

PREFACE

This thesis is the terminating paper of the master study in Environment Physics and Renewable Energy at the University of Life Science (NMBU), Ås Norway. My interest for sustainable fuels for the transportation sector, and my interest for farming led me to thougts about yielding the birch tree. This thesis is a theoretical study in the possibilities of making biofuel, especially biodiesel from wood, especially birch, as biomass feedstock.

Ås, april 2015

Rune Haukeland



Acknowledgements

I would like to give specially thanks to my advisor, professor Jorge Mario Marchetti, at Norwegian University of Life Sciences, Departement of Mathematical Sciences and Technology (NMBU), at Ås. He has been my teacher through several cources at the University, and he has the ability of parallel pushing and drawing, such that I as a student could learn as much as possible. He also encourages me to think, to solve problems by reading, doing and thinking. As a teacher myself, I appreciate that way of learning.

I also have to thank my family. To do a full sivil engineering education through 5 years, have to take some time, which have been taken from normally family activities.

Rune Haukeland



Abstract

This master thesis is a preview of some of the latest results from research on fuels from renewable energy sources. Because more outdrawing of fossil oil contributes to more emissions of climate gases, it is a very important goal to reduce yielding of fossil hydrocarbons as fuel for transportation. Especially heavy transportation vehicles, aeroplanes and boats, will demand liquid fluid to drive their engines. It is therefor important to do more research in using biomass as raw material for biofuels. Also because it is competition about using agricultural area for food production, it is important to have knowledge about how to tild cellulosic biomass from trees, as feedstock for biofuels.

Several processes are presented, and it look like also hardwood tree species now more and more are used for feedstock for biofuels. Norwegian forests have increasing standing volume of cellulosic biomass, and is a great potential for biofuel production in the future. In Finland, UPM Fortum, the Finnish biopower plant company has done a lot of research of yielding waste from cellulosic industry as raw material for biodiesel production. Recently, they opened the world's first commercial plant for biodiesel production, based on their own cellulosic waste as feedstock. Knowledge from this industry should also come to Norway. Then we can yield pine, spruce and birch to biofuel production.



Sammendrag.

Denne master oppgaven er en gjennomgang av noen av de siste resultatene fra forskning på drivstoff fra fornybare energikilder. Fordi stadig mer uttak av fossile hydrokaroner bidrar til utslipp av klimagasser, er det et særdeles viktig mål å redusere bruk av fossile hydrokarboner som drivstoff. Spesielt tunge transportmidelr, som lastebiler, båter og fly vil ha behov for flytende drivstoff, og det er derfor viktig å forske videre på bruk av biomasser som råstoff til drivstoff. Også fordi det er konkurranse om areal til matproduskjon, er det viktig å ha kunnskap om hvordan man kan utnytte trær, det vil si cellulosemateriale som råstoff til biodrivstoff.

Mange prosesser blir gjennomgått, og det kan se ut som at også hardwood tresorter blir mer og mer brukt som biodrivstoff råstoff. Norske skoger har økende stående volum av biomasse, og er et stort potensiale for fremtidig biodrivstoff produksjon. I Finland, har UPM Fortum, det finske kraftkonsernet forsket mye på bruk av avfallstoff fra celluloseindustien som råstoff for biodiesel. De har nylig åpnet verdens første kommersielle biodiesel produksjonsanlegg, basert på avfall fra egen celluloseindustri. Kunnskap fra denne industrien bør også komme til Norge. Slik kan vi i fremtiden utnytte både furu, gran og bjørk til drivstoff produksjon.



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Abbreviations and glossary

ASTM American Standard For Testing & Materials

Bpd barrels per day

FT Fischer-Tropsch

FTP Fisher-Tropsch processes

FTS Fischer-Tropsch synthesis

CO₂ Carbon di oxide UN- United Nations

CH₄ Methan

N₂O Nitrogen di oxide

UPM A Finnish Company, The worlds first commercial biorefinery for producing

wood based renewable diesel started up January 2015.

NMBU Norwegian University for Life Sciences.

DME Di methyl ether

Syngas Synthesis gas, CO and H₂. Used as feedstockin FTP, or FTS

ATF Aviation Turbin Fuel
GTL Gas to Liquid process
HT High Temperature process
LT Low Temperature process
FPBO Fast Pyrolysis Bio Oil
LNG Liquid Natural Gas



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1.Introduction

1.1 General

The situation with huge amounts of CO_2 emissions is one of the most important issues of the world today. The effects of the global climate in temperature change, ice decreased in arctic summer, and global sea level increasing the latest 160 years, is showed in figure 1.

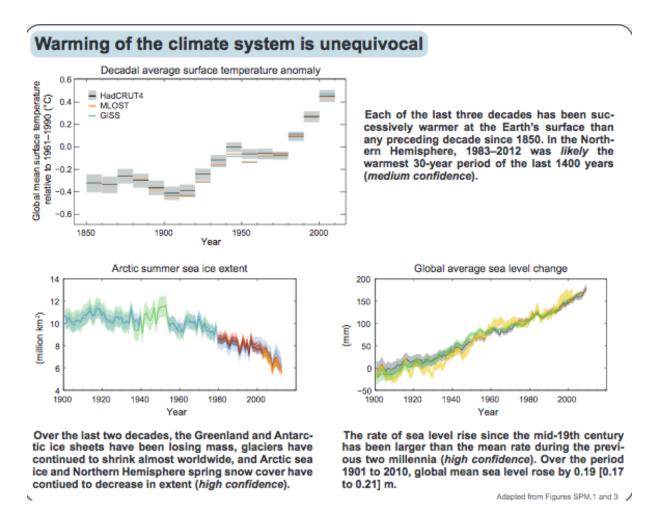


Figure 1; A) The average temperature increasing the last 160 years. B) The arctic summer sea ice extent. C) Global average sea level change (increasing) [1].



Due to UN Climate Conference in 2013, the emissions of CO_2 . CH_4 , and N_2O , now are on so dangerous levels, that the goal to not exceed 2 degrees of global warming is difficult not to reach [1].

The worlds needs of fluid oils will increase by 2.02 billions barrels of oil from 2014 to 2016, according to "Teknisk Ukeblad" [2]. One of the arguments is that the transportation fluid oil needs is increasing more than the results of more efficient engines is decreasing the oil consumption [3]. Use of fossil oil is negative of at least two reasons; emissions of stored carbon to the atmosphere, and expected smaller amounts available from the oil resources, and therefore expected higher oil prices. For the time being, the world is experience a fall in the oil prices from the very high level last year, but this is connected to difficulties in the worlds economics and politics, and is not an issue discussed here. It is discussed when the worlds oil peak will be, but it is agreed that the peak point exist, and that the worlds fossil oil resources will have an end [2].

The "traditional" biodiesel, which is defined as "fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats" [4], seems not to take woody biomass as feedstock for making alternativ biodiesel. This paper will seek to investigate the possibilities of using wood biomass as feedstock for biodiesel.

The last couple of years there have been several researchers funded interesting new ways to yield wooden biomass. Here will be presented some traditional pathways to make biodiesel, and some results which could give new possibilities to make biodiesel directly, or indirectly, from wooden based biomass.

It will also be discussed different species of trees as feedstock, especially birch, a leaf tree, and conifer trees as pine or spruce. All trees have carbon bounded in cellulose, hemicellulose and lignin molecules. A great challenge is to find enzymes which do the process properly; to give the wanted results from wooden biomass [5].

Norway is in the boreal belt, that is a "belt" covering the northern part of the earth, from 45th to the 70th northern latitude. It covers about 14 % of the worlds vegetated surface, but contains around 38 % of the worlds forest area [6]. It will also be discussed why yielding of the wood biomass from the forest for making biodiesel is worth investigating.

There are several benefits of using wood as feedstock for making biodiesel.



- The change of fossil fuels to biodiesel will lead to zero carbon emissions.
- Income for some farmers or forest owners could increase if it were a biodiesel plant in which to deliver the wood resources.
- Use of wood resources could save the environment by need of less transportation, the biofuel plants could be placed near the feedstock.
- According to less transportation needs, it is an argument that biodiesel production from local forests could be seen as better from a democracy point of wiew [7].
- Cellulose is not a food resource for human beings. Oil from seeds, like soy or raps could be used in competition with food resources.
- Energy potential from biomass from the forest in Norway is high, and that the wood today is growing much more than the output [8].

Different trees give different fraction of sugar yields when treated by preheating and enzymes [9]. Wood from pine and spruce is more used as feedstock for cellulose industry than birch. Birch has different chemicals construction, which makes it more difficult to use as directly feedstock to oil-based products.[9]. In Finland however, UPM Biorefining opened a new biodiesel from wood plant January 2015. The production comes from crude tall oil, a waste product form pulp production. This is the first full biodiesel from wood biomass plant in the world [10].

1.2 Fuel oil from fossil resources or biomass resources

Fossil oil contains hydrocarbons in different length. Through refinery it comes gases (at standard temperature and pressure), like methan, ethan, propan and butan, and liquids as gasoline, diesel, aeroplane fuel (jet fuel) and heavy oil fuel. In addition the longest carbohydrates is solid compounds, like asphalt.

Figure 2 shows chematic the processes and the different oil types as result. As shown, diesel is more visceous than for example gasoline.



