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BIOFUEL SPILL RECOVERY FROM WATER

With a focus on sorbing materials

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Abstract

Oil spills into natural water bodies are common environmental disasters and there is a plethora of well-researched and generally accepted methods and technologies for dealing with this problem. An extensive legislative apparatus also exists to prevent these occurrences and ensure the liable parties defray the costs of such catastrophes. With the increasing production volumes of renewable fuels, the question arises of whether it is a viable option to apply the same recovery methods and legislative standards to some little-researched fuels and their unpredictable behaviour. The research done for this thesis consisted of investigating how biofuels can be recovered and what legal matters this entails.

Oil spills recovery operations most often rely on applying skimmers, sorbing materials, booms and burning the fuel. This thesis consists of conducting a theoretical study of the existing methods and testing protocols for conventional fuels, especially those that have to do with sorbent materials, and developing laboratory tests that would provide us with the information of how the problem of mitigating biofuel water spills could be approached. Five different fuels were tested in the laboratory, amongst them three renewable fuels – NExBTL (provided to us by Neste Oyj), pyrolysis oil (provided by Fortum Oyj) and ethanol blended gasoline E85 . Two other fuels were conventional diesel and gasoline.

NExBTL is a renewable diesel that is very similar chemically to conventional diesel. E85 dissolves in water and pyrolysis oil has a very complex and little-studied behaviour when added to water. Part of it completely dissolves in the upper layer with a dense tarry layer emerging on the bottom. This makes recovery of these two fuels impossible by applying the current technology that is widely used. Another big issue that this bring us to is the necessity to classify these fuels differently in environmental protection legislature created for fuel spills. One possibility for mitigating a pyrolysis oil spill could be of biological nature in order to speed up biodegradation.

Subject headings, (keywords)

biofuels, behaviour in water, renewable diesel, pyrolysis oil, fuel spill

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1 INTRODUCTION

Fuel spills of conventional fuels have become a common occurrence ever since humanity has set itself on a path of rapid industrialization and energy intensive production. We are highly reliant on many kinds of combustible substances depending on what purpose a particular fuel is used for. The main point is that all fuels are more or less harmful to the environment. Petroleum-based products emit lots of pollutants such as SO_2, NO_x's, PM_x's and greenhouse gases into the atmosphere (How Does Oil Impact the Environment? 2016). Despite the significance of this environmental problem genrally, this thesis will focus only on its one aspect - the emission of fuels into water.

Fuels spills often turn into big news when stories about them seep into the mainstream media. For example, the article by the Telegraph in 2011 presented to the readers of this newspaper the catastrophic scale of 10 biggest oil spills in human history. According to the article, the famous Gulf War oil spill that occurred in 1991 released around 360 million gallons of crude oil into the Persian Gulf. The most recent undeniable catastrophe, that most of us are well familiar with, thanks to the extense media coverage, which occurred in the Gulf of Mexico pinned the number of spilled gallons of crude oil at around 210 million (10 Largest Oil Spills in History 2011). Surprisingly, it is not the oil spills that contribute the most to the petroleum based products' pollution in water. Despite this popular belief (largely caused by the media), it is mostly vehicles, boats, industry and machinery and intentional dumping that release oils that eventually reach water (Sources of Water Pollution 2014).

Oil is extremely toxic to the marine environment and birds producing numerous negative effects in organisms. Fuels damage birds' plumage and reduces the insulating ability of fur-bearing animals. When fish are exposed to petroleum-based products, they develop enlarged livers and experience reduced growth and other adverse health effects (How Does Oil Impact Marine Life 2014).

1.1 Biofuels

This thesis presents biofuels in particular and ways to deal with them as the main object of this research. As our biofuels industry is developing at a rapid pace (Dufey 2006, 4), it has become increasingly important to start doing numerous and concrete research on

assessment of the behavior of biofuels in water and methods to mitigate biofuel spill disasters. Biofuels include various types of fuels (these will be discussed in much more detail later in this thesis). Fortunately, we can already at this point note that many of them have similar behavior and physical properties to those of conventional fuels. However, there are some biofuels, which are commonly used or quickly emerging as new alternatives, that appear to be unlike any conventional fuels that are currently in use and this dilemma of whether this is the direction our industry should go in must be attentively looked upon as we are considering the prospects of using them. Additionally, despite a seemingly successful biofuel spill recovery, there are water soluble fractions in fuels that can be toxic to aquatic organisms (Leite et al. 2015, 576). Another study confirmed this by discovering toxic effects of three types of biodiesel (produced from castor oil, palm oil and waste cooking oil) on microalgae and sea-urchins (Leite et al. 2011, 895).

The research on biofuels' behavior when their spillage occurs has been lagging behind the development and the scale of biofuels' use. Their spill into water is only one area of the multidimensional problem that emerges as a necessary consequence for substituting conventional fuels for their biological counterparts as we integrate them into the everyday economy. Some other complex issues that heir usage may entail include spills into soils and pollutants emitted into the air.

1.2 Behavior of conventional fuels and biofuels in water spills recovery operations

Generally in fuel spill operations, three very important key oil properties must be taken into account at the very beginning of the recovery operation. These are the relative density to water, pour point (simply put – the temperature that gives us the point at which the fuel stops flowing) and viscosity. Oils can also be categorized as some type (usually 4) where each types represents its natural ability to evaporate and disperse (Transportation Research Board and National Research Council 2014, 69.).

As mentioned earlier, many bio-fuels such as biodiesel, renewable diesels, NExBTL are comparable to the behavior of their petroleum-based counterparts in water. However, even these seemingly identical substances might behave slightly differently when studied closely. In addition to this, some other biofuels, such as pyrolysis oil and ethanol fuel, behave like no other conventional fuel; therefore, it will be of utmost importance

to describe their behavior in water and try to develop ways to mitigate oil spills of these substances.

In addition to this, pyrolysis oil and biodiesel can cause serious damage to the materials used in the mitigation processes done for these fuels due to their acidity and other chemical properties that differ from their traditional counterparts.

1.3 The ÄLYKÖ project

This thesis is a part of the ÄLYKÖ project of South-Eastern Finland University of Applied Sciences (Xamk) .The project was launched in the beginning of 2015 and continued until the end of February 2017. The project aims at minimizing and preventing environmental risks and damage from transportation and storage of hazardous materials and oil in Eastern Finland and the water shed area of Lake Saimaa (MAMK University of Applied Sciences 2015). The project ÄLYKÖ was financed by the South Savo Centre for Economic Development, the South Savo Fire and Rescue Department, the North Karelia Fire and Rescue Department, Meritaito Oy, Metsäsairila Oy and South-Eastern Finland University of Applied Sciences. Marko Hintsala from Knorring Oy AB also kindly provided some expertise and samples (listed later in the text) for this project during our meeting with him on 14.10.2016.

My thesis is a continuation and completion of the work done by one of my group members in her thesis on the behavior of biofuels in soil (Zhaurova 2016). In this thesis we investigated what current technologies and methods of recovering fuels in case of large spills exist and whether these methods can be transferred and applied to biofuels. The main focus of this work was on how effective are sorbents in this regard and what existing protoclos and testing standards are beneficial to the tests developed for this work. It was also important to investigate if the current legislature is applicable to these new types of fuels. Additionally, it must be mentioned that this thesis does not contain any unusual and complicated terminology. Some terms that might be confusing to the reader are explained in APPENDIX 3.

2 OIL SPILL RECOVERY OPERATIONS

The current studies on oil spill recovery have been applied in labs as well as real-world simulated conditions. Due to our long and rich history of dependence on petroleum-based products, the amount of studies and papers published on this issue is enough to garner a very clear view on what products and materials are preferable for using in handling petroleum-based fuels as well as for transportation and storage of such fuels. However, all these go only as far as we are considering conventional fuels. Very little information is currently available for sorbents and damage tests as applied for biofuels. For some fuels such as NExBTL (which is a renewable diesel) and biodiesel, the assumption that they will behave in a very similar way to the already well-studied conventional fuels is quite realistic. However, this is not aways the case depending on the conditions a spill occurs in as well as the equipment and tools used for the recovery and mitigation operations. That is why this assumption must be well examined and checked whether it holds any truth to it in the case of oil spills.

Very little research exists on the behavior of pyrolysis oil (bio-oil) in nature and no information on its behavior in oil spill situations has been found. Thus, it was quite motivational and challenging for me to acquire completely novel data and insights into its behavior.

2.1 Methods for combating oil spills

There already exist some very well established ways of mitigating the consequences of oil spills. The methods range quite a lot. Here we can in some detail describe the widely applied techniques that have proven to be more or less successful.

First of all, there are tracking systems that help to detect and collect data on oil and chemical spills as well as tracking contamination. Oil booms are used for corralling off the oil slick and directing it to a particular location or containing it until further measures are taken. Skimmers are boats that utilize brushes and pumps as well as some other tools for extracting oil from the water surface. There are international standards to test the recovery performance of skimmers (ASTM F2709-15, 2015). Skimmers are usually combined (i.e. used in coordination) with a boom system. In a brush skimmer a fine-bristled brush would be used for lighter oils and a hard-bristled one for heavy fuels.

There are also chemical dispersants and mechanical ways of cleaning oil as well as burning the oil slick in-situ and letting it bio-degrade.

Many different tools that are commonly used in fuel spill recovery operations will not be discussed in great detail in this thesis. For instance, in real life situations booms (depending on the shape, material and mass) would behave differently and this would give us the very important data on how high the boom floating on top of the water is after it had absorbed some volume of fuel. As Schrader notes: "a boom must continue to act as barrier to oil, even after the total absorption." (Schrader 1990a, 589). These are very particular problems that require their own specialized research.

2.2 Legal matters and difficulties in conducting experiments in real-world conditions

There are very strict laws that govern oil spill recovery processes. For example, in the UK, under the oil recovery codes of practice, only those vessels granted the Oil Recovery Certificate by the Marine Safety Agency are given the official permission to operate as an oil recovery vessel. This particular code's scope of requirements includes training of the personnel, knowledge of fire protection, ventilation, gas detection and alarm systems and many more strict demands (Code of Practice for Vessels Engages in Oil Spill Recovery Operations 1996.).

It can be difficult to obtain the permit for conducting realistic large-scale experiments on oil spill mitigation in real-world conditions (US Congress, Office of Technology Assessment 1990, 32). In some countries like France, UK, Norway and Canada this can be done easier than in, for example, the US. For instance, some dispersants used in oil spill clean-ups, when submitted for tests, must undergo different screening depending on the country (Committee on Effectiveness of Oil Spill Dispersants, Marine Board, national Research Council 1989, 86). To see the interaction and interdependence of the various countries in their research regarding the fuel spills we can look at a lage-scale study done in Canada described by Richard Lazes in his paper published in 1994 in Spill Science and Technology Bulletin that has shown that in-situ oil slick burning is not as harmful as initially thought and this has paved the way for allowing this method to be used in some U.S. areas by Region 6 of the Regional response team and evaluation of this method by other countries. SYKE in Finland lead a similar study in 2012 where a

simulation of a huge oil spill was conducted in the Baltic Sea (Weaver 2012). These types of simulations test the readiness of countries to combat huge environmental disasters.

