. The high investment costs needed for electrolysers do however make cost-competitive hydrotreatment with renewable hydrogen unlikely in the foreseeable future. Hydrotreatment of lignin with electrolysis H_2 is estimated to cost about 50 % more but would instead double the GHG savings (Jafri et al., 2020).

Some factors to keep in mind for optimisation and streamlining the process is the choice of raw materials. Hardwood would be preferred over softwood, since the lignin produced from this source has a lower M_w, which enhances the degree of solubilisation. Out of the lignin types currently available at amounts worth mentioning, the sulphur-free types of soda and organosolv lignin would be preferable, due to the advantages and benefits the lack of sulphur can give; circumventing the problems with catalysts that the sulphur could cause, as well as being able to compete with the higher-priced low-sulphurous fuels on the market.

Location-wise, it would be optimal for the plant to be located at the waterfront with an adjacent harbour. Ships regularly visiting the harbour could then be the first ones to switch over to using the new fuel, minimising transportation costs and ensuring a smooth market introduction.

For a lignin fuel to become competitive, a mixture of external incentives and optimisation of the existing production processes is required. The feasibility also depends largely on if a fuel that is compatible with the current engines and fuel infrastructure can be produced, or if the engines will have to be changed and adapted to suit the fuels. A lignin fuel that is usable in the current engines is more likely to be attractive to larger markets, and shipowners are assumed to be more willing to pay a premium for a greener fuel, rather than investing large sums into retrofitting or technologies that are still under development. In regard to the incentives that could improve the competitiveness of a lignin fuel, an emissions trading system forced onto the maritime sector could be the solution, but as the sensitivity analysis of this study suggests, an EUA price as high as 160–190 euros could be needed for lignin fuels to become directly competitive on a cost basis. With the recent price surge on the EU ETS market of almost 1,000 % in the last four years, only a threefold increase from today's prices of around 50 EUR per EUA would be needed.

It is important to remember that the economics behind producing marine fuels from lignin are not just reliant on finding an optimal production process. Most research projects associated with lignin valorisation are focusing on producing high-value products, and in the case of success, the allure of producing a fuel from the lignin could easily diminish. The prudency when it comes to investments made in this sector could be explained by this, and long-term commitment agreements would have to be put in place between suppliers and shipowners to entice investments in this type of novel technology.

9 SWEDISH SUMMARY – SVENSK SAMMANFATTNING

Ligninets potential som marint biobränsle

Den globala uppvärmningen som just nu sker på jorden orsakas till stor del av de växthusgaser som släpps ut. Även sjöfarten, som står för en betydande del på ca 3 % av de totala årliga utsläppen, har börjat titta på olika lösningar som kan bidra till de utsläppsminskningar som Parisavtalet, och tidigare Kyotoprotokollet, haft som mål att uppnå (United Nations Framework Convention on Climate Change, 2015). Det är främst koldioxidutsläppen, som år 2012 uppskattades till 938 miljoner ton, som anses vara den stora boven inom sjöfarten (International Maritime Organization, 2015).

Majoriteten av de fartyg som rör sig på hav och sjöar använder sig idag av fossila bränslen såsom diesel och tung brännolja, vilka avger stora mängder koldioxid vid förbränning. Det är främst en befarad implementering av EU:s krav på utsläppsrätter inom sjöfarten som fått rederier, motortillverkare och övriga berörda parter att satsa allt mer på att hitta alternativa och mer miljövänliga bränslen.

Biobränslen är något som av Europeiska Kommissionen anses vara koldioxidneutrala, trots att de avger en del CO_2 vid förbränning (2003/87/EC). Orsaken till det är att bränslen kan definieras som biobränslen då de produceras av råvaror som antingen är förnybara eller restprodukter från andra processer. Till båda dessa kategorierna hör *lignin*, som dels är en av de mest rikliga naturliga polymererna i vår omgivning, och dels är en oftast outnyttjad biprodukt från främst kemisk massaproduktion.