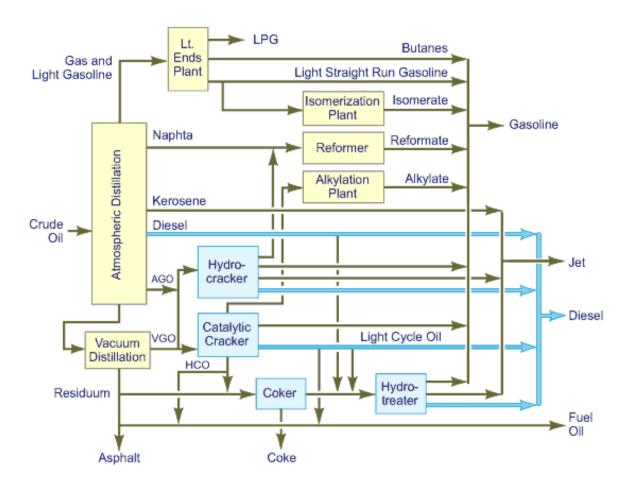


Figure 2. Diesel streams in modern refinery. (AGO=Athmospheric gas oil. VGO=Vacuum gas oil. HCO=Heavy cycle oil) [11].

Biodiesel is defined to be the fatty acid methyl esters from vegetables or animal fat[12]. Figure 3 and 4 show possible paths making biodiesel, figure 3 in detail from soy beans, figure 4 in principles from vegetable oils or animal fats.

Biodiesel is more complex than fossil diesel. While petroleum is clean hydrocarbon chains, biodiesel is an ester with oxygen atoms as a binding part. Fossil diesel has mostly 13-17 carbon atoms in plain chains, esters could have different length of carbons. Biodiesel can contain hundreds of different compounds. Making usable fuel for car, truck, and airplane engines is then a challenge. The gasket and seals have to resist another pH than fossil diesel. Biodiesel has various viscosities, which can be a problem for modern diesel pumps. Filter has to be made so that the viscosity fit the fluid. Use of



the fuel in winter with low temperature could demand some blends to give the right viscosity [13].



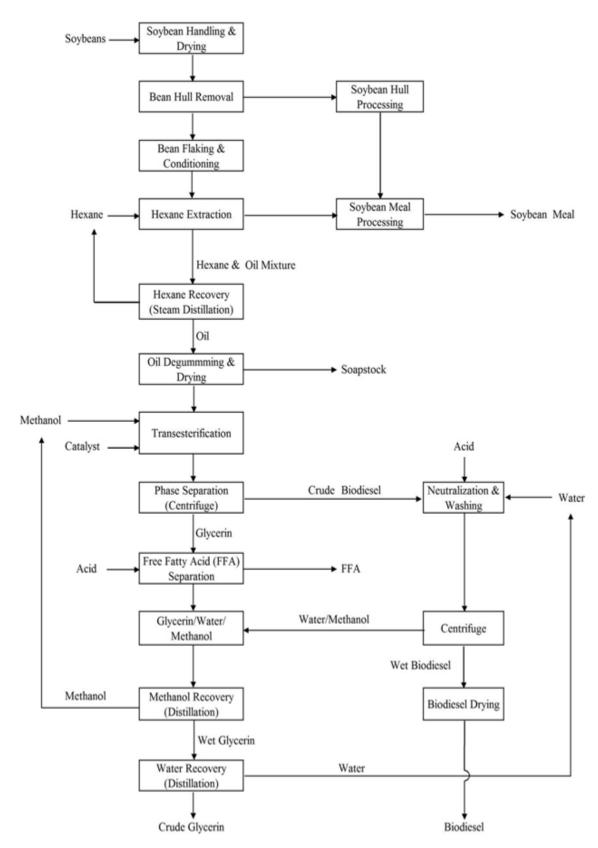


Figure 3 Biodiesel from soy beans [14].



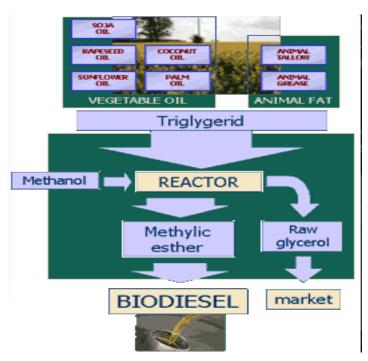


Figure 4 Biodiesel from vegetable oil or animal fat [14].

1.3 Fuel from cellulosic biomass

Fuels made from cellulosic biomass covers several fuel types. In chapter 3 it will be shown different routes ending up with different products, which can be used as fuels; ethanol, methanol, FT diesel, DME, hydrogen, synthetic diesel and solid fuels. Diesel from cellulosic biomass is called 2nd generation biodiesel [12].

1.4 Algae as resource for biofuel

The third generation biofuel, is biofuel with algae as feedstock. It has several advantages, but also a huge disadvantages; algae needs large volumes of water, nitrogen and phosphorous to grow. Algae is not the issue for this paper, but can be highly yielded in the future [15].



1.5 Different needs for small and big transportation vehicles.

Renewable energy is important to be developed further. For some use, e.g. private cars or small boats, battery packages and electric engines are available. For heavier transportation elements, like trucks, big boats or aeroplanes it would probably still be necessary with fluid fuels, as diesel for trucks, and fluids with stronger spesifications for aeroplanes. Therefore developing processes of making biofuels, amongst them biodiesel, would be of great significance.



2.Raw material.

2.1 General

The three dominating tree species are spruce, pine and birch. Spruce and pine are the two most growing trees in Norway. Both belong to the Pine family. Despite they are in the same family, they differ from each other in many ways[16]. Together they takes over 90 % of the volume of all trees in Norway.

Table 1. Standing volume included barch in 2010 of trees in Norway[16].

Tree Specie	Standing volume included
	barch[1000 m ³]
Pine	439.768
Spruce	317.757
Birch	181.536
Other	100.946
Total	1.040.007

Table 2. Standing volume excluded barch in 2010 of trees in Norway[16].

Tree species	Standing volume without
	barch[1000 m ³]
Pine	275.000
Spruce	389.000
Broadleaf	243.000
Total	907.000

Table 1 shows the volume of the trees in Norway in 2010, divided in tree species. All the other species is given in a sum called others. Stein Tomter in "Skog og Landruk"



lists up 25 other tree species which are included in "others" [16]. Table 2 shows the volume of standing trees without barch in 2010. Here is the term "broadleaf" including both birch and other broadleaf trees. The two tables are made for different purposes. The figures for birch in table 1 is therefore not direct comparable with the figure for broadleaf in table 2. In table 1, the sum of birch ant others would be comparable with broadleaf in table 2. The total volume calculated without barch is 907 million m³.

From 1925 to 2012 the volume has increased ca. 300%, from 300 millions m^3 in 1925 to over 900 millions m^3 in 2010 [16].

In the period 2008-2012, the yearly average net volume increased 24 millions m³. But the yearly average logging was only 11,1 millions m³.

Of several reasons, the wood production in Norway has decreased, and for the year 2012 the logging was only 8,4 million m³.

For the year 2011, the net increasing of tree volume corresponds to 32,4 million tons CO_2 -equivalets. The total emission of climate gases in Norway was in 2011 53,4 million tons. The increasing volume of the Norwegian trees equivalents then 60% of the totale emission of climate gases [16].

2.2 Comparing spruce, pine and birch.

2.2.1 History of pine, spruce and birch in Norway.

Pine came to Norway 9000 years ago, spruce is known from 3000 years ago, but birch has been found as fossil roots as long as 17.000 years ago. As the ice disappeared from the Norwegian coastline, the birch followed [17].

Spruce is still moving westwards in the country.

As a result of the warmer climate, also the tree line is increasing by altitude, and then the spruce and pine is found higher up in the mountains in the whole country than some decades ago. This level is a line called the treeline. It indicates that above this level only birch is growing, but not pine and spruce. In the latest 70 years it is documented that the tree line has increased with 70 meters on Ringebu near Lillehammer, but in



Finnmark, and more north, as in Svalbard, the speed of increasing treeline is much slower. The reason seems to be the change in climate conditions, with higher average temperature.

The treeline varies from ca 1000 meter over the sea level in the south, to nearly sea level in Finnmark. (Polar treeline).

There are also other explanations for increasing tree lines than climate changes. Less mountain farms, more mouse and reindeer could influence on the tree line [18].

2.2.2 Geographical distribution of pine, spruce and birch in Norway.

Geographically and conditions

The forest in Norway cover today about 12 millions hectare of land. Among 78 % of the forest areal is covered by pine and spruce, and of that again, the pine forest is 33%, and then the spruce is 67 %.

The rest of the total forest areal is covered by leavtrees. 90 % of this is birch forest.

The pine and spruce forest is mainly in the south and middle of Norway, but it is spread over the whole country. A forest is almost consisting of one single tree specie [16].

2.2.2.1 Birch

Birch is presented all over the country. It grows in humidity areas, often nearby rivers. It is often seen a few meters of birch forest between the farmers land area and a river or lake.

In addition birch grows in the mountains, nearby or higher than the tree line. It is often called Mountain Birch, but is only growing slow because of temperature and weather conditions. It is genetically an ordinary birch [19]. Different types of birch trees are shown in figure 5.





Figure 5. Birch. A) Mountain birch. B) Birch forest in Maridalen in Oslo. C) Hanging birch in front of the University of Stockholm, Sweden [20].