Two test protocols have been developed by MMS (Minerals Management Service) in 1992 for testing skimmers and booms. The purpose behind this is to help governmental authorities to plan better for what equipment should be used in the case of an oil spill. This organization cooperates closely with American Society for Testing and Materials to create new and further improve existing protocols for oil spill response (U.S. Department of the Interior. Minerals Management Service 1996, C-13.).

2.2.1 Legal matters involving recovery of biofuels

There are quite a few types of biofuels and and the behavior of some of them matches the behavior of the traditional fuels they are supposed to substitute quite well. They behave similarly because they are also often diluted with their non-biological counterparts. Biodiesels are a different matter due to their chemical composition. They degrade faster than petroleum diesels and their toxicity is less strong. They also speed up the degradation time of petroleum diesel when diluted with it (Handbook of Oil Spill Science and Technology 2015, 88). However, given the slight differences even in the most favorable scenarios, we cannot rely on the same regulations and methods to mitigate oil spill occurrences that are applied to petroleum-based fuels. For example, in 2007 Washington State expanded its Oil Spill Act to cover biofuels as well. This practice might not seems sensible but, given the current situation, we simply do not have enough data and research done to do otherwise (Marten Law 2007).

2.3 Using sorbents for the recovery of fuels

Once an oil slick is contained, sorbent materials can be utilized to recover/extract the liquid. There are quite a few differend kinds of sorbents used for this purpose but the main categories are natural organic sorbents, natural inorganic sorbents, synthetic sorbents. We worked with all three types in the tests conducted for this thesis. It is necessary to study the properties and behavior of these sorbents when applied to various types of fuels to get the best results out of their application. For the purpose of this thesis

we can define sorbents as materials absorbing and adsorbing liquids (more on this in APPENDIX 3).

Sorbents can first be divided into two main classes – oil only and universal sorbents. The first type is strongly oleophilic and hydrophobic whereas the second type should in theory be able to sorb all chemicals, solvents, water and oils (Environment Agency 1998, 3). Further, sorbents can be divided into some basic groups (as mentioned above): inorganic, natural organic and organo-mineral, synthetic.

Good absorbing materials should have the following properties: high uptake capacity, high rate of uptake, good retention capability over time, possible oil recovery from sorbents, re-usability and biodegradability of sorbents. The range of synthetic sorbents is quite large. They are made in different ways for varying purposes (e.g. for all types of chemicals or only hydrophobic materials). It is worth noting, that synthetic sorbents are usually given their distinctive color code indicating what a particular sorbent is used for. Product meant for oil only are typically blue or white, universal sorbents are grey and sorbents designed for all chemicals are yellow (West Coast Spill Supplies 2016). The most commonly used materials for oil spill clean-up operations are currently polypropylene and polyurethane.

Due to the lack of this type of research for biofuels, the current methods widely applied for sorbents used for conventional fuels are assumed to produce similar results for biofuels with similar properties. In practice, there shouldn't be any real distinction between these methods anyways, as bio-fuels are supposed to replace traditional fuels and used for the same purposes.

2.3.1 Research and tests for sorbing materials

Once again, there is, unfortunately, no universally accepted testing methods for determining what standards sorbents manufacturers should be following. But Environmental Canada has already developed an official Canadian standard for testing sorbent materials. These include desirable properties that the tested sorbents should have and the methods for testing them (Cooper, Keller 1992). In addition to that, Environment Canada is attempting to develop a comprehensive testing program that will provide extensive information on initial and maximum sorption capacity, water pickup, buoyancy, re-use

potential, retention profile (this one had already been integrated into my tests done for this thesis), material durability and disintegration as well as such important factors as ease of application and retrieval. Many end users of sorbents require non-biased and reliable information about the product before considering their acquisition. Environment Canada is aiming to incorporate as many useful methods as possible from the ASTM standards that have top status amongst all protocols in existence so far (Cooper David & Gausemel Ingvil 1993, 549-551).

A standard protocol, given the code ASTM F726-99, is relied upon by the Environment Canada Sorbent laboratory. It tests the ability of a sorbent to pick up some quantity of liquid. Sorbents are tested for liquids of differing viscocities and two time intervals are used. A long and extensive report was published in 1999 testing adsorbing and absorbing properties of materials in adherence to this protocol. One important factor contributing to how good a sorbent's performance is in practice, according to this protocol, is shown by the buoyancy tests. It states that if over 10 % of the sorbent sinks under a dynamic degradation test, the material is shown to be defective for real world applications, where wave motions can produce a similar effect. Our test methods are very similar to the ones presented in this protocol when it comes to testing sheets, pads, blankets, mats (Type I) and loose – unconsolidated particulate material (Type II) (SAIC Canada 1999). However, we have simplified the procedures slightly and made them more suitable for the equipment and resourced that were available for our work.

Despite the seeming successful attempts at creating comprehensive testing protocols and standardization, I encountered many problems even in my own research on this topic. Bazargan et al. in their paper Standardization of Oil Sorbent Performance testing (2015, 1271-1278) argue that there is a good reason for why the testing protocols deveoped by ASTM are not used uniformly and have not become the univeral standard for testing oil sorbent properties of materials. The authors of this paper find fault with no clear standard for dripping time and argue that reporting a complete dripping profile (uptake capacity vs. time) gives a lot more information about the interaction of the sorbent with the sorbate. Secondly, the mesh size used for holding a fine-particle sorbent during the test might produce a noticeble impact on the measurements due to the trapped sorbate between the sorbent and the net. Another important factor that needs to be taken into consideration when conducting absorption tests are the properties of the sorbate that can change depending on many factors. The authors also propose some solutions

for imroving this protocol. In our tests we have tried to use this research to obtain more reliable results.

2.3.2 Benefiting from the existing studies on sorbent testing

Although the process of testing sorbents for their rate of absorption, uptake capacity and retention time seems simple at first, there is some nuance involved as shown above. Thus, we have tried to benefit from the range of the exisiting protocols and studies and transfer these techniques onto the conditions we had at hand. The other significant work that must be mentioned, that gave us some very useful tips and data, that I rely for sorbing testing throughout my research is Kauko Himanka's Bachelor's thesis in which he investigated a wide range of sorbents used on the Finnish market (2006).

3   BIOFUELS

The five types of fuels we focused on in this thesis are the following (amongst them two types of fuel that are considered conventional): diesel, 95E10 gasoline, renewable diesel NExBTL, E85 ethanol fuel blend (containing 85 % of bioethanol) and fast pyrolysis oil. NExBTL as expected to behave in a very similar to conventional diesel. In fact, its chemical composition very closely approximates that of petroleum-based diesel. Therefore, we had some confidence that this fuel wouldn't pose many difficulties based on the research done before we even started doing the tests (Neste Corporation 2016a). E85 and pyrolysis oil are challenging in this regard because their behaviour is not at all comparable to the fossil fuels that we are so familiar with. More information about their chemical composition and behaviour upon mixing with water will be presented in the next few sections. The difference between renewable diesel like NExBTL and biodiesel will also be discussed, as these two are still very often confused and renewable diesel hasn't yet acquired the reputation of a great substitute for conventional diesel that it will, in my opinion, gradually acquire in the future. In fact, the production volumes of renewable diesels are already much higher than those for biodiesel in Finland.

3.1   Diesel and 95E10

Before the biofuels are discussed, it would be informative and necessary to mention quickly what we expect from these two conventional fuels upon their spillage into water. Then this can be counterposed to the behaviour of the biofuels and the challenges that the recovery process for these fuels involve when compared with the two fuels presented in this section.
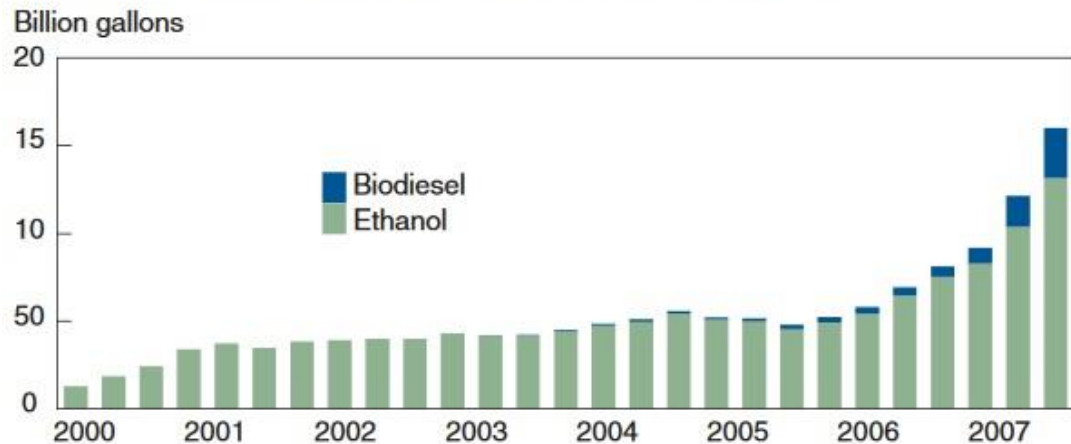
We are all well familiar with the famous image of a very thin dark-colored slick on the surface of water that instantly arises when we think of oil spill catastrophes. This is what crude oil in water looks like. It spreads over a large area until it forms a very thin film floating on top of water. Spilled diesel and gasoline have very similar behaviors, they can be collected or the spills can be mitigated by the methods presented in chapter 2.

3.2   Defining and classifying biofuels

Biofuels are fuels produced out of living matter or, to simplify it slightly, from biomass. The main goals are to decrease the dependence on fossil fuels, decrease the release of greenhouse gases into the atmosphere and to provide a more stable, more geographically uniform and more controlled way of energy production with better linking of rural areas with urban centers (Naik et al. 2010). Biofuels can be prepared from different types of biological feedstock. Thus, it becomes quite important to develop industries that take advantage of using cheap, easily-replaceable feedstock that does not strain human resources and does not come from food production, which is not only an economically dubious solution but is also a psychologically unappealing one. For example, bioethanol is produced from sugars such as sugar beet and sugar cane, starch such as wheat and corn, as well as cellulose that comes from, for instance, different species of trees and switchgrass. Biofuels are produced from waste in Finland, mostly out of the residues from the forest industry (Bayar 2013). Biodiesel can be produced out of lipids, which are often exracted from seeds, cooking oil, algae (Jaliliannosrati et al. 2012a, 145). The energy balance of a particular type of biofuel (energy input vs. energy output of the final product) must always be estimated along with the costs. These net balances are more favourable, for example for biodiesel than for bioethanol (Coyle 2005, 28).

Figure 1 demonstrates well the rate of growth in biodiesel and bioethanl production on the world scale from year 2000 to 2007. The volume of production of NExBTL and pyrolysis oil can still be considered miniscule when compared with these well-established fuels on the world market.