Av lignin finns det väldigt många typer, och de namnges oftast enligt den process som använts för att extrahera ligninet från dess ursprungliga plats inne i cellväggarna på lignocellulosisk biomassa. Ligninmolekylernas struktur påverkas i sin tur av de kemikalier som används i extraktionsprocessen som ger dem specifika egenskaper – och även den ursprungliga råvaran påverkar vissa karaktärsdrag, såsom den genomsnittliga molekylvikten.

Sulfitmassafabrikernas ligninsidoström kallas lignosulfonater och har redan en del kommersiella användningsområden som bl.a. dispergeringsmedel inom cementindustrin, dammbindningsmedel och tillsatsämne i ett antal industriella applikationer. *Kraft-lignin*, som kan tas ut från sulfatmassaprocessens svartlut, är däremot det lignin från industrin som har störst potential att göra skillnad som marint bränsle. Sulfatprocessen har i dagsläget en marknadsandel på runt 90 % av den totala massaproduktionen, och den mängd Kraft-lignin som årligen kunde tas ut utan att nämnvärt påverka processförloppet har uppskattats kunna producera över 2 EJ energi (Dessbesell et al., 2020). Även andra lignintyper kunde ha fördelar som marint bränsle, t.ex. svavelfria lignin kunde användas vid tillverkning av bränslen med låg svavelhalt, men tillgången på dem är än så länge alldeles för liten.

Fokuset i det här arbetet har således legat på Kraft-ligninet och dess möjligheter som råvara för bränsletillverkning. Andra lignintyper har haft en sekundär roll i den experimentella delen av arbetet, men vissa tester har även gjorts på dem för att kunna dra vissa slutsatser om deras potential som bränslen. Trots att relativt ringa mängder lignin extraheras i dagsläget, främst för att det saknas incitament för företagen att investera i de relativt kostsamma processer som finns på marknaden, kunde fem olika typer av lignin erhållas som donationer från företag inom branschen. Två olika typer Kraft-lignin från barrträd erhölls från UPM Biochemicals (BioPiva™ 100 och BioPiva™ 300, i det här arbetet nämnda som **BP100** respektive **BP300**), natriumlignosulfonater med namnet **DA30** donerades av svenska Domsjö Fabriker Ab, ett icke-kommersiellt björklignin (**BLN**) från finska CH-Bioforce Oy:s egna BLN-process samt ett enzymatiskt hydrolyslignin (**EHL**) från en anonym etanoltillverkare togs också med trots att deras produktionskapacitet än så länge är väldigt begränsad.

Efter en inledande undersökning av de olika lignintypernas värmevärden med en bombkalorimeter av märket Parr 1341 Oxygen Bomb Calorimeter i kombination med en ”Parr 1672 Thermometer” (Parr Instrument Company, Moline, IL, USA), kunde snabbt lignosulfonaterna uteslutas som lämplig kandidat. Dess kalorimetriska värmevärde uppmättes till 17,6 MJ kg^{-1}, i jämförelse med 26,9; 27,1; 26,5 respektive 23,5 MJ kg^{-1} för de övriga i ordningen BP100, BP300, BLN och EHL. Även om lignosulfonaternas vattenlöslighet kunde underlättat framställningen av ett flytande bränsle, är energidensiteten en av de störst vägande faktorerna när det gäller marina bränslen, och en eventuell blandning med vatten hade försämrat detta värde ytterligare.

På de fyra kvarstående typerna gjordes sedan en elementäranalys med en PerkinElmer Optima 5300 DV Optical Emission Spectrometer (PerkinElmer, Inc., Waltham, MA, USA), för att bl.a. testa kol-väte-förhållandet, samt svavel- och syrehalterna i ligninproven, då dessa är av väsentlig betydelse för bränslenas lämplighet. Resultaten, som kan ses i Tabell 5.3, gav inga större överraskningar – BLN- och EHL-ligninens bekräftades som svavelfria, medan Kraft-ligninen enligt förväntningarna innehöll en dryg procent svavel. Det största problemet med ligninets elementära innehåll är dess höga syrehalt, mätt till runt 30 % för alla typerna, då korrosionsbeständiga material kan behövas vid hela bränslets kretslopp tills att det förbränts.