2.2.2.2 Pine

Pine can grow under very different conditions. Both in the inland where there are dry climatic conditions and along the coast, with wet and cold windy weather, pine forest is growing. It tolerate high temperatures in the summer time and low temperatures in the winter time. It accept both long periods of rain, as dry periods. Pine can grow in nutrient-poor soil. It is growing from the sea level to over 1000 meter elevation. Though the most concentrated pine woods is found in the south and the inner east parts of Norway [16, 21]. A typical pine forest is shown in figure 6. It is charachteristical light at the ground between the tree trunks.





Figure 6. Pine forest, Hedmark in Norway [22].

2.2.2.3 *Spruce*

Spruce is less tolerant for dry areas, and grows mostly in areas with rain. Spruce require more nutrition than pine. It is very big spruce forests in the south and east of the country. It is found up to 700-800 meters over the sea level [16]. A spruce forest is shown in figure 7. The trunks are hidden behind the branches.





Figure 7. Spruce forest. One can see that the branches are growing from the whole trunk, while pine have only branches growing from the top of the tree [22].

2.3 Chemical and physical properties

2.3.1. Birch

Birch has small cellulose fibres. The cellulose fibres wall is thick, and consist of regular mostly six edged glucose molecules. Some of the glucose molecules consist of 5 carbons in the chain, called C5. The amount of C5 is higher in birch than in spruce and pine [23]. Hemicellulose is smaller molecules and lignin act like "glue" between the cells. Another difference between birch on the one side, and pine/spruce on the other side, is that the lignin content in birch is lower. Birch also contents extractives which means



that it demands different enzymes to cleave the polysaccharides into smaller parts. The hemicellulose content of birch is higher than in pine/spruce. Also the chemical construction of the lignin and the hemicellulose molecules differ form birch to pine/spruce [24].

Birch has spread pores which carry water from the cellulose walls. [24]

As a broadleaf tree, the hemicellulose content appr. 30 % C5 means sugar, often called tree sugar. Monosaccaride $C_5H_{10}O_5$ is made from polysaccharides Xylan from the hemicellulose [9, 25].

Birch has highest density of the three trees birch, pine and spruce. The values varies from different sources. One of the explanations could be that it differs according to water content. The values from birch differ from 505 kg/m³ to 670 kg/m³.

The burning value also differs from different sources. Here are presentated the values from Skog og Landskap at NMBU, Ås, Norway. Birch has burning value 5.17 kWh/kg [26-28].

Birch has 47,4 content of Carbon, and 5.2 % of Hydrogen in the wood [26].

The content of the main elements is shown in Table 2.

Table 3. Main elements shown as content % in conifer vs leavtrees [24].

Main elements in different trees			
	Conifer trees	Leavtrees	
Cellulose	40-42%	40-45%	
Hemicellulose	28-34%	25-35%	
Lignin	27-32%	22-26%	
Ash	0,1%	1%	



2.3.2 Pine

91-95 % of the pine wood contains of long celluloce fibres. They are 70-200 times longer as their width. Between and in the cells it is resin, a thick, viscous matter containing aldehydes, phenylpropanoids (makes lignin), and rubber substances. This is as concrete between the cells, and explain why timber has strong properties.

One of the differences between spruce and pine, is that pine has small pores in the cells, which allows impregnate liquid to penetrate the wood, to give it long life properties, and resistant against fermentation. The pores also allows water to leave the cellulose walls faster than birch, that means that it will reach its fibre saturation point earlier than birch.[29]

The hemicellulose is build op by C6 sugars mainly in pine, named galactaglucomannan [30].

Because pine mostly is build up by C6 sugars, and because this C6 sugars have been the feedstock that is easiest to make pulp and other product from, pine and sprue are the common used trees for cellulosic production in Norway [9].

Pine has density 490 kg/m^3 to 530kg/m^3 , depending on source. Burning value is 5.36 kWh/kg [26-28].

Pine has 52.4 % content of Carbon, and 5.9 % of Hydrogen in the wood[26].

2.3.3 Spruce

Spruce is very similar to pine, but it has some differences. The pores in spruce are smaller and fewer. That means that it is not suitable for impregnation. Impregnation in pine will go much deeper into the tree. The cutted tree from spruce is lighter and whiter than pine, because the sap pipes in pine goes both radially and up/down through the wood, and give the tree more deep and dark colours [16, 24, 29].

Spruce has mainly C6 sugars in its hemicellulose [9].

Spruce has density from 390 kg/m³ to 450 kg/m³, and a burning value of 5.28 kWh/kg. Spruce has 52.3 % content of Carbon, and 6.1 % of Hydrogen in the wood [26].



2.3.4 Comparing density and burning values of pine, spruce and birch.

A comparison of the trees density and burning values is given in table 4. The figures from 2008 and 2011 is partly based on different measurement methods, and partly of species from different places. A comparison is given in figure 8.

Table 4. Density value from different sources, burning value and content of C and H in different tree species [26-28].

		2008	2011	Burning	Content %	Content %
	Density	(kg/m ³)	(kg/m ³⁾	value.	Carbon.	Hydrogen.
	(kg/m ³)	[26]	[26]	[28]	[26]	[26]
	[27]			(kWh/kg)		
Birch	670	580	505	5.17	47.4	5.2
Pine	530	490	430	5.36	52.4	5.9
Spruce	450	430	390	5.28	52.3	6.1

Birch is often said to be the best fire-place wood. In addition to a subjective explanation, like the fire smell, birch is also known as the most economically wood to buy. The sale is in volume, and table 5 shows the burning value per volume.

For transportation of timber, it is the volume which is the limiting unit. Based on the three different measured values from two different institutions, and two types of measurement, table 5 shows the similar burning values from the three tree species, for each of the three measurements, by volume. Table 4 shows the values per weight units. Both firewood and fuels for transportation are sold per volume. It is therefore interesting to see if there is a correlation between burning value per volume firewood, and the degree of yield it is possible to get out of the wood in liquid fuel for transportation.



Table 5. Burning values pr volume for birch, pine and spruce. Volume figures calculated from the values in table 4.

	Burning value CI-	Burning value	Burning value	
	metric	Skog og Landskap	Treteknisk(kWh/m³)	
	(kWh/m³)[27]	kWh/m³)[26]	[28]	
Birch	3190	2999	2611	
Pine	2840	2626	2304	
Spruce	2376	2270	2059	

Figure 8 shows a comparison of the three tree species, compared with which institute have given the values. All three institutes have birch as the tree with the highest burning value per volume, the pine in all three institutes have spruce as the tree with lowest burning value per volume.

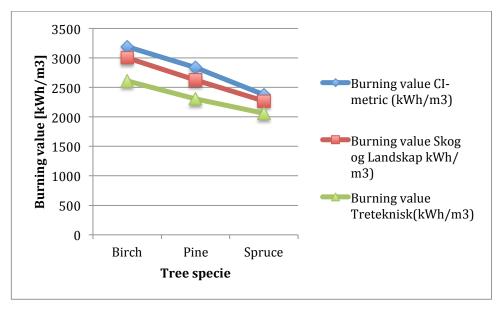


Figure 8. Burning value per m3 for the three tree species, compared with three different values for density, given from three different sources



2.4 Yielding areas of pine, spruce and birch.

Both pine and spruce are used for building construction materials. 50% of spruce is used for building materials, the rest is used for paper, celluloce and biomass.

The core wood of pine is very strong, and resistant for small organisms. Pine is used for building materials, especially for constructing wood, and is the one used for impregnating materials. Spruce is used for outdoors constructing in the inland of Norway, where the summer is dry, and the winter cold, and therefore the need of impregnating is not so deep. Spruce is also used for indoor construction, and floor, wall and roof outer layer [17].

Some farmers in Norway are cultivating spruce for Christmas trees.

Birch is mostly used for firewood. There is some minor furniture factory, which use birch because of its beautiful colors in the wood.

Only 0,5 % of the trees taken in 2010 was leavtrees, of them birch was 90 %. Table 4 and 5, and figure 8 shows that birch has the highest burning value pr m³ of the three tree species. In figure 8 it is easy to see that birch is the most economically fire wood to buy, when one compare burning value with volume [17].

Feedstock for bioenergy is mostly waste from celluloce industry, but also whole timber is used in small amounts. In 2012, 1,65 million tons were burned in Norwegian houses and cottages. The use of biomass as source of energy in district heating is measured in Watt, and the total amount was in 2011 6 072 GWh. From this, bark, tiles and wood gave 1265 GWh, or ca 20 %, The main resource for district heating was waste from industry and housholds, with 3227 GWh [16].



2.5 Characteristica of pine, spruce and birch.

2.5.1 Forest

Forests seem to have mainly only one kind of tree species. So also in Norwegian forests. This could be based on different growth conditions, all trees prefer different temperature, humidity, soil, nutrition and so on. This is an observation done by the forest researchers [16].

2.5.2 Description

Pine has a straight-line formed tree trunk, and has branches as a crown in the top. It is found as high as 1000 meter over sea level, and is hardy with respect to dry periods, wind and low temperatures.

Spruce has branches sitting as pairs nearly from the ground to the top.

The colour of the spruce wood is white-yellow, the colour of the pine wood is darker yellow. It is a clearly mark between the darker core wood and the lighter outerwood in pine.

Hanging birch can in the right conditions give double volume biomass as ordinary birch [16].

2.5.3 Height

In Norway, both spruce and pine can be more than 40 meters high. In Germany, there are examples of trees around 50 meters.