FIGURE 1. Biodiesel and bioethanol production on the world scale.

However, according to Timilsina's estimates (Timilsina 2012), this growth decelerated rapidly after around 2008 and biodiesels comprised only 2,7 % of all fuel consumption for transportation purposes.

The next figure (Figure 2) illustrates well how the type of feedstock affects the efficiency of the oil yield production. By looking at this figure, it becomes clear why a lot of research is currently done on using algae as the feedstock material. It is many times more efficient than its next competitor – palm oil – and it is completely unexhausting on arable land when compared to some common crops that are used for production of biofuels.

Oil Yield/Acre/Year

Feedstock	Soy	Safflower	Sunflower	Rapeseed	Palm Oil	Micro Algae
Gallons	48	83	102	127	635	15000
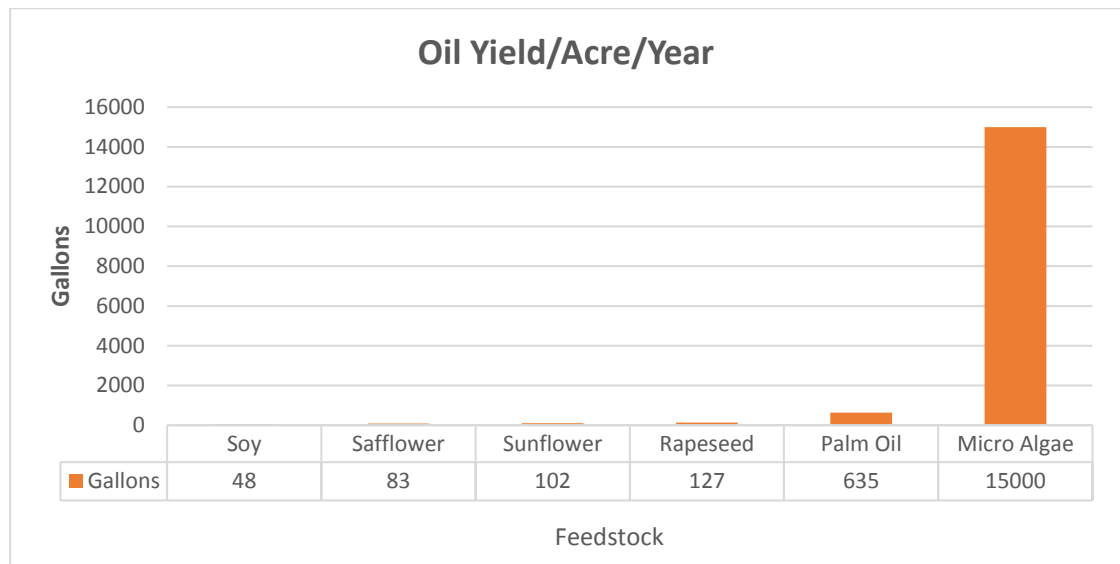
FIGURE 2. Yield in gallons depending on feedstock (Jiliannosrati et al. 2012b, 145).

It is also important to make the distinction between primary and secondary usage of biofuels. That is, primary biofuels are used in the way that is well familiar to us – wood chips, firewood and other types, by direct combustion for our everyday requirements of heating and electricity production. Whereas secondary biofuels undergo a chemical process to produce an intermediate energy-containing substace (solids, gases and liquids) to be used as, for example, transport fuels later on (Food and Agriculture of the United Nations 2008, 11).

Defying biofuels can also be problematic because it depends on what ratio of a particular biofuel (e.g. bio-ethanol) is mixed in with a conventional fuel. For example, E85 that was used for our tests is considered a biofuel, although it still contains 15 % of conventional fuel, usually – gasoline. Last but not least, the classification based on the type of feedstock must be discussed, which is necessary to understand the efficiency and economical value of a particular biofuel.

Secondary biofuels can be neatly divided into first, second and third generation biofuels. The first generation biofuels use edible crops as their feedstock materials, which often means growing such nutritional staples for producing fuels. This is obviously a dubious way to deal with the fossil fuel problem from the ethical perspective. First generation biofuels have gained popularity through the benefits they provide for energy security

and their ability to easily blend with traditional fuels, as well as almost identical compatibility with the already existing technology and infrastructure. Still, global food security is endangered and valuable arable land is used up for this purpose. Second generation biofuels are produced out of residues of edible or non-edible (leaves, bark, fruits, seeds) foodstock used for the first generation biofuels or from non-edible biomass such as grass or lignocellulosic biomass. This is much less straining on the environment and a good way to approach it is by using more efficient feedstock material and less dependence on edible crops (Fakhruddin 2017). The following figure (Figure 3) illustrates succinctly the chemical and thermal pathways involved in the production of the second-generation biofuels:
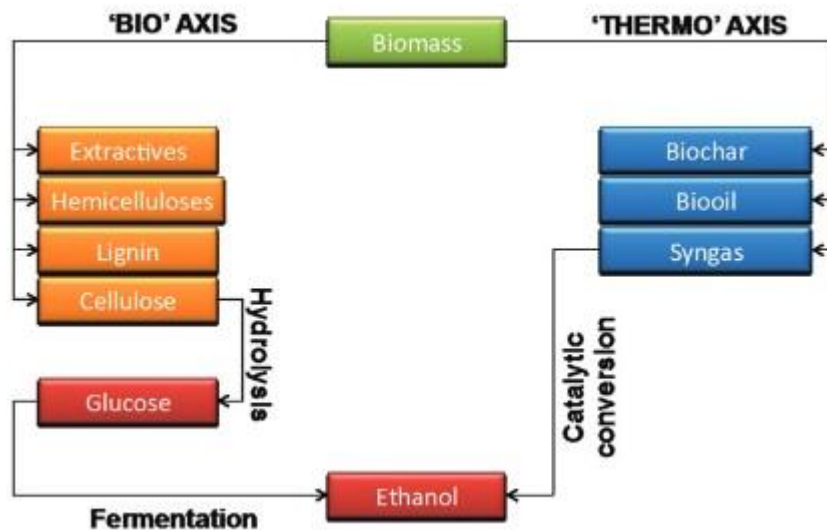
FIGURE 3. Simplified pathways through chemical and thermal means to produce biofuels out of lignocellulosic feedstock material (Lee & Lavoie 2013a, 8)

Third generation biofuels are very energy-rich and are, in principal, CO_2 neutral. Mostly, microalgae is used for their production, thanks to the very high lipid content of these organisms. The problems, of course, include the large volumes of water needed as well as high dependence on geographical location. This is still a highly-researched area in the production of biofuels and the technology is still under development to produce fuels made out of algae efficiently and cheaply (Lee & Lavoie 2013b, 10) . Mainly, the technological processes are converting by biochemical reactions, for example, to produce biogas via anaerobic digestion or biodiesel through transesterification (Alaswad et al. 2015, 1459).

3.2.1 NExBTL

For this thesis we received a sample of renewable diesel NExBTL from the Finnish company Neste Oyj for using in our tests, which is chemically almost identical to conventional diesel, unlike biodiesel. NExBTL is produced by hydrotreating vegetable oil, whereas biodiesel is produced by transesterification. Due to the aerobic conditions of production, oxygen molecules are present in this type of diesel fuel (i.e. biodiesel) and this, in turn, produces different chemical and physical properties (e.g. less sulfure emissions, difference in biodegradation rates, more efficient burning, stronger solvency and corrosity), as well as requirements for modifying the engine. Most modern engines can handle blends of diesels of which around 100 % percent is biodiesel. However, older engines and piping systems might have to be converted due to these differences in the chemical compositions (Biofuel Chemistry: What Are Biofuels and How Are They Made? 2010).

NExBTL, as mentioned before, closely approximates the conventional diesel in its chemical and physical properties, which guarantees easy subtitution of the conventional counterpart by this version of diesel fuel in any type of equipment or blending with conventional diesel to any ratio of NExBTL to diesel. It is a valuable product also due to the much lower harmful emissions of, for example, NO_x's, PM, PAH's and CO. A large range of biomass materials can be used for the production of this fuel (Neste Corporation 2016b). The following table (Table 1) gives a good general overview of the differences and similarities between NExBTL (Neste Corporation 2016c) and conventional diesel (Properties of Diesel Fuel 2017):

TABLE 2. Comparing NExBTL with conventional diesel.

Property	NExBTL	Conventional Diesel
Appearance	Clear & bright	Colorless to amber
Cetane number	> 70	> 40
Cloud Point (maximum) (°C)	-34	-34
Water and sediment (maximum volume) (% V/V)	≤ 0,02	≤ 0,02
FAME content (% V/V)	0	7
Density (kg/m³ at ATM)	770-790	832
Sulfur content (mg/kg)	≤ 5	15-500
Cold filter plugin point (°C)	-5	-5
Calorific Value (MJ/kg)	44	45,5

Flash point (minimum) (°C)	> 61	40
Viscosity at 40°C (mm²/s)	2,0-4,0	2,5-3,5
Carbon residue (% m/m)	< 0,10	< 0,10
Ash (% m/m)	< 0,001	< 0,001
Oxidation stability (g/m³*h)	< 25	< 25
Conductivity (pS/m)	≥ 50	≥ 50

Finally, the different chemical reactions that oils undergo to yield either renewable diesel (NExBTL in our case) or regular biodiesel are shown in the following figures (Figure 5):
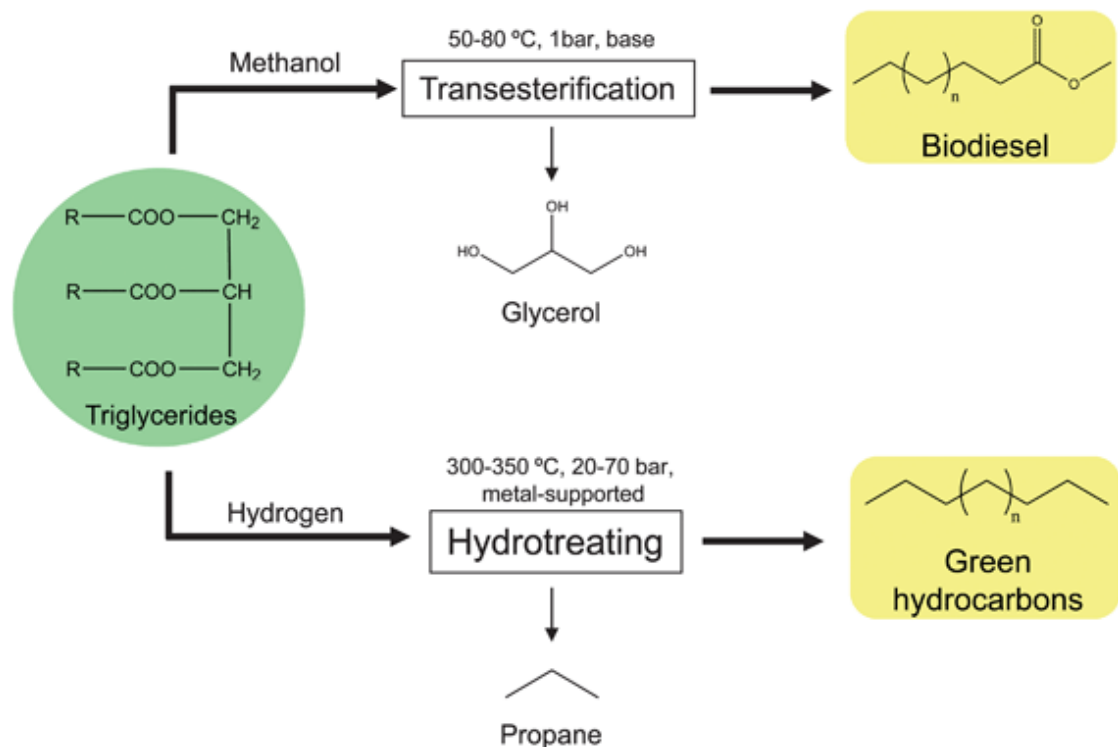

FIGURE 5. Different types of diesel produced by transesterification and hydrotreating (Serrano-Ruiz et al. 2012)

Note the presence of the oxygen molecules in the final product of the transesterification process and the need for a catalyst in the form of base or acid. This final product is also known by its chemical name as methyl ester.