De stora problemen uppkommer då de oftast svårlösliga ligninpulvren som extraherats ur sina respektive processer ska omvandlas till ett flytande bränsle – vilket krävs för den befintliga infrastrukturen för bränslen ska kunna användas, och då eventuella omställningskostnader skulle bli väldigt stora. En del metoder, såsom *solvolys*, pyrolys och förgasning, har redan undersökts, men än så länge finns det inga fullskaliga produktionsanläggningar på marknaden.

De två huvudsakliga metoderna som valts av processtekniskt kostnadsmässiga skäl är solvolys av ligninet i ett polärt lösningsmedel samt en empirisk metod där ligninet kunde malas (och eventuellt ultraljudbehandlas) till en så liten partikelstorlek att det kan röra sig genom de marina bränslesystemens filter med en porstorlek på 10 µm. Trots att den senare nämnda processen är väldigt simpel, kunde mha uppföljning av partikelstorlekarnas utveckling med en Mastersizer 3000 (Malvern Panalytical Ltd, Malvern, Worcestershire, UK) konstateras att dels energin, dels tidsåtgången som skulle krävas för att finmala ligninet vore oändamålsenligt stora och kostsamma. Ett ytterligare problem vore dessutom att hitta en möjlig blandning av ytaktiva ämnen, s.k. *surfaktanter*, som kunde bidra till att motverka de typiska problemen med dispersioner: koalescens, flockulering, gräddbildning och sedimentation. För att kunna avgöra om det är möjligt att få en eventuell dispersion med ligninpartiklar att hållas stabil en längre tid behövs ytterligare forskning inom speciellt ytkemin.

För den andra metoden, solvolys, är det främst lösningsmedlen metanol och etanol som anses vara de bästa alternativen. I en studie visade det sig att löslighetsgraden för ett soda-lignin var 61 % och 57 % i metanol respektive etanol efter en mild solvolysprocess i en satsreaktor, med temperaturen 200 °C, 50 bars tryck och en reaktionstid på 30 minuter. Efter att den förhållandevis stora mängden partiklar som fanns kvar i form av bl.a. oupplöst lignin filtrerats bort kunde en del av lösningsmedlet destilleras eller förångas bort och återanvändas, varvid en lösning med en ligninhalt på upp till 80 vikt-% kunde erhållas (Kouris et al., 2019).

Även om inte lika höga halter kunde uppnås i den experimentella delen av det här arbetet, är det ändå en lovande process. Något som ännu krävs för att göra den producerade ligninoljan användbar är en katalytisk vätgasbehandling för att frigöra syre. En lägre syrehalt minskar dels på risken för korrosionsskador, men förbättrar också stabiliteten och blandbarheten med fossila bränslen – något som krävs i de många riktlinjer som finns för marina bränslen (ISO, 2017). Ett problem som ännu återstår att lösa är identifiering av en optimal katalysator, som både bör vara hållbar och i bästa fall även tåla förekomst av svavel.

Personligen rekommenderas en bevakning av IDEALFUEL-projektet, som är ett EU-finansierat forskningsprojekt med mål att kunna kommersialisera den tidigare nämnda ligninoljan producerad enligt den av Kouris et al. (2019) patenterade metoden. Deras huvudfokus tycks ligga på framtida bioraffinaderier och deras potential att producera svavelfritt lignin som biprodukt vid t.ex. etanolproduktion, men trots det finns det en chans att deras teknologi kunde implementeras även på svavelhaltigt Kraft-lignin, som dock bevisligen har en sämre löslighetsgrad. Fördelen med svavelfria ligninbränslen vore att de kunde konkurrera med dyrbarare lågsvavliga fossila bränslen vilkas pris är ca 25 % högre än för den vanliga tjockoljan. Däremot kan den höga produktionskapaciteten för Kraft-lignin vara gynnsam och därmed pressa ner dess pris.