Birch is divided in three main types; Ordinary birch, hanging birch and dwarf birch. The two first is usually 20-30 meters, but dwarf birch is usually not over 2 meter. Mountain birch is a variation of ordinary birch. Because of strong conditions with low temperature, a lot of wind and others, it is not growing so high [16].



2.6 Planting and increasing volume.

In 2012 it was planted 22 million new spruce plants. Totally 28 million plants were seed, under 1 million was birch. This is much more than logged. Yearly increasing standing volume, is 12.9 mill m^3 [16]. The potential for more yielding of cellulosic biomass is then absolutely existing.





3 Producing fuel from biomass

3.1 Definition of diesel and biodiesel.

3.1.1. Fossil diesel.

Fossil diesel is hydrocarbons, with longer carbon chains than gasoline. The number of carbons in fossil diesel is 12-20. Sometimes it is called diesel oil, and that indicates that diesel has higher viscosity than gasoline. Boiling point for diesel molecules are from 180-360°C. Density of diesel is 0.84 kg/L, while gasoline has 0.74 kg/L. That also means that diesel has more energy per litre, 10,7 kWh/L against 9.7 kWh/L for gasoline [31].

3.1.2 Biodiesel.

Biodiesel is defined as mono alkyl ester derivate from lipid feedstock, such as vegetable oils or animal fats [12]. It is then not the same chemical substance as fossil diesel oil, but can substitute the fossil diesel. Fossil diesel burn million year old carbon, and is hence called not renewable. Biodiesel burn carbon which have been collected by the vegetables for perhaps a period of months, and is then called renewable.

Diesel engines may be modified to work properly with biofuels. Gaskets, seals, filters, needles and diesel pumps are among the parts that is replaced with more resistant ones, due to change in pH values, water content or blending of components with different properties, as flame point.



3.2 Storing challenge

Because biodiesel contents biological degradable fats, biodiesel looses its quality if stored over long time [12]. Also bio-oil from fast pyrolysis processes, is recommended not to store for a period over 6 months.

3.3 Making biodiesel from wood biomass.

3.3.1 Paths to different biofuels.

There are many known paths of processing biomass to fuels. Figure 9 shows different paths from different feedstock, while figure 10 shows the different paths based on which of the two main processes are followed.



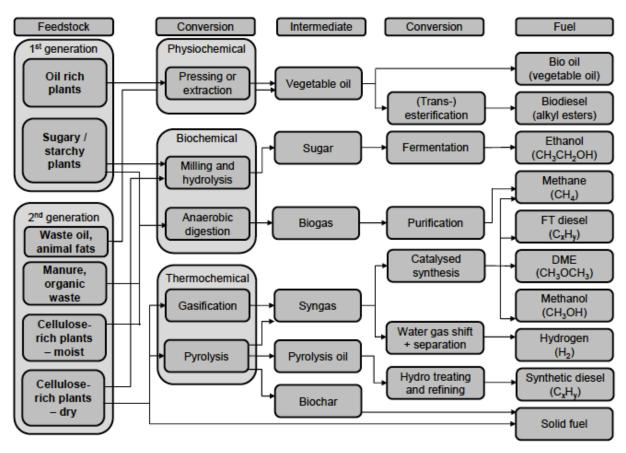


Figure 9 Main conversion routes from different biomass feedstock to different fuels [32].



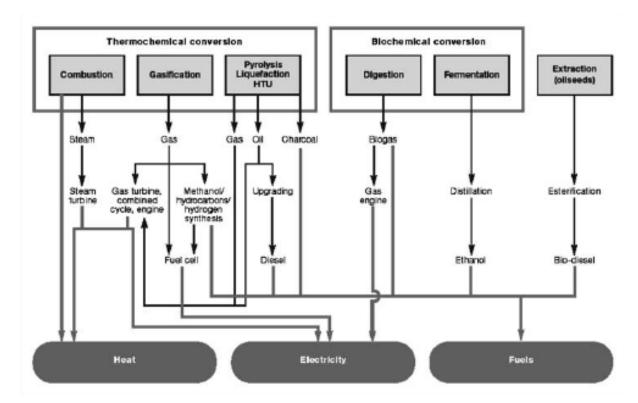


Figure 10 Routes of processing biomass to different types of energy [33].

3.3.1.1 Thermochemical conversion.

3.3.1.1.1 Combustion.

Combustion of wood or any biomass feedstock gives energy in form of heat. Wood can be combusted as firewood [28], or it could be residues from pulp industry, agriculture and more. There are several studies which deal with the amount of energy which could come from huge plants, or small scale combustion units. The combustion units could give hot water to nearby houses, or be converted to electricity [34].

3.3.1.1.2 Gasification

Gasification of biomass means that the C, H and O atoms in the biomass form H_2 and CO gases [35]. Those gases can in turn be used in a fuel cell engine or go through a water gas shift process. A membrane reactor could increase the effect of the separation



of H₂ gas.[36] The Fischer-Tropsch-Process (FTP), using the syngas (H₂ and CO) to from hydrocarbon chains and water, would be treated in chapter 3.3.3.1.

3.3.1.1.3 Pyrolysis

Pyrolysis is processes where biomass in the absence of oxygen is converted to char, bio-oil, or biogases. Several investigations have been done recently, to maximize the outcome due to different variables. The feedstock itself, the heat, the different enzymes, different reactor types, biomass feed rate, carrier gas flow, the size of the particles involved, the reaction time varied. As an example of such research, Heidi Nygård at NMBU, Ås has recently published her PhD thesis of "The Potential of molten salt as heat transfer media in fast pyrolysis of wood" [32]. Molten salts have three properties, which can make them well fit for pyrolysis processing; They have good heat capacity, can act as catalyst, and is a solvent which allow the medium (waste wood, or small particles of wood, coming in close contact with the catalyst. However, the yield of Nygård's work, was under 40 % bio-oil [33]. While table 6 in chapter 3.3.3.3 shows that it is possible to have as much as 75 % yield of bio-oil form fast pyrolysis.

A theoretical study over different pyrolysis outcome from bio-oil production in Colombia was published late in 2014 [37]. Wood exist of cellulose, hemicellulose and lignin. Cellulose and hemicellulose, which are long-chained polysaccharides can cleave into disaccharides, and then to monosaccharides. To cleave the bonds there are several processes, some involving enzymes. Humans don't have such enzymes in the digestive system, and cellulose is then not cleaved into usable nutrients in human bodies. Figure 11 and 12 show polysaccharide and disaccharide. The grey marked atoms in figure 12 is founding water when treated with special enzymes, and is the transformed to monosaccharide.



Figure 11 Cellulose is polysaccharide with many glucose molecules, from a few hundred, up to about 6000 for cotton [38].

Figure 12 Disaccharide is formed by two monosaccharides. The -OH and -H in grey forms water, and the glucose molecules will link together. It is this bond that is important to break to form monosaccharides [38].

3.3.1.2. Biochemical

Biochemical engineering is studying processes of chemical engineering methods and industrial approaches to living cells and how different components react when blended with biological components under different conditions [39].

3.3.1.2.1 Digestion

Lignocellulosic biomass is usually not digested in animals. Termites however, are able to digest 79-94 % of the cellulose from wood [40]. Some termites are using a mix of endogenous and bacterial cellulases [41]. Ruminants guts digest lignocellulosic biomass,



and both anaerobic and aerobic bacteria used in ruminants is investigated by Ali Bayane, to find mechanisms which could be applied to biogas digesters, in order to improve converting lignocellulose biomass to methan.[42].

Figure 13 shows a path to ethanol. In the figure, picture number 3 could be the "digest" place, where celluloce molecules is broken down to simple sugar molecules.

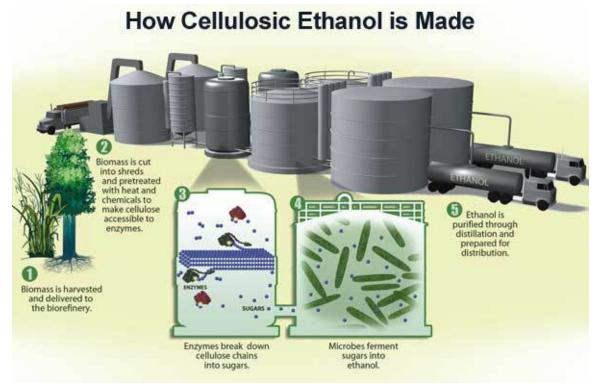


Figure 13 How to make ethanol from woody biomass [43].

3.3.1.2.2.Fermentation

Fermentation is the part of the process where microbes (bakteria, yeast) is breaking down the sugar molecules to carbondioxid (CO_2), and ethanol (CH_3CH_2OH). The process has to be in a given temperature, not too cold. If it is too cold, the microbes, which start the fermentation, could die.



3.3.1.3 Extraction (to biodiesel)

Extraction could both be in a mechanical way, through an oil seed crusher. The cost of a mechanical oil seed crusher is not so high, but up to 1/3 of the oil can remain in the oilseeds cake. The cake could be used as animal feed. However, an extractor which use solvent, could remove almost all the oil from the meal. But both the mechanical tank, and the solvent, could increase the cost, according to SRS, a California based engineering company [44].

Figure 12 shows extraction from algae, where electromagnetic field is used to separate the components.