3.2.2 E85

E85 is considered a biofuel due to the large part of bio-ethanol that is mixed with 15-30 % of gasoline in Finland. E85 is a more efficient transportation fuel than 95E10 gasoline and it is meant for usage in so-called flex-fuel vehicles that can run on fuels consisting

from differing proportions of gasoline and ethanol (Korkeaseosetanoli E85, 2016). The main purpose of using this fuel is to decrease the amount of released CO_2 into the atmosphere. It is produced by utulizing the well-known fermentation process that relies on large masses of feedstock materials rich in sugars and then simply mixed with gasoline. In countries like Brazil and USA most of this feedstock material is corn. Adding ethanol to gasoline raises the octane number. The equipment used in combination with this fuel must be converted by using suitable materials. For example, rubber to Teflon and aluminium for stainless steel (E85 as a Vehicle Fuel). One of the most interesting and problematic properties for our work in particular is that E85 separates into two phases upon adding it into water with the lower layer completely miscible with it and a very thin upper layer of undissolved gasoline on the top that can also be homogenized with the rest of the solution by stirring or shaking it (Vakkilainen 2016, 9). The following figure (Figure 6) demonstrates the growing production volumes of ethanol on the global scale:
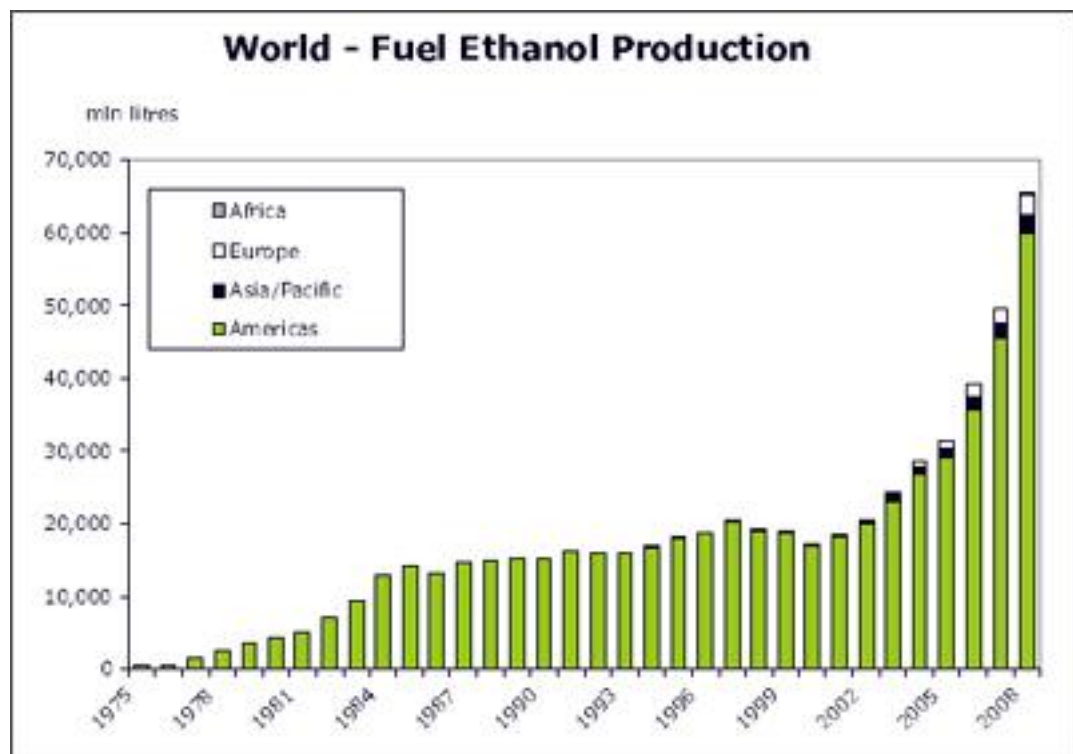
**FIGURE 6. Fuel ethanol production on the global scale (Licht 2009, 175)**

It can be seen from the figure that most of this ethanol comes from the Americas, particularly US and Brazil. Cultivating corn for the production of ethanol in Brazil has produced an outrage from the general public and still remains a contentious topic to this day because of the problem of deforestation (Allen 2011, 3). Finally, for our research it

is important to state that ethanol spills can be extremely dangerous for the marine environment and are, practically, impossible to mitigate. Ethanol is toxic to fish and marine life in high concentrations ((e) Science News 2012). As mentioned before, there is no limit to how much ethanol can be dissolved in water. Therefore, the traditional methods do not seem to be very effective at its recovery. The light non-aqueous phase that ethanol fuels produce on the surface of water disappears very quickly due to the mixing caused by natural conditions and evaporation. At this point it is only possible to really "clean" this "mixture" by adding oxygen into water, which is viable only for small and closed-off water bodies (Renewable Fuels Association 2013).

3.2.3 Pyrolysis oil

Pyrolysis oil (The Finnish company Fortum Oyj has kindly provided us with the samples of their pyrolysis oil for our tests), also often referred to as bio-oil, are biofuels that are produced by pyrolysis (fast pyrolysis is applied more often now) out of organic materials (most often - lignucellusosic materials) and they are nothing like the traditional fuels such as petroleum-based fuels because they differ immensely in their chemical composition and physical properties. The water content is high and the heating value is much lower. Because of their chemistry and the high oxygen content, they are highly polar liquids that are very acidic. However, their composition also includes hundres of other chemicals, amongst them esters, phenols, ketones and different acids. There is a lot of and economic demand to establish this type of fuel as replacement for heavy fuel oils and for direct heating. Despite the wide range of biomass that can be used for producing bio-oils, this development looks especially promising for countries with lots of pulp and paper, and sawmill industry. Sourcing this biomass requires lots of investment and integration into the existing demands for the forest industry (Lindfors 2009a, 8 – 10). The following pie charts (Figure 7) demonstrates the complicated chemistry of a typical pyrolysis oil sample (more about the phase separation in the next paragraph):
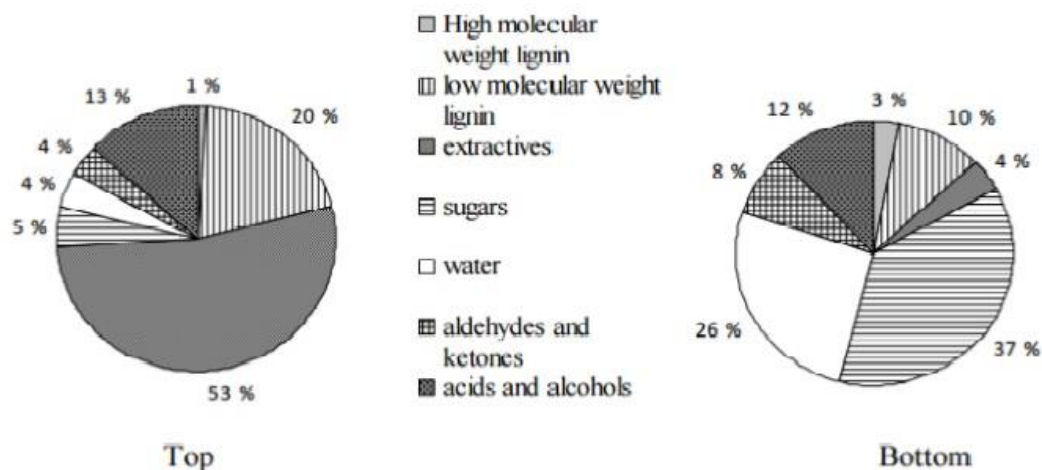
FIGURE 7. Complicated chemistry of pyrolysis oil (Lindfors 2009b, 18)

It is very difficult to control where exactly the macromolecular chains are broken by the thermal process, that's why pyrolysis invariably yields decomposition products with a wide range of chain lengths. As a result, gases and liquids (oils) as well as solids (char) are produced in different ratios, mainly depending on the process parameters and catalysts used. Therefore, raw pyrolysis oil is a mixture of many different hydrocarbon components and, in this regard, can be compared to crude oil. Despite the fact that bio-oils are categorized as homogeneous single-phased fuels, there are some reasons for why this fuel can turn into a two- (or even more) phased liquid during the production or storing stage. This is highly dependent on the concentration of water in the feedstock and the alkaline metal content. The solvents that can be said to work well for polar bio-oils are alcohols of low molecular weight. By applying solvent fractionation, fast pyrolysis bio-oil can be separated into water-soluble and insoluble fractions (Lehto et al. 2013, 15-16).

Fast pyrolysis oil quickly separates into an organic and aqueous phase upon its dilution with water. If pyrolysis oil is pilled into water in large volumes its vapour can cause an explosion. Explosion-proof equipment and gas detectors must be used at the site of the spill. It is toxic to fish and aquatic organisms. Its range of components makes its behaviour in the case of a spill difficult to predict. The major components might degrade fast, whereas other components degrade much slower (The Dow Chemical Company 2015, 4). The difficulty in containing or remediating a pyrolysis oil spill lies in the fact that it partitions between air, water, and soil. The proportion that partions to sediment is quite

small and, therefore, might not be worth the trouble that its remediation requires. For large spills soil remediation is necessary (NOVA Chemicals 2016).