För en eventuell framtida marknadsintroduktion av processen kunde massafabriker eller bioraffinaderier belägna vid vatten och med egen hamn vara ett utmärkt ställe att lansera bränslet. De ofta reguljärt pendlande fraktfartygen kunde således vara de första att genomgå en eventuell eftermontering (eng. *retrofitting*) för att ta i bruk bränslet, som kunde produceras i anslutning till fabriken. Detta skulle eliminera eventuella transportkostnader och följaktligen vidare förbättra biobränslets konkurrenskraftighet. Trots de optimeringsförslag som getts i det här arbetet, tyder känslighetsanalysen som gjorts för att undersöka effekten av de tidigare nämnda framtida kraven på utsläppsrättigheter att ett pris på upp till 160–190 euro per ton CO_2-utsläpp skulle krävas för att en ligninolja innehållandes 70 % lignin och 30 % metanol skulle bli direkt konkurrenskraftigt med de fossila bränslen som idag används inom den marina sektorn.

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APPENDIX

Appendix I. *Data used for the sensitivity analysis.*

Kraft lignin price (€/t)	200 €	Ethanol price (€/t)	1 082 €	(Average for USA, Thailand, Brazil, France, Sweden, Spain)
Lignin oil production cost (€/t)	250 €	Bioethanol price (€/t)	1 244 €	(15 % premium added)
Lignin ratio	70%	Methanol price (€/t)	410 €	(Fixed price for Europe Q2/2021)
Solvent ratio	30%	Biomethanol price (€/t)	472 €	(15 % premium added)

Item	Price estimate (€/t)	HHV (GJ/t)	LHV (GJ/t)	Price per GJ (€/GJ)	Emissions (t CO_2/t fuel)	Fuel price incl. CO_2 tax (€/t)	Fuel price incl. CO_2 tax (€/GJ)
Raw materials							
Kraft lignin (BP100)	200 €	26,9	25,7	8 €	0	200 €	7,8 €
Lignosulphonates	415 €	17,6	15 *	28 €	0	415 €	27,7 €
Ethanol	1 082 €	29,7	26,7	41 €	1,91	1 082 €	40,5 €
Bioethanol	1 245 €	29,7	26,7	47 €	0	1 245 €	46,6 €
Methanol	410 €	23,0	19,9	21 €	1,37	410 €	20,6 €
Biomethanol	472 €	23,0	19,9	24 €	0	472 €	23,7 €
Fuels							
IFO380 (< 3.5 % S)	354 €	41,8	39,0	9,1 €	3,2	354 €	9,1 €
MGO (<1.5 % S)	517 €	45,9	42,8	12,1 €	3,2	517 €	12,1 €
VLSFO (< 0.5 % S)	442 €	44	41 *	10,8 €	3,2	442 €	10,8 €
LSMGO (< 0.1 % S) - DMA	447 €	45,1	43,0	10,4 €	3,2	447 €	10,4 €
ULSFO (< 0.1 % S)	432 €	45,4	43,1	10,0 €	3,2	432 €	10,0 €
Lignin oils							
Ethanol-lignin (BP100)	715 €	27,7	26,0	27,5 €	0,57	715 €	27,5 €
Methanol-lignin (BP100)	513 €	25,7	24,0	21,4 €	0,41	513 €	21,4 €
(Bio)-lignin oils							
Bioethanol-lignin (BP100)	763 €	27,7	26,0	29 €	0	763 €	29,4 €
Biomethanol-lignin (BP100)	531 €	25,7	24,0	22 €	0	531 €	22,2 €

**estimated*