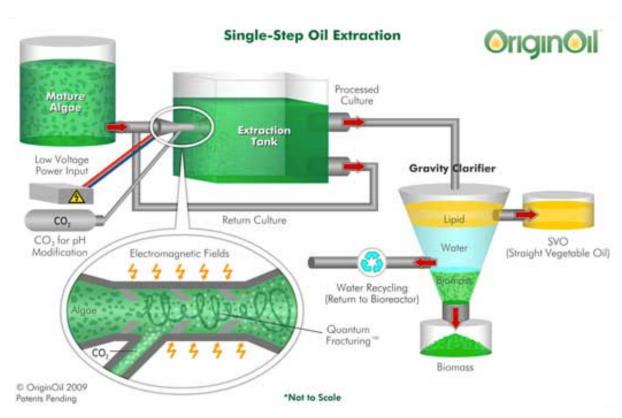


Figure 14 Extraction of vegetable oil from algae [45].



3.3.1.4 Ethanol from sugars. Blending in fossil or biodiesel.

Ethanol can be made from fermentation of sugars. To make biomass to sugars, it needs some pretreatment, which is described above. Ethanol can then be used as fuel as it is, or can be blended in gasoline. The fraction of blending can be from 0-100 %. If the gasoline is blended with more than 15 % ethanol, the gasoline engine has to be some modified. In Brazil, approximation 40 % of the cars are running on pure ethanol. In Sweden both blending of ethanol in gasoline and diesel is much used, both also the exhaust is treated by catalyst converters to reduce the emissions of carbon monoxide, hydrocarbons and nitrogenoxides. It is also possible to use ethanol as blending in diesel fuels. Buses several places in the fuel runs on blended diesel fuel with ethanol. Also diesel engines are possible to convert to tolerate pure ethanol [46].

3.3.2 1st generation biodiesel

3.3.2.1 Biodiesel from vegetable oils or animal fats

According to the general definition biodiesel is transposed under a process called transesterification. It means that the vegetable oil or animal fat, through some reactions, (explained under), form esters and glycerine, The glycerine has to be removed, to give the esters in a pure form.

The reaction is a three step reaction, one from triglycerides and alcohol to diglycerides and esters, the second from diglycerides and alcohol to monoglycerides and esters, and the third is from monoglycerides and alcohol to glycerol and esters.

Each reaction is reversible, and each reaction gives the esters, which is biodiesel.

The principle of the reactions is shown in figure 13.



$$\begin{array}{c} \text{CH}_2-\text{COO}-\text{R}_1 \\ | \\ \text{CH}-\text{COO}-\text{R}_2 \\ | \\ \text{CH}_2-\text{COO}-\text{R}_3 \\ \end{array} + \begin{array}{c} \text{3R'OH} \\ \\ \text{Catalyst} \\ \end{array} \begin{array}{c} \text{R}_1-\text{COO}-\text{R'} \\ | \\ \text{R}_2-\text{COO}-\text{R'} \\ | \\ \text{R}_3-\text{COO}-\text{R'} \\ \end{array} \begin{array}{c} \text{CH}_2-\text{OH} \\ | \\ \text{CH}_2-\text{OH} \\ \end{array} \\ \text{CH}_2-\text{OH} \\ \end{array}$$

Figure 15 The transesterification reaction, from triglyceride to esters and glycerol

The triglycerides are different for different vegetables, or different animal fat. The diesel engine is able to run with a lot of different esters. In the Biodiesel Handbook, there are listed more than 70 different plant oils, which are used for biodiesel engines. They have slightly different properties, which gives the fuel needs of some blends, to avoid that wax crystals agglomerate, and then destroying of diesel pumps and plugging fuel filters. Different fuels also have different viscosity at cold temperatures, which gives the need of blending with fluids that lower the waxing temperature [47].

3.3.3 2nd generation biodiesel

While diesel oil from vegetables and animal fats are called the first generation biodiesel, yielding of more of the vegetables, like leaves, and the cellulose parts, is called the second generation. One of the main issues in yielding vegetables to make transportation fuel, is the use of eatable resources. If it is possible to break down the lignin and cellulose molecules, and form usable molecules, we can get several positive factors:

- Use the waste from the cellulose industry and the households, will reduce the storing problem og waste.
- Replace the use of fossil fuels.
- The CO₂ emissions will be reduced, and the CO₂ used will be captured by the growth of new green plants.
- Using areas which could be used for food production could be reduced.
- Using plants which is not used for food.



3.3.3.1 Routes to 2nd generation diesel from dry wood feedstock

First is presentated a full list of the routes to different fuel from dry wood feedstock. There is also other work, i. e. Bridgewater, who has made a similar table over routes to biofuel. The routes can have slightly differences. Bridgewater has more detailes i.e for catalysed synthesis [48].

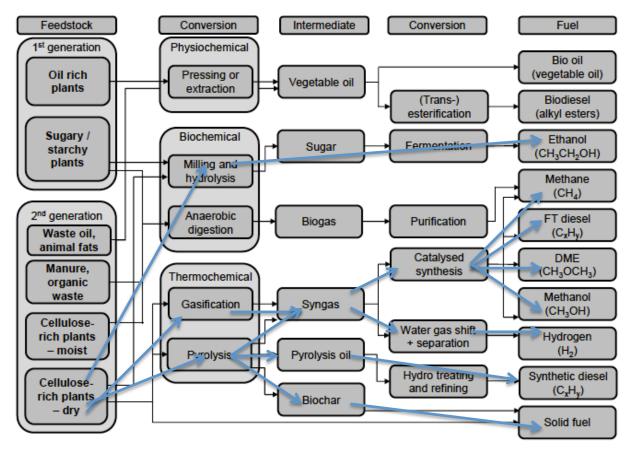


Figure 16 The routes from dry cellulose-rich plants to different fuels [33]. The arrows made by the author.

Routes from dry cellulose-rich plants:

- 1. Via milling and hydrolysis to sugar, then via fermentation to ethanol.
- 2. Via gasification to syngas. Then via catalysed synthesis to methane.
- 3. Via gasification to syngas. Then via catalysed synthesis to FT diesel.
- 4. Via gasification to syngas. Then via catalysed synthesis to DME. (Dimethyl Ether)
- 5. Via gasification to syngas. Then via catalysed synthesis to methanol.



- 6. Via gasification to syngas. Then via water gas shift and separation to hydrogen.
- 7. Via pyrolysis to syngas. Then via catalysed synthesis to methane.
- 8. Via pyrolysis to syngas. Then via catalysed synthesis to FT diesel.
- 9. Via pyrolysis to syngas. Then via catalysed synthesis to DME.
- 10. Via pyrolysis to syngas. Then via catalysed synthesis to methanol.
- 11. Via pyrolysis to syngas. Then via water gas shift and separation to hydrogen.
- 12. Via pyrolysis to pyrolysis oil. Then via hydro treating and refining to synthetic diesel.
- 13. Via pyrolysis to biochar. Then to solid fuel.

(the last route, direct from cellulosic biomass to combustion, is not treated here. This last route is the traditional way to yield biomass,; direct heating in fire-places or for coocking.)

Here is of interest to end up with diesel, either FT diesel or synthetic diesel. Then is route 3, 8 and 12 of special interest.

Since the aim of this paper is to investigate the possibilities of making diesel from dry wood, especially comparing birch and pine, the routes to other biofuels are not treated more here.

3.3.3.2 Dry wood gasified to syngas. Then via catalyses synthesis to FT diesel. (Route 3)

3.3.3.2.1 Gasification

Gasification of biomass feedstock involves partial oxidation. The processes are generally designed for low- to medium energy fuel gases or synthesis gases for producing chemicals, such as methanol (CH₃OH), and other hydrocarbons [32]. It is well known processes, and is described in thousands of articles. Biogases have relatively low energy density, which make it expensive for transportation. Most biogas is produced as it is used. However, it is possible to store it for some time, but the cost will reduce production for storing [49].

Under the 2. World War, more than one million small-scale plants, using wood or biomass-derived charcoal were build. They were air-bown gasifiers using biomass feedstocks. The low-energy gas was used to power vehicles and to generate electric power. In the decades after the war, researchers all over the world continue to develop biomass gasification processes. In Sweden, Volvo and Saab (now unfortunately broke),



have made programs to develop a standard gasifier design, which could be used in mass production for vehicles [50].

There are three basic types of biomass gasification processes:

- 1. Pyrolysis
- 2. Partial oxidation
- 3. Reforming.

With chosen temperature and pressure conditions, pyrolysis products from biomass are primary gases. If the stoichiometric amounts of oxygen needed for full combustion not are present, there will be partially oxidized products. Reforming is a term which was used for fossil oils, i. e. in cracking, but for biomass it refers to gasification in presence of another reactant, i. e. steam-oxygen or steam-air. The stoichiometric with cellulose as feedstock is presented here; (taken from Klass; Biomass for Renewable Energy) [53].

Pyrolysis
$$C_6H_{10}O_5$$
 \rightarrow $5CO + 5H_2 + C$ (1)

Partial oxidation
$$C_6H_{10}O_5 + O_2 \rightarrow 5CO + CO_2 + 5H_2$$
 (2)

Steam reforming
$$C_6H_{10}O_5 + H_2O \rightarrow 6CO + 6H_2$$
 (3)

3.3.3.2.2 Syngas

Syngas is defined as hydrogen (H_2) and carbonmonoxid (CO). In a process called Fischer-Tropsch Synthesis,(FTP), it is converted to methan (CH_4) and water (H_2O) . Based on feed rates, reactor sizes and catalysts type, the reaction can form long carbohydrate chains, showed as the principal reactions in equation (4);

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \tag{4}$$

This is the classic Fischer-Tropsch reaction, mentioned in thousands of articles. It was the German physicists F. Fischer and H. Tropsch who developed and build up the process to commercial scale 1925-1935. The reaction was known form French scientist early in the 1900th. The principle was to use syntese-gas (syngas), hydrogen and



carbonmonoxid, and let them react to form hydrocarbon chains and water. The process takes place at about 200°C, at normal pressure, and using cobolt or nearby metal as catalyst. Before the first world war, they used coal to make syngas, and it became an important source for the German making synthetic oil and gasoline. After the war, this production was laid down. In the decades after the second world war, it has been used for methan production [51]. A lot of work had be done to develop the process in order to give expected outcome, e.g. hydrocarbons chains with more than 5 carbons in the chain [52].