Fast pyrolysis oil quickly separates into an organic and aqueous phase upon its dilution with water. Based on the phase diagram (Figure 8) provided by Oasmaa and Peacocke in their extensive publication on the properties of bio-oils, we can see the composition of the organic and aqueous phases of pyrolysis oil:
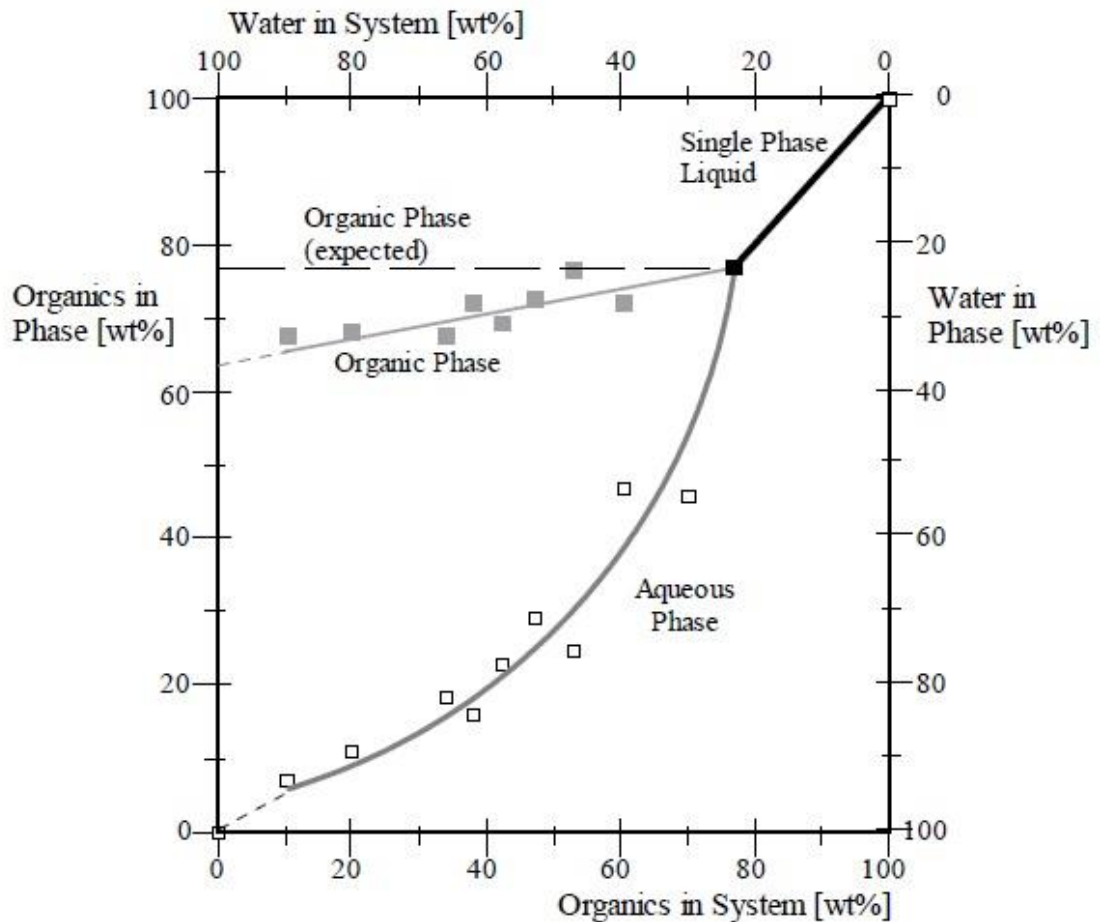
FIGURE 8. Pyrolysis liquid – water phase diagram (Oasmaa & Peackocke 2001, 46)

Picture 1 gives us a visual image of the complex behaviour of pyrolysis oil immediately and 1 day after adding it into water. A very dense tarry layer is formed almost right away on the bottom. This layer is very stable and doesn't dissolve even upon stirring it or shaking the container. The water layer becomes much less opaque after storing it in a cold place (around 3°C):
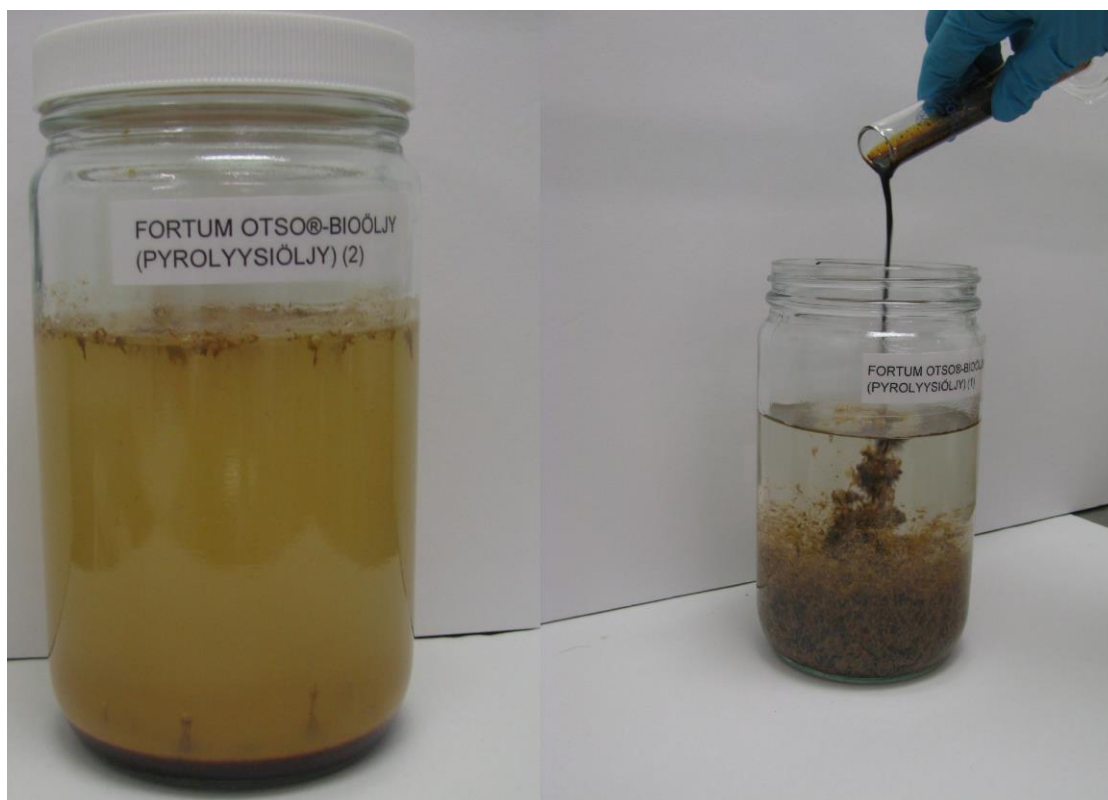
PICTURE 1. Pyrolysis oil in water 1 day and immediately upon adding into water (photos: Mariia Zhaurova 2016).

3.3 Some more comments on the compatability of fuels with various materials

Materials used for any industrial activity must undergo important tests to prove that they are durable enough to undergo a certain task they will be subjected to. In the case of oil spill clean-ups, we are talking about pipes and hoses, storage containers/tanks, brushes used in skimmers and many other types of tools and equipment. Many tests are done to ensure a material is able to withstand these processes and testing protocols have been developed. ASTM has a long list of standard protocols for testing corrosion and wear resistance of materials (Corrosion Standrads and Wear Standards 2017). Many mechanical properties of materials are the specific concern of materials engineers and scientists; these are ductility, strength, impact resistance, bending, fatigue and creep behaviour among many others. Common tests to measure these properties include tensile, impact, hardness and corrosion, resistance tests (AZO Materials 2014).

A common standard on chemical resistance of materials ISO/TR 10358 provides us with and extensive classification system that in our case can be useful for deciding which materials with which fuels can be combined safely (ISO/TR 10358 1994). For example,

as mentioned earlier, the same infrastructure can largely be used for biodiesel as for conventional diesel if modified slightly. Nonethelss, it has higher solvent characteristics and, therefore, suitable materials must be applied. These include steel, aluminium, fluorinated polyethylene or polypropylene, and Teflon. Whereas NExBTL, due to its strong chemical similarity to conventional diesel, doesn't require any kind of infrastructure change, which makes it a particularly enticing prospect in cases where the infrastructure has only been developed for the conventional fuels. Bioethanol does require specially developed equipment and for its production and transportation.

4 MATERIALS AND METHODS

The practical part of our research consisted of conducting various tests and simple observations to have a concrete understanding of how effective traditional or well-known methods of fuel recovery are for biofuels. These methods were developed by us relying heavily on the existing protocols and critique of these protocols (described in the previous sections) developed for conventional fuels. As this research is pretty much non-existent for the biofuels we were using for our tests, we took the liberty to approach it the way we deemed practical, given the equipment and tools at hand as well as time and pecuniary constrains.

The tests can be categorized neatly into the following separate sets of measurements:

- Screening tests
- Basic absorption capability tests
- Static degradation tests
- Dynamic degradation tests
- Damage tests

The materials for the tests were kindly provided by companies and organizations operating in Finland (Knorring Oy Ab, Meritaito Oy, Lamor Oy, KK-Module Oy, Finnish Environment Institute and the South Savo Fire and Rescue Department) that have allowed us to test a wide range of various sorbents and materials. The fuels were acquired either from companies (Fortum Oyj for pyrolysis oil and Neste Oyj for NExBTL) and the most common ones from a gas station in Mikkeli, Finland (95E10, diesel, E85).