The process is also suitable with biomass as feedstock. It is then need for gasification before the FTP. E.g. Martin and Grossman from the department of chemical engineering, Carneigie Mellon University in Pittsburg, [53] has done a work to optimize the FTP in using Switchgrass as feedstock to make biodiesel. Then some of the efforts was to make lignocellulosic biomass to usable syngas before the FTP. Both the cleaning of the gases, and the ratio H_2/Co was issues. They used a mathematical equation to optimize the biodiesel output. The production cost was calculated to be 0,72 \$/gallon, which means under 2,00 NOK/L. Then the production cost seem to be very promising[53].

The production of syngas is not included in those calculations, and it is then a question if syngas production from green lignocellulosic resources could be as low as to be competive to fossil oil resources.

While hydrocarbons with chain length 13-17 is defines as diesel, aviation turbin fuels (ATFs) are a complex mixture of hydrocarbons with 8-17 carbon atoms in the chain [54].

According to Yan et al [55], the most highly developed route to produce alternative fuels from lignocellulosic biomass is by gasification process and cleaned, then catalytically converted via Fischer-Tropsch synthesis, or CO hydrogenation (alcohol synthesis). They describe a process involving a multifunctional catalyst, made of iron (Fe), potassium (K), Cobalt, (Co), Molybden, (Mo), and γ –aluminia (Al)catalyst. It is described a laboratory investigation, which resulted in clean aviation turbine fuels, that means hydrocarbons from C5 to C13 [55].



3.3.3.3 Dry wood pyrolysed to syngas. The catalyses synthesis to FT diesel. (Route 8)

Pyrolysis is thermal decomposition in the absence of oxygen. In order to get maximum yield of bio oils which is storable and transportable, *fast* pyrolysis is of great interest.

Table 6. Different methods of pyrolysis give different wanted products [48].

Typical product yields (dry wood basis) obtained by different modes of pyrolysis of wood

Mode	Conditions Wt%	Liq	quid	Char	Gas
Fast	~500°C, short hot vapour residence time ~1 s	75	5%	12%	13%
Intermediate	~500°C, hot vapour residence time ~10-30 s	50	0%	25%	25%
Slow - Torrefaction	~290°C, solids residence time ~30 mins		-	82% solid	18%
Slow - Carbonisation	~400°C, long vapour residence time hrs -> days	30	0%	35%	35%
Gasification	~800°C	5	5%	10%	85%
•	·				

The blue arrow point at the highest fraction of gas one can achieve from gasification by pyrolysis.

The next step in the process is using the syngas, which can be done by the FT process. According to Fedou et al (Axens, 2008), Fischer-Tropsch (FT) technologies which are developed to make diesel, can be divided by four paramters;

- 1. FT catalysts, two main types.
 - a. Iron-based catalysts.
 - b. Cobolt-based catalysts.
- 2. FT reactors. Three main types.
 - a. Fixed bed, the catalyst is located inside the tubes.
 - b. Fluidized bed, the catalyst is maintained in suspension by the syngas.
 - c. Slurry, bubble column, a three phase reactor, with synthesis gas, waxes, liquid products and solid catalysts.
- 3. Operating temperature.
 - a. HT-FT; high temperature Fischer-Tropsch, around 350°C and above.



- b. LT-FT; low temperature Fischer-Tropsch, around 220-240°C.
- 4. Final products obtained, after FT upgrading.
 - a. Middle distillates (diesel), paraffinic naphtha. (also in some cases waxes or lube bases).
 - b. Gasoline, olefins and chemicals specialities.

Those parameters are not independent of each other. Three combinations have been developed or used of different companies as shown in figure 17.

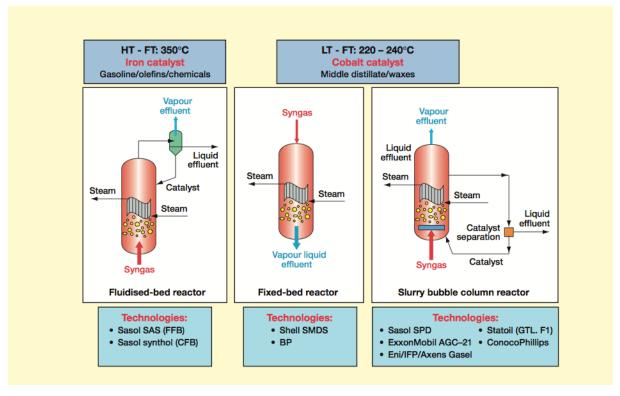


Figure 17 The three main families of FT technologies [55].

Category 1 is a fluidised-bed reactor with iron catalyst. A such reactor was opened in South Africa in 1993, with a capacity of 200.000 bpd. The main products is olefins speciality and liquid fuels. This technology requires expensive work to make pure diesel.

Category 2 is a fixed-bed reactor with cobalt catalyst. It was developed by Shell in the 70's. The catalyst is located inside tubes. It has opportunity to produce waxes and lube base, but the yields after product upgrading of ultra clean FT diesel or middle distillates, is very high. It has two important advantages;



- It is not difficult to scale up to industrial scale, it is simple to make many tubes following each other.
- As the catalysts in inside the tubes, it is normally no problem with separation of liquid and solid products.

It has also some disadvantages;

- The temperature gradient along the tubes could be difficult to control., due to the thickness of the tube shell.
- Transfer limitations of the gas liquid phase and the solid catalyst could give limited capacity per train.
- The catalyst maintaining is also an issue. It could take two weeks to empty, clean and fill the tubes if the catalyst should be changes, according to Shell.

Due to the long period of down time during catalyst change, this is the reason for why such catalyst are not good for iron catalysts. Cobalt catalysts is known to last much longer.

Category 3 is a low-temperature on cobalt catalyst Fischer Tropsch reactor (LT-FT). It is a slurry bubble column reactor (SBCR). It has been developed the last 20 years for producing kerosene, diesel, naphta and waxes. Compared to the two other categories it has severale advantages:

- It has the best utility of the catalyst.
- The capacity is at least 5 times higher per train than category 2 reactor. The
 capacity is at least 15000 bpd per train, and it can have reactor diameter up to 10
 m.
- Easy isothermal operation in the reactor.
- Easy maintaining; the reaction could go continuously through a catalyst change.

Nevertheless, it has a couple of challenges to be solved before it could be classified as a product finished for cellulose FT-diesel production;

- The separation of liquid and gas fuels.
- When the reactors is huge, it seem to mechanical stress on the catalyst.

The first reactor of this type started in Qatar in 2007 by Sasol [55].



Figur 7 shows the three reactors, with information of which company involved, which main products after refining, start-up year and capacity.

Table 7 The main FT reactors in the world, with capacity, start-up year, products and company [55].

Main FT industrial applications in the world

HT-FT in fluidised bed with iron catalyst: Sasol CFB and FFB in South Africa

GTL

South Africa (Petro SA & Sasol) Main products
Capacity: 200 000 bpd Olefins specialities

Last start-up: 1993 Liquid fuels

LT-FT in fixed bed with cobalt catalyst: Shell SMDS in Malaysia

GTL

Malaysia (Shell) Main products

Capacity: 14 500 bpd Diesel

Last start-up: 1993 Naphtha/waxes

LT-FT in slurry bubble column with cobalt catalyst: Sasol SPD in Qatar

GTL

Qatar (QP/Sasol) Main products

Capacity: 33 000 bpd Diesel Last start-up: 2007 Naphtha



3.3.3.4 Dry wood pyrolysed to pyrolysis oil. Then via hydro treating and refining to synthetic diesel. (Route 12)

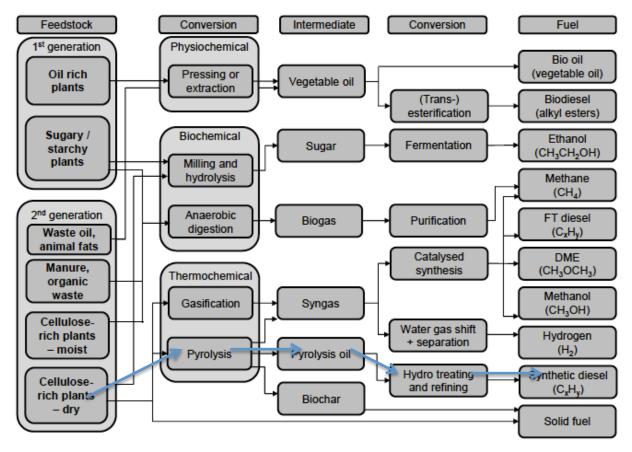


Figure 18 The route from dry cellulose-rich plants to pyrolysis, then to pyrolysis oil, via hydro treating and refining to synthetic diesel [33]. Arrows made by the author.