4.1 Screening tests

These tests are qualitative tests that provided us with the basic understanding of how fuels behave when applied to a wide range of sorbents and helped us establish what sorbents should be used for the future more thorough tests. For the first part we placed 17 different sorbents on a white sheet of paper (around 5 cm x 5 cm for the mats and one tablespoon of each particulare sorbent) with a gap between them and pipetted 3 ml. of each fuel onto each sorbent (Picture 2):
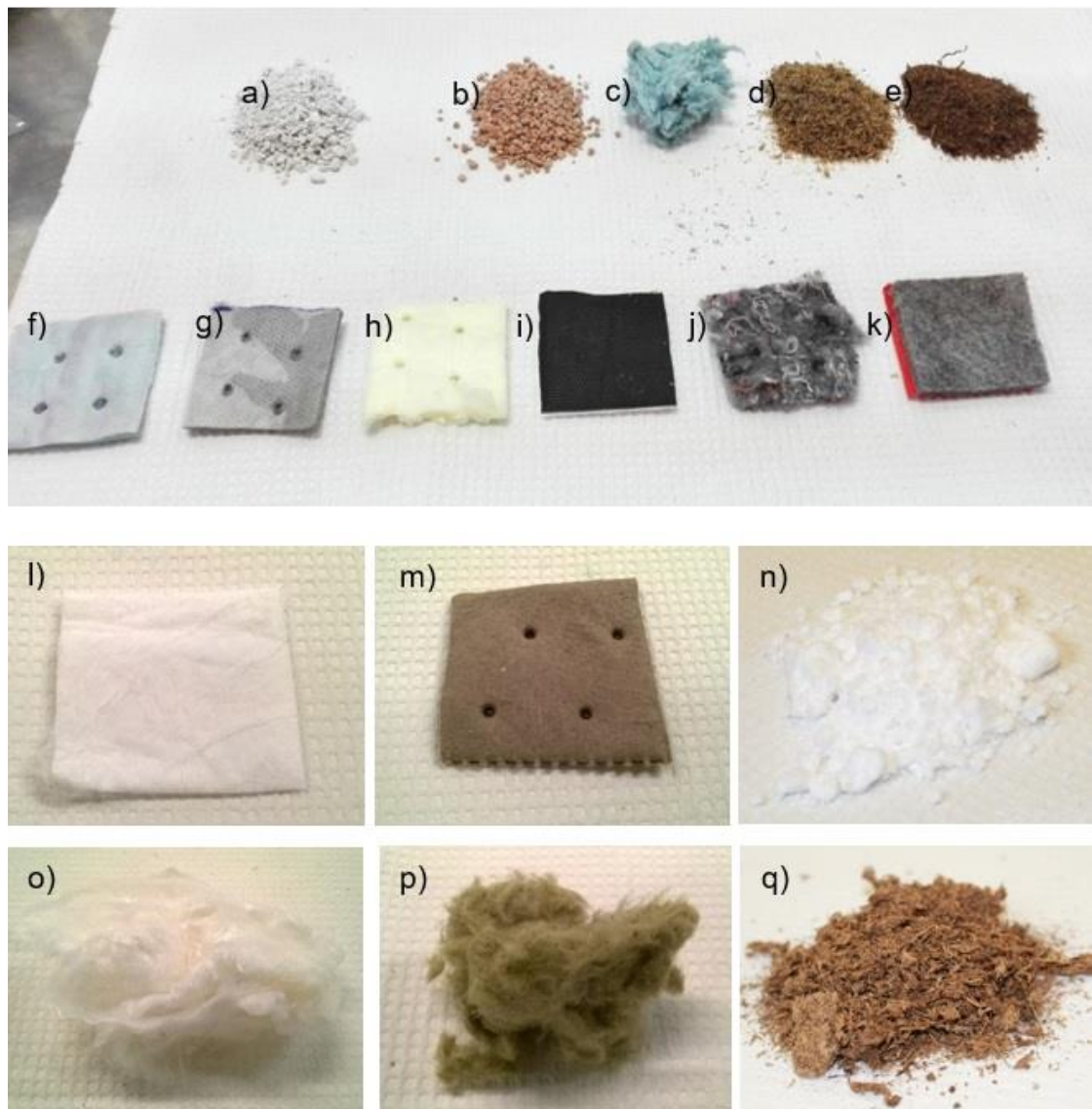
PICTURE 2. Sorbents used in the screening test : a) Light sorbent granules b) Brown sorbent granules (Imu Hirmu) c) PP Oil Only particulate d) peat moss e) Finnish peat f) Knorring Oil Only mat g) Knorring UNIVERSAL mat h) Knorring

Chem mat i) Knorring beach protection mat j) Wool mat k) Syke sorbent mat l) White mat m) Brown mat n) ORSORB very finely ground polypropylene o) Cotton waste sorbent p) Green Oil fiber glass q) VAPO peat

All the observations were written down in a matrix where a combination of each fuel and sorbent was assessed according to its rate of absorption and fuel retention capability on the scale from 0 to 3 (0 – doesn't absorb at all; 3 – everything is absorbed quickly and retained). The results were also described and photographed.

The second part of these screening tests consisted of tests in water only and tests in a water – oil (diesel) mixture. The same samples of sorbents used in the previously described screening test were chosen again. For the first part of this test approximately 0,5 l of water was poured into a container and the sorbent pads cut into 4cm x 4cm squres were placed onto the surface. A table spoon of each of the particulate sorbent was added to approximately 70 ml. of water in a separate bottle. Visual description of what happens right after this was given and then the containers were transferred onto a shaker table. The number of cycles was set at 80 for the big container and 100 for the glass bottles. After 5 min. the samples were taken out (2 min. rest), photographed and described again. After another 10 min. this was repeated (2 min. rest). Then the samples were left to rest for another 24 hours and then were describe in a similar manner for the last time. For the second part of these tests the same process was applied except for the fact that, before placing the sorbents in the containers, enough diesel fuel was added to reach a top layer of approximately 6 mm.

4.2 Basic absorption capability tests

This quantative test was done for two sorbents (Knorring Oil Only mat and Knorring Chem mat). It can be considered quite simple, yet it is the basis for the following tests. A 5cm x 5 cm pieces of both of these maths were immersed in each of the 5 fuels (always weighed beforehand), left for 15 minutes and then the mass was measured immediately as well as at the intervals of 1, 2, 3, 4, 5, 15 minutes. Three replicates of the test were produced. The absorption capability can be calculated by applying the following Formula 1 (Schrader 2004, 596):

$$A_c = \frac{m_w - m_d}{m_d} \qquad\qquad\qquad (1)$$

Where A_c is the absorption capability, m_w is the mass after sorption and m_d is the dry mass.

4.3 Static degradation tests

For this test each of the fuels was added to 150 ml. of water. The amount of the fuel added was estimated based on the sorption capability in pure fuel tests (previous section). Since the best performing fuel for both sorbents was conventional diesel (except pyrolysis oil, which we didn't choose fot this task because it separates into different phases in water), the amount of each fuel used was calculated based on this value. This mass added is the precise theoretical value based on the previous test, in reality slightly more fuel (+0,05 g or +0,1 g) was added.

After each fuel had been added to water (in a beaker that would allow for the top fuel layer to reach a few mm. in height), it was left to settle and then a sorbent pad was placed onto the surface of the mixture. It was once again left to settle for around 15 minutes and then the mass of the sorbent was measured at the same time intervals as in the sorption capability tests in pure fuel. Then some observations were made after the sorbents had been extracted from the mixture as well as squeezing them to see whether it absorbed any water along with the fuel.

Total petroleum hydrocarbons left in water after extracting the sorbents were also measured using InfraCal 2 ATR-SP analyzer and hexane as the solvent. These values were obtained only for the diesel and NExBTL mixtures, since the analyzer cannot be used for highly volatile chemicals such as gasoline. The VOC concentrations were also measured inside the beakers with a Tiger PiD detector for diesel and NExBTL.

4.4 Dynamic degradation tests

In the dynamic degradation test fuels were added to 100 ml. of water. As mentioned earlier, the amount of fuel was estimated according to the sorption capability in pure fuel tests (this was done in the same manner as for the static degradation test). The rest of the set-up was very similar to what had been described previously, except for the fact that the mixture was mixed by a magnetic stirrer for 15 minutes before weighing the

sorbents. The magnetic stirrer was set at around 200 cycles per minute to imitate natural windy conditions and waves in a water body. The measurements were done the same way as in the static degradation tests. The general set-up is demonstrated in Picture 3.

PICTURE 3. Left – mixture of diesel and water on a magnetic stirrer. Right – 5 mixtures of each fuel and water waiting for the sorbent mat to be placed onto them.

4.5 Damage tests

For this test a sample of a storage bag, containment boom, storage container and skimmer brushes was immersed in each kind of fuel in a petri dish and covered to prevent the evaporation of fuel. The tested materials were: storage tank by KK-Module Oy, storage bag by Knorring Oy Ab, skimmer brush by Meritaito Oy, oil boom by Lamor Oy, open-water boom by the Finnish Environment Institute. After 7 days the materials were inspected for any change in durability and any other damage that the fuels could have caused. The following picture shows the set-up of the test and the materials used:

PICTURE 4. Materials used in the damage tests: a) storage tank by KK-Module Oy b) skimmer brush by Meritaito Oy c) storage bag by Knorring Oy Ab d) oil boom by Lamor Oy e) open-water boom by the Finnish Environment Institute.

5 RESULTS

The most important results obtained in our tests will be presented in this chapter in a manner that shows how one result leads to another. This is especially important in the case of the screening tests, because it showed us the best sorbents that had to be used for the following tests. The appendices contain some important detailed results as well as test potocols that we utilized in the process of testing the fuels.

5.1 Screening tests

The screening tests provided us with the basis for deciding which sorbents have the most suitable properties. Given the large range of different types of sorbents (synthetic, organic, mineral, mats, particulates), this information can be later applied to future re-search that would only focus on a particular type of sorbent that might be tested for some fuel. A matrix for the sorbents and fuels with the rate of absorption and retention capacity is attached to this thesis as an appendix with some descriptive information.

5.2 Absorption capability tests

As described above, this test is an important prerequisite for the future tests because it allows us to calculate the theoretical value that a sorbent could possibly absorb in just pure fuel and then add this fuel to water for the static and dynamic degradation tests. This test was done for each fuel but only for two types of sorbents (blue Oil Only mat and yellow Chem mat) that showed really good performace in the screening tests. The results were written down and the following table created for each mat and replicate that helped us calculate the absorption efficiency:

TABLE 3. Example of the table for calculating the absorption capacity:

Knorring Chem mat for chemical spills	Mass when measured with the liquids below (g):				
	Diesel	Gasoline	E85	NExBTL	Pyrolysis
Before immersion (dry):	0,89	0,96	0,88	0,94	0,96
Immediately after immersion (extra oil shaken off):	10,99	9,21	9,97	10,70	18,51
1 min.	10,07	8,72	9,59	10,01	16,06
2 min.	9,85	8,44	9,29	9,73	15,24
3 min.	9,69	8,18	9,05	9,33	15,02
4 min.	9,56	7,97	8,92	9,31	14,78
5 min.	9,47	7,74	8,77	9,27	14,58
15 min.	9,40	6,71	8,08	9,16	14,27
Absorption capability:					
Immediately after immersion (extra oil shaken off):	11,35	8,59	10,33	10,38	18,28
1 min.	10,31	8,08	9,90	9,65	15,73
2 min.	10,07	7,79	9,56	9,35	14,88
3 min.	9,89	7,52	9,28	8,93	14,65
4 min.	9,74	7,30	9,14	8,90	14,40
5 min.	9,64	7,06	8,97	8,86	14,19
15 min.	9,56	5,99	8,18	8,74	13,86

5.3 Static and dynamic degradation tests

Three replicates for each test were done and the results are summarized in the following fashion:

TABLE 3. Example of the results table for the static and dynamic degradation tests.

	Chemicals/ Knorring Chem mat				
	Diesel	Gasoline	E85	NExBTL	Pyrolysis
Mass of fuel added (g)	8,01	7,32	7,11	7,83	7,29
Initial mass of the sorbent (dry) (g)	0,89	0,82	0,79	0,87	0,81
Immediately after immersion (g)	9,16	8,34	11,48	9,04	10,05
1 min. (g)	8,85	8,00	10,78	8,74	9,92
2 min. (g)	8,72	7,79	10,49	8,60	9,77
3 min. (g)	8,58	7,64	10,31	8,51	9,63
4 min. (g)	8,48	7,53	10,15	8,42	9,51
5 min. (g)	8,41	7,45	9,92	8,37	9,41
15 min. (g)	8,29	6,71	9,53	8,23	8,75
	Absorption capability				
Immediately after immersion (g)	9,29	9,17	13,53	9,39	11,41
1 min. (g)	8,94	8,76	12,65	9,05	11,25
2 min. (g)	8,80	8,50	12,28	8,89	11,06
3 min. (g)	8,64	8,32	12,05	8,78	10,89
4 min. (g)	8,53	8,18	11,85	8,68	10,74
5 min. (g)	8,45	8,09	11,56	8,62	10,62
15 min. (g)	8,31	7,18	11,06	8,46	9,80

| Analysis of the water left in the beakers after removing the sorbents		
	Infracal analysis (ppm)	ProTiger VOC (ppm)
NExBTL	268,3 (over calibration range)	≈ 32,0
Diesel	42,1	≈ 60,0

The results in this form (averaged out for all the replicates) can easily be converted into a much more visually pleasing and informative format, as presented in the following chart (Figure 9). The values presented in this chart are given for the measurements done at 1 min. after extraction, because after that the sorbents most often stop to release any more fuel and the mass goes down most likely due to evaporation. Also, note that the dynamic tests were done only for diesel and NExBTL.
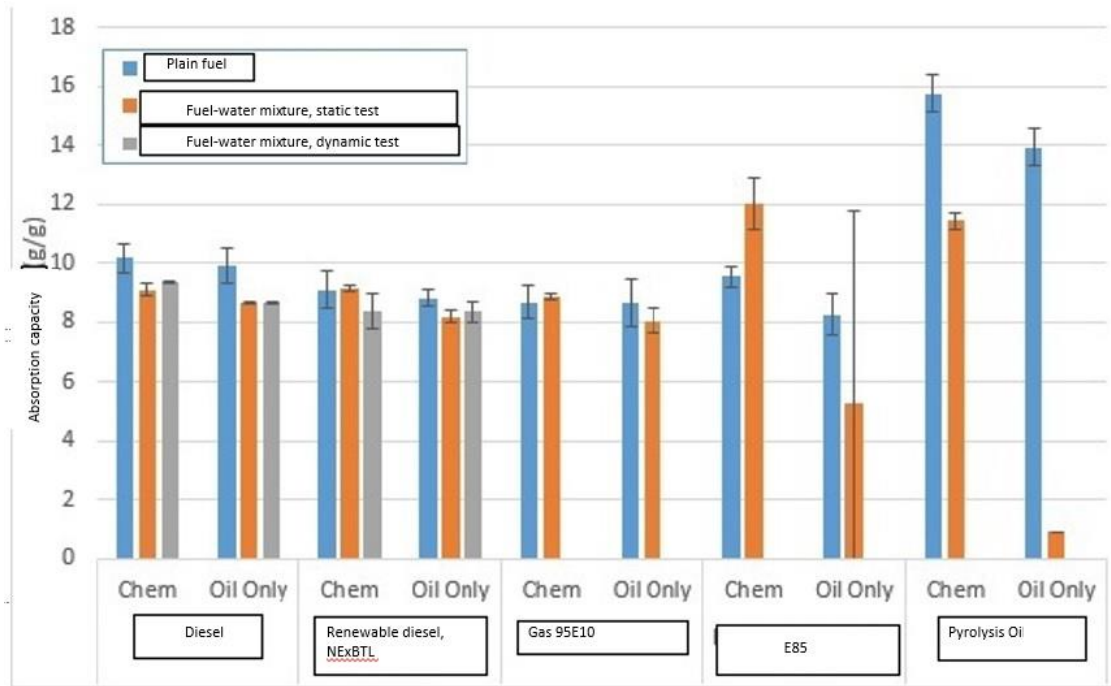
FIGURE 9. Absorbance capacity of the Knorring Chem and Oil Only sorbents in different tests.

The following chart illustrates what was the concentration of the total hydrocarbons in water after the extraction of the sorbent as measured by the InfraCal 2 ATR-SP analyzer and the concentration of the VOC's in the air inside the beaker also after the sorbent had been taken out:
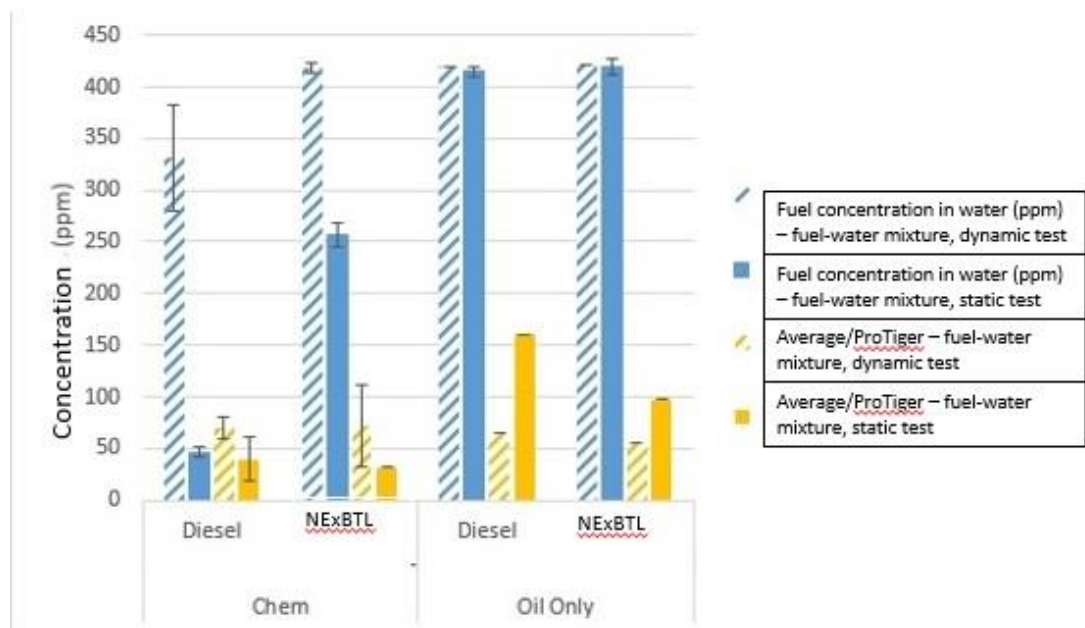
FIGURE 10. The concentrations of hydrocarbons in the water VOC concetrations in the air inside the beaker after the removal of the sorbent mats.

5.4 Damage tests

The results included careful inspection and photographing of the materials. Any visual change or change in the haptic sensation was described as well as how easy it was to clean the material by means of paper tissue and water. The following picture (Picture 5) demonstrates damages of gasoline (95E10) to a piece of the open-water boom (this change in the appearance can be easily seen when compared to Picture 4). However, this damage was probably due to cutting of boom material. Any other visual damages due to exposure to fuel for tested materials was not observed. The appearance of the inside of the sack changed slightly depending on the fuel. In some cases it was opaque and in some clear and transparent. All of the materials were easy to clean by means of rinsing and paper tissue.
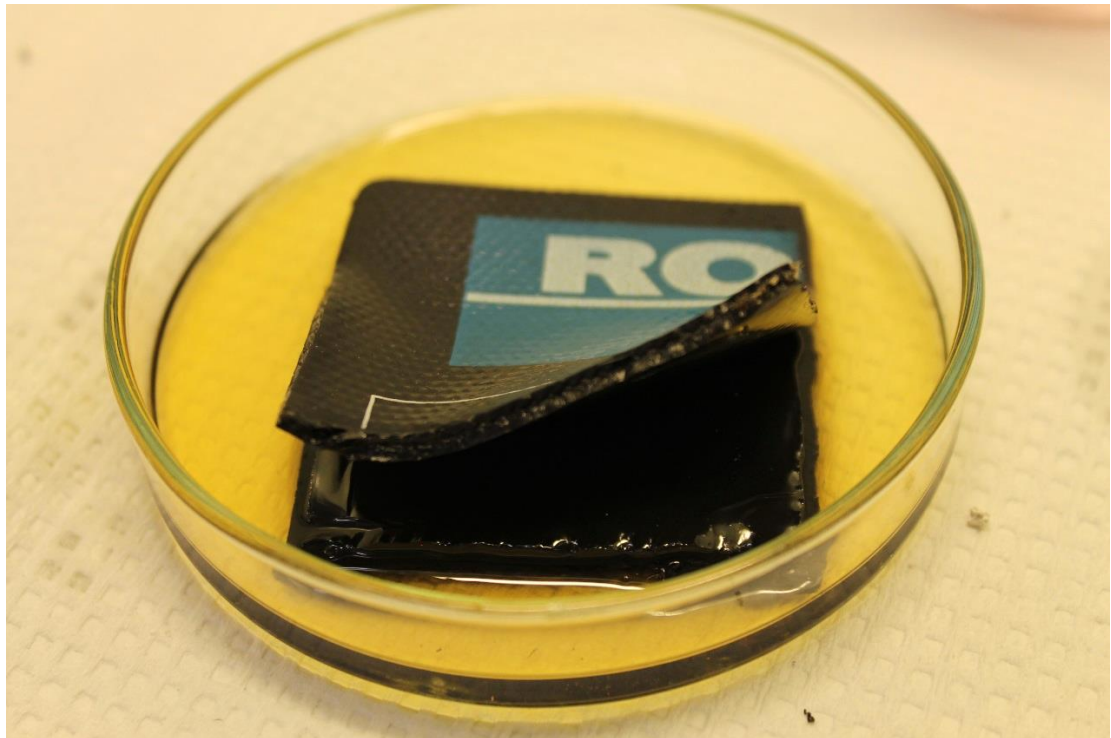
PICTURE 5. Open-water boom after immersion in gasoline.

6 DISCUSSION OF THE RESULTS

The matrix for the effectiveness of sorbents in screening tests is presented in detail in Appendix 1. Many sorbents produce good results with a good retention capability as

well as rate of absorption. However, the differences between fuels were obvious, despite the fact that this screening test is supposed to only give a general picture of what sorbents might produce good results in mitigating fuel spills. Slightly less of NExBTL was retained than conventional diesel by some sorbents. Many of the sorbents work as well for E85 as for gasoline, but E85 goes through the Oil Only whereas gasoline is well retained by it. In the case of the fiber glass the situation is reversed – E85 was contained well whereas gasoline wasn't. Pyrolysis oil was usually absorbed very slowly when compared to the other fuels. Surprisingly, a product that might be good for the rest of the fuels (e.g. the beach protection mat) couldn't contain the pyrolysis oil at all. Most sorbing mats did not absorb any water but the Chem mat and the Sykes sorbing mat did.

Organic materials produce much worse results for the tested fuels than do the synthetic materials. For example, amongst the organic materials the wool mat works the best and does really well when compared with many synthetic materials. However, these materials might work much better in a situation where they are placed onto a spilled chemical or fuel as opposed to the liquid being pipetted onto these sorbents. The particular sorbents can be especially useful in situations where it can be stuffed into crevices or cracks in order to prevent the fuel from getting into the ground.

The beach protection mat and Oil Only mats were still completely dry after being placed in water for 24 hours. The Universal mat and especially the Chem mat as well as the wool mat were floating on top of the water but did absorb some of it. The Syke absorption mat sank. The peats were mostly floating on the surface but after some time many particles started sinking or got suspended in the water column. The peat moss sank more than the peat. In the water-diesel tests all the sorbent mats absorbed the fuel but remained floating on the surface. The peats absorbed the fuel and floated on the surface more stably than in water only.

Clear differences were observed between the fuels in the quantitative tests that were done to measure the absorbance capability (refer to Figure 9). Usually, the following type of graph is expected to be produced when a sorbent oversaturated with fuel is releasing fuel gradually and the graph shows exponential decay (Figure 11). This behavior in the uptake capacity depends on sorbate as much as it depends on the sorbent:
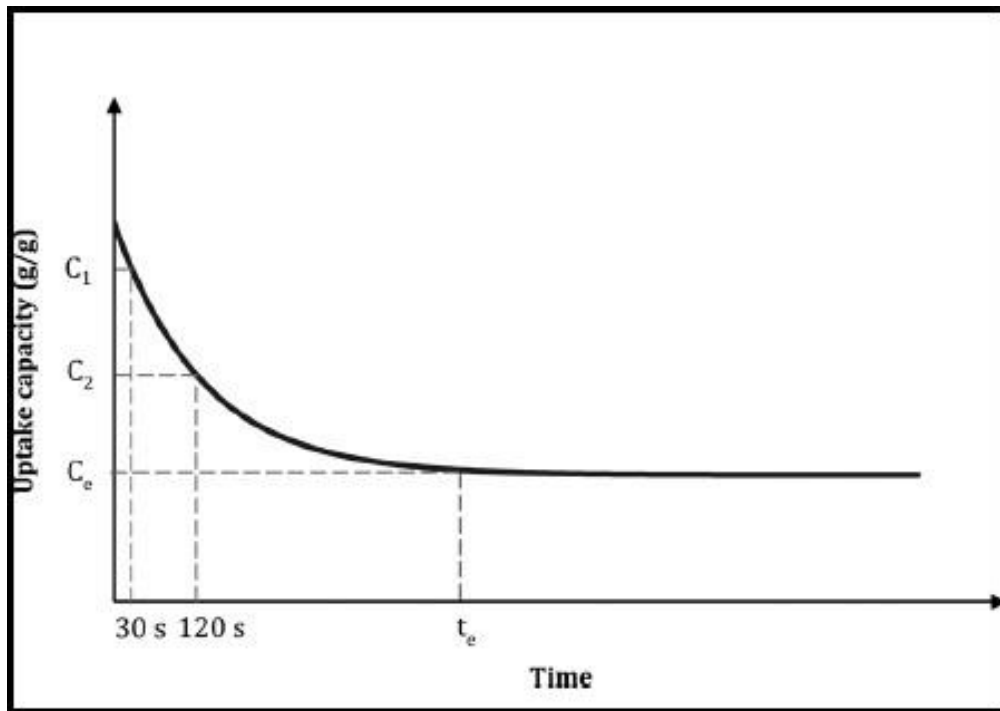
FIGURE 11. Theoretical uptake capacity vs. dripping time allowed. C_e is the equilibrium is the absorbance capacity reached at some time t_e (Bazargan 2015, 1275)

However, in practice, given the various possibilities for error (evaporation, unwanted squeezing and shaking of the sorbent, fuel stuck in the mesh of the sieve), our measurements produced the following graph (Figure 12). In this figure you can also see that the equilibrium capacity is never reached due to the evaporation of the fuel:
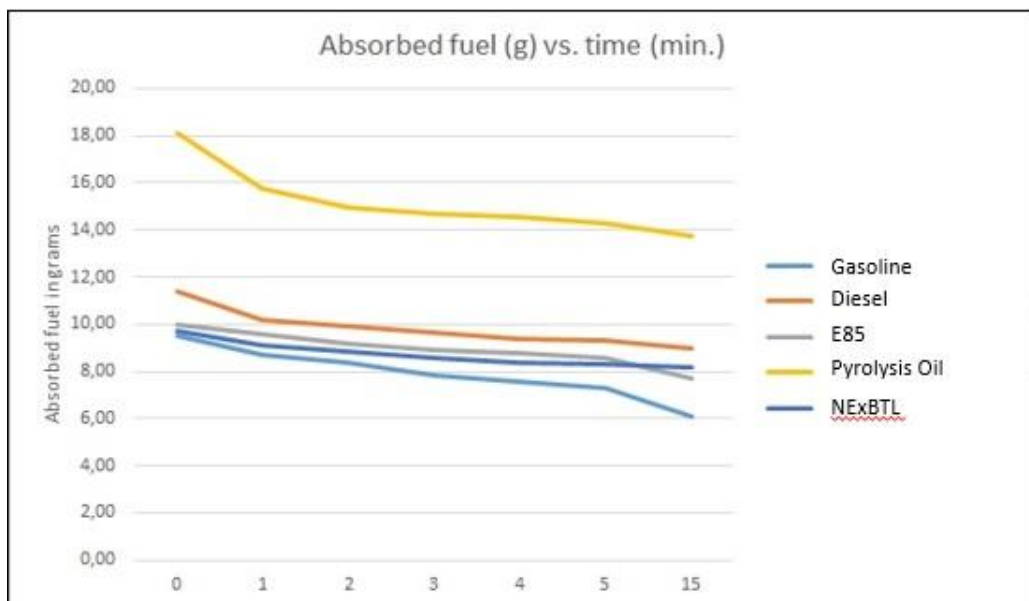
FIGURE 12. A more realistic graph showing how absorbance capability of a sorbent changes.

The absorbance capacity of both the Chem and the Oil Only mats was much higher for bio-oil than for any other fuel due to its high viscosity and density. For the same reasons the absorbance capacity for conventional diesel was slightly higher than for NExBTL. The Chem mat was slightly more efficient for all fuels than the Oil Only mat. The difference in values between different tests was the largest for the E85 fuel, mainly due to the fact that upon slow addition to water, a thin upper layer of the fuel is formed but most of it is dissolved and cannot be recovered by the Oil Only mat. In fact, if the fuel is added to the water quickly or mixed afterwards, no discrete upper layer is formed. This interesting difference can be seen from the following picture (Picture 6).


PICTURE 6. Right – E85 is added quickly and stirred. Left – slowly without stirring.

This is an important phenomenon because mats meant for hydrophobic materials can absorb this upper layer well, whereas if a mat like that is placed into the beaker that's shown on the left side of Picture 6 it will float on the surface without absorbing any liquid. The absorbance capacity for Chem all is much higher in any case due to the fact that it can absorb this solution and the density of water and ethanol is much higher than the that of the upper layer that is absorbed by the Oil Only mat.

The fact that the absorbance capability is nearly the same for the dynamic and static tests (Figure 9) is a good sign because it shows that there is no clear change in this property whether the water is moving or not. This is a very useful property if a sorbent is used in real-life conditions. Note the higher values for the absorbance capacity in pure fuels.

When the pyrolysis oil is added to water and a Chem mat is applied to the mixture, the water with the dissolved compounds released from the pyrolysis oil in the upper layer is absorbed by the mat without producing any noticiable "cleaning" of the water. Nothing whatsoever was absorbed by the Oil Only mat. This test quickly proves that there is no possibility for recovering any of spilled bio-oil by applying this commonly used method. There is also a very dense tarry layer emerging on the bottom of the beaker. In reality this means that this substance would be formed on the bottom of a water body which is most likely very harmful to aquatic organisms living near or depending on this habitat. Picture 8 shows these results:
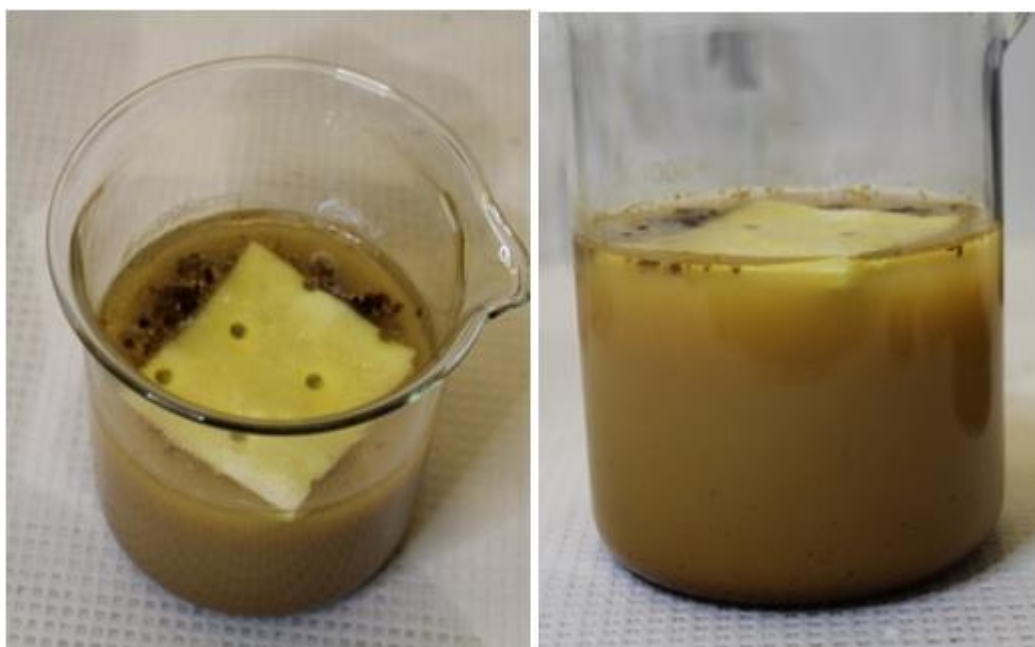
PICTURE 8. Sorbents are not effective at all for pyrolysis oil spills.

The concentrations of TPH (total petroleum hydrocarbons) in the water (around 0,08 ml, if scaled to the volume of water used) indicate that both types of sorbents are very good at removing the diesel and NExBTL from the water. There was also no visible sheen on the surface of the water after using the sorbents. The concentrations of the VOC compounds as well as TPH were lower after using the Chem mat as opposed to the Oil Only one. The concentrations of TPH left in the water were clearly much lower for conventional diesel than for NExBTL after using the Chem mat, whereas they were pretty much the same after using the Oil Only mat. The VOC concentrations were lower for NExBTL than for conventional diesel, due to the lower vapor pressure as well as volatility of NExBTL.

The damage tests yielded very promising results because the biofuels did not cause damages to tested materials. The other samples were hapticly inspected and were cleaned really easily. It was decided not to conduct any more damage tests (more specialized test of the mechanical properties and micro-imaging of the surface) because of our results. However, in more specialized research these tests are necessary. Pyrolysis oil is quite an