From Table 6 one can see (the red arrow) that fast pyrolysis can give up to 75 % yield of liquid bio-oil from wood. The time is very short, about 1 s. If the process time increases, i. e. up to 10-30 s, the yield of liquid bio oil will be reduced to about 50 %.

The design of the reactor is very important part of fast pyrolysis processes. [48] It is three important criteria in the designing of the reactor for yielding high parts of pyrolysis oil:

1. Rapid heat transfer, and high heating rates. This is to prevent for carbonization.



- 2. The reactor temperature should hold about 500° C.
- 3. Short vapour residence and rapid reducing the temperature in order to prevent from unwanted secondary reactions.

Back in 2004, Czernik and Bridgewater stated that the process of producing bio oil from fast pyrolysis of cellulosic biomass to make different chemicals was developed far enough to be commercial success. But it still remained some research to have the bio oil for use in transportation engines a commercial success [56].

So, in 2015, it has come so far that it is necessary to define what bio-oil from fast pyrolysis is. Depending on the components of the woody feedstock, both the feedstock and the products are very different. In order to have components which is useful as fuel in different engines, it is necessary to define standards. Then Oasmaa et al this year (2015) present both a suggestion for standards and definitions, but also an overview of fast pyrolysis plants all over the world [57].

Fast pyrolysis bio-oil (FPBO) concist of several components. International Energy Agency (IEA) Bioenergy task34 suggest a definition, such that FPBO could be uniquely defined;

"Liquid condensate recovered by thermal treatment of lignocellulosic biomass at short hot vapour residence time (typically less than about 5 seconds) typically at between 450-600 °C, at near atmospheric pressure or below, in the absence of oxygen, using small, (typically less than 5 mm), dry (typically less than 10 wt % water) biomass particles. A number of engineered systems have been used to effect high heat transfer into the biomass particle, and quick quenching of the vapor product, usually after removal of solid byproduct "char", to recover a single phase liquid product. Bio-oil is a complex mixture of, for the most part, oxygenated hydrocarbon fragments derived from the biopolymer structures. It typically contains 15-20 wt % water. Common organic components include acetic acid, methane, aldehydes and ketones, cyclopentenones, furans, alkyl-phenols, alkyl-methoxy-phenols, anhydrosugars, and olgomeric sugars and water-insoluble lingo-derived compounds. Nitrigen- and sulphur containing compounds are also sometimes found depending on the biomass source."[58]



There are two different fuel oil grades established by ASTM in march 2015; Grade G and grade D. The main different is that grade D has 10 times less solid contents than grade G, 0,25 mass%, compared to 2,5 mass% of solids in the pyrolysis oil [57].

January 20i5 Europe's first commercial size installation for fuel production opened in Finland by Fortum UPM. Also in Netherland a full size plant for fast pyrolysis bio-oil is opened, and in Brazil there is designed one [57].

In Finland the FPBO is used for heating buildings by replacing heavy oil. It is also used for biodiesel (from woody feedstock) production. Also many other places in the world have made plant for fast pyrolysis to make bio-oil. The company Ensyn has the last 25 years produces bio-oil by fast pyrolysis in commercial scale, to give chemicals for the food industry, and products for heating [57].

In Germany the company Pytec in 2007 has investigated use of FPBO in diesel engines, using a modified Mercedes-Benz 450 kW diesel engine. They achieved totally 10 hours of running, starting with 4 % diesel blending, but reduced blending after starting [59]. Together with the experiments by Wärtsila in Finland, the modifying of the diesel engine needs to be made in

- The gasket and seals must be changes to resist the pH (acids).
- The valves and needles need to be made of stainless steel.
- The temperature of the inlet has to be justified.
- The compression of the engine could be some higher.
- The lubrication of the engine requires some more lubrication products, or some products should be removed from FPBO.
- The fuel tank must have some mixing equipments to avoid segregation of the FPBO [57].

There are several plants making bio-oil from fast pyrolysis wood based feedstock in the world. Table 8 shows those with feeding capacity over 1000 kg/h. The original table also have plants with capacity down to 10 kg/h. The commercial plants are shown here. The other plants are for the most research tables, not commercialized.



Table 8. Fast pyrolysis from wood based feedstock bio-oil plants [57].

host organization	country	technology	capacity (kg dry feed/h)	capacity (kg FPBO ^a /h)	applications	status
		Feeding	Capacity of >1000	kg/h		
KiOR	USA	circulating fluidized bed, catalytic	20 833	4542	catalytic bio-oil for HDO^b	dormant
Ensyn/Fibria	Brazil	circulating fluidized bed	16 667	11 470	fuel	in design phase
Fortum	Finland	fluidized bed	10 000	6313	fuel	operational
BTG BioLiquids/EMPYRO	The Netherlands	rotating cone	5000	3200	fuel	commissioning
Ensyn Technologies	Canada	circulating fluidized bed	2500	1720	fuel	operational
Genting	Malaysia	rotating cone	2000	1200	fuel	dormant
ABRI Tech.	Canada	auger	2000		fuel	dormant
Red Arrow/Ensyn	USA	circulating fluidized bed	1667 (3 each, 1 smaller)		separation of chemicals and fuel	operational
Red Arrow/Ensyn	USA	circulating fluidized bed	1250		separation of chemicals and fuel	operational

Of all the plants, only Fortum in Finland has succeded in making a commercial amount of clean diesel product. According to Fortum's own Web page, the wood based biodiesel can be blend or used unblend without modifications of the diesel engines in most cars[60].

The process from crude tall oil to clean diesel for use in diesel engines cars is shown in figure 19.



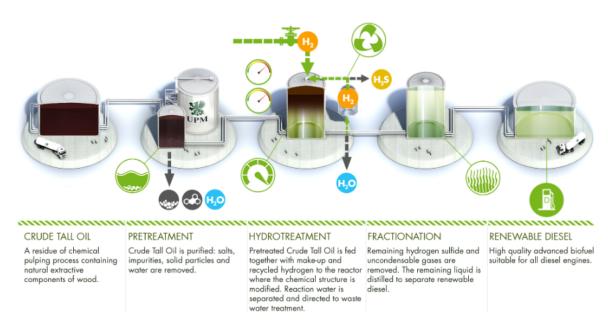


Figure 19. The processes from crude tall oil to renewable diesel usable for all diesel engines as shown by UPM in Finland. The production started January 2015 [60].

The wood based biodiesel from Fortum is the first diesel reported working unblended in existing diesel engines without modifications.

A very interesting master thesis from Iowa State University from 2012, by Jing Zhang, different pyrolysis (fast and primary), gave different chemical reactions. That is not so new, but he found that both pine and oak gave nearly the same result in yieldable levoglucosis (57,31% vs 56,04% wt%). (Levoglucose is the C6 glucose molecules bound in long chain, building celluloce fibre.) Pine is an example of softwood and oak is an example of hardwood[61]. Oak and birch are different trees, but both has high contents of C5, compared to pine. Zhang's results indicates that with pyrolysis conditions, the possible yielding of softwood as bio-oil feedstock should be a possibility[62].

3.3.4. 3rd generation biodiesel.

The research of use of algae as feedstock for biodiesel production, is called the 3. generation of biodiesel. Still it is not produced in commercial scale, but a company in the US, Sapphire Energy, is planning to have the commercial production ready during the next months this year, 2015. The algae oil plant is located in the desert outside



Colombus, New Mexico. They have contract with Phillips 66 and Tesoro, an oil and gas company. Phillips 66 became partners in 2014, and together they test out these days, to see if they could upgrade Sapphire's "green crude oil" to on-spec diesel, meaning it could be used directly in a diesel engine [62, 63]. Articles which deal with algae production, all say that algae could be a valuable feedstock, but point on one great challenge; The high water content. Also the cost seem to be too high for commercial production today. On of the companies is Linde Group in Germany . They also point on Sapphire Energy as the world leader in yielding algae to useable transportation fuels.[64] It will be extremely exciting to follow this project!

On the other hand, both Gerd Klöck in 2010 [65], and Donald. L Klass in 1998, say that yielding bioenergy form algae is interesting, but energy demanding. Klass states that yielding energy from algae is technically possible, but energetically unfavourable [50].

Yielding of algae to combustible fuel made in transportation engines is a great topic, which deserves more discussion. However, the goal of this paper is to go deeper into the possibilities of yielding diesel from cellulosic biomass, especially birch.



4 Results and discussion.

4.1 General

There is a lot of ongoing research for yielding biomass for fuels. Some, like using syngas for making biodiesel, has come to commercial level. Research on cellulosic or lignocellulosic biomass as feedstock for transportation fuels is a part of all that research. It is, as shown in table 8, some biofuel plants which are dormant for some reason, and at least one in design phase (in Brazil), and one resently opened in commercial scale in Finland.

It is an important issue that is has been difficult to find papers which describe yielding of dry birchwood biomass as feedstock for making biodiesel. Stein Tomter at "Skog og Landskap" at NMBU, confirmed that little research has been done in yielding birch as feedstock for bio oil or biodiesel production. He assumes that there are two main reasons; One is that the amounts of C5 sugars in the celluloce molecules makes it more difficult to get usable oil. The second is that the standing volumes of birch trees are much lower than pine and spruce, and is then assumed to not be sustainable for commercial yielding [66].

Gudbrand Rødsrud at Borregaard stated that is more difficult to yield birch as feedstock for their production than pine or spruce, because of the high content of C5 sugars in birch compared to pine and spruce[68] Borregaard has a very modern plant in Sarpsborg, yielding wood as feedstock for a lot of products; vanillin, glue, amongst many others[9, 67]. However, studies with different hardwood trees has resently showed that it is possible to use processes and mix catalysts such that lignocellulosic cells also is possible to yield to make biofuel, I. e Yan et al [54].

Also the result from the master thesis of Zhang from Iowa State University, indicates that it is possible to use hardwood as feedstock for bio-oil, though this work was based on comparing pine and oak, (not birch).



4.2 Gas or liquid fuels driven engines?

Gasoline engines can easily be modified to work on gas[68]. The gas has to be compressed. Therefore a tank with sufficient strong walls has to be used. Then big ships would need a tank, which would be too big and heavy, if the tank should store gas for weeks of sailing. Security issues with storing such big volumes of a combustable and explosive gas would also say that this is not a good idea. However, in 2014 several ships were built with gas engines, or gas as an alternative fuel to diesel, in hybrid boats. Still it is a security question to make the tanks safe enough to avoid emissions and explosions [69]. For heavy trucks, especially long-distance trucks, the same objections could come. Especially would gas engines for aeroplanes of the same reasons be unwanted. For heavy transportations engines, and especially aeroplanes, therefore liquid fuels are preferred.

However, gas is used today in small vehicles, and also in town buses. Both natural gas, biogas and hydrogen is known as fuels for town buses and local small lorries [65].

There are 50 gas ships in the world. (44 owned by Norwegian ships-owners). Some new ship today is built with LNG gas engines, which means that they have up to 80 % lower emissions [70].

Then research and developing plants for liquid fuels for transportation diesel engines is and will be of great importance.

4.3 Diesel from syngas or bio-oil from fast pyrolysis? Sustainable process and use of transportation fuels.

As reported in chapter 2.2.3.3 the plants from Petro Sa & Sasol, Shell, and QP/Sasol in South Africa, Malaysia and Qatar, produces FT-diesel from syngas. The plants in Malaysia and South Africa have operated since 1993, so it is not wrong to assume that there is sustainable economy in these plants. The plant in Qatar has the



latest start up date. Then the thermodynamically technic had developed since the two earlier; both with the reactor design and the catalysts, with separate of the catalyst.

In chapter 2.2.3.4 was presentated the wood based bio-diesel from Fortum in Finland.

There is common knowledge that it is dangerous level of carbondioxide in the atmosphere. Both drilling of new and force more oil of old fossil oil fields will lead to more CO₂ emissions. Use of biofuels will reduce this emission, according to UPM, with their new technology, up to 80 lower CO₂ emission. Figure 20 shows the reduction potential of greenhouse gases, according to UPM's own web page.

FIVE TIMES LESS GREENHOUSE GAS EMISSIONS PER EQUIVALENT JOURNEY

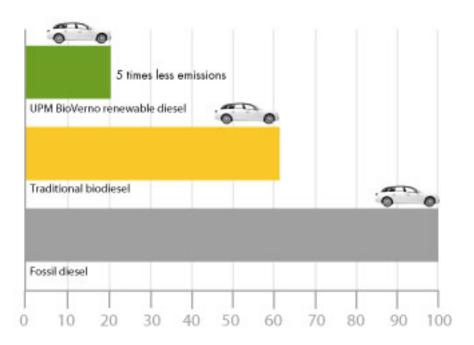


Figure 20 Greenhouse gas emissions reduction potential if changing to UPM renewable diesel.[60]

It is very exciting with the production of clean renewable diesel from cellulosic biomass in Fortum UPM, Finland. Because it still is so short time since the factory opened for commercial production, we wait for more articles about the topics. It is also some



difficulties because it is a commercial production. Fortum UPM is a commercial company, with own employeed researcers.

The UPM plant in Finland has invested over 175 million Euros, and has a capacity on 120 million litres of yearly biodiesel production.

In the future, ordinary cars could be driven by electricity, gas or biodiesel from renewable sources. From reasons mentioned in the last paragraph, heavier trucks, boats and aeroplanes still would demand liquid fluid. To get that fluid from renewable resources is now possible for diesel engines, according to UPM [60].

From figure 16 and 18, there were shoved that the yielding of cellulosic biomass could go through path number 3, 8 or, 12. The processes, both at UPM in Finland, but also the FT diesel made in South Africa, Malaysia and Qatar, could follow slightly different routes. From figure 16 the box "Hydro treating and refining" could mean the same as in figure 19 from UPM shows as fractionary. Figure 16 is only one of many overview over routes from different sources to different fuel products.

From chapter 3.2.3.2 Yan et al stated that the most developed process from lignocellulosic feedstocks so far was the gasification process followed by cleaning and then FTS, or CO hydrogenation. However, UPM in Finland claim to have the world's first plant to produce clean diesel form lignocellulosic feedstocks. Since Yan et al talks about aviation fuel, and UPM about diesel for transportation units, for use in diesel engines, there is perhaps not the big contradiction like it seems.

Yan et al has produced clean aviation fuel at Departement of Agricultural and Biological Engineering, at Mississippi State University, USA. They have not done the test in a full scale plant, but they assume that it is possible. Their experiment was successful in making pure aviation turbin fuel, but only a few liters.

On the other hand, UPM in Finland has succeded in building a full scale plant, with capacity of 120 million liters biodiesel pr year. They won 5. March this year (2015) Commercial Scale Plant of the year award in Amsterdam.

Neither of the two special mentioned plants here used birch as feedstock. UPM uses waste from their mills, where a little fraction is birch, while Yan et al used oak-tree



wood chips in their investigation for forming aviation turbine fuels. They did not say why they used oak. Both syngas and waste from cellulose industry is used for raw material in fuel production.

4.4 Feedstock of residues or fresh timber?

The forests in the boreal belt, in Scandinavian, Russia and Canada, have the last decades grew much more every year than logged. The potential for using wood as raw material for liquid biofuel seem to be large. The growth is expected to increase even more because of global warming and longer growth periods each year[6]. Replacing fossil fuels with fuel from biomass could force more activity over to use wood as feedstock. It is a question if it is enough waste in the world to fill the needs for transportation fuels. Bio oil from fast pyrolysis, and clean biodiesel from wood based feedstock, both can use wood as raw material.

4.5 Definition of bio-oil or biodiesel.

Biofuel have many names; diesel, biodiesel, bio-oil, synthetic diesel, wood based biodiesel, and other combinations. In addition there are several fluids that are blended in fossil diesel, or in some kind of biodiesel. The standard definition of biodiesel is from the first generation of biodiesel; mono alkyd ester from long chained fatty acid derived from vegetable oil or animal fat [70].

Diesel is defines as hydrocarbons with chain length from 12-20. Biodiesel is a quite different liquid. Both has the properties that is combustable in a diesel engine. Through a FTP it is possible to make hydrocarbons like the fossil diesel. Then the liquid is called FT-diesel, or synthetic diesel.

According to ASTM, there is 7 kind of fossil diesel (different amounts of C12-C20). This is ASTM 975[71].



My opinion is that all liquids suitable for diesel engines could have the name diesel. The most important way to separate those liquids is to say if the liquid comes from fossil resources, or from biomass resources, due to the carbon life circle. Then we could separate in biodiesel from vegetable oil, animal fat, some kind of biological waste or cellulosic biomass. Then the main choice would be if the diesel product is environmental sustainable. Fossil diesel free up carbon stored million of years ago, and biodiesel has a sustainable carbon circle, with zero emission, depending on how many decades it take for the bio resource to grow to the harvestable size.

4.6 Summary.

The economy in UPM's new plant in Finland is done without subsidies from the government. Today it is used waste from pulp industry. If the plant should pay for wood as raw material, the economy would not be sustainable.

It have been difficult to find papers describing birch as biomass resource for yielding any kind of biofuel. Many papers describe other hardwood, as use of oak, through fast pyrolysis making ATF [54]. Probably birch is useful as a resource. Research can be done with trying processes and different mix of catalyst. The work and results from UPM shows that woody biomass is a reliable resource in making biofuel. Yielding of wood as biomass for transportation fuels can result in

- Fewer greenhouse gas emissions.
- Yielding the most abundant biological polymer in the world.
- Cellulose is not digestive for human being.
- Wood does not use food supplies.
- Wood can grow on land not suitable for eatable vegetables.

There are several advantages for using biomass, especially wood as resource, and further research should be done.

UPM has been used as source in this paper. It has been difficult to find reliable articles direct on the processes used at UPM. Several mail has not been answered. This could be because some processes are hidden due to commercial secrets. The knowledge



of how to develop renewable wood based diesel usable for ordinaire diesel engines should be known by more companies. More work should be done to find and develop this knowledge in Norway.

This paper has showed that Norway, and the boreal belt, contains increasing huge amounts of cellulosic standing volume biomass. This is both an important carbon storing, and an energy resource which could be yield in a renewable way.

Cellulosic biomass with relatively huge amount of C5 sugar in the cellulose mass as switchgrass and oak, has been shown as usable feedstock for biofuel production. No paper was found in direct yielding birch as feedstock for biodiesel. Since the content of C5 in birch is about the same as in oak, one can assume that birch could be yielded as bodiesel feedstock. More research of processes, including reactor tank design, heat transfer medium (as molten salt (Nygård)), temperature level, catalyst compounds and more, should be done.

A personal opinion, is that Norway, with such huge amount of economical resources, has a moral duty to finance such research in order to reduce the emission of greenhouse gases.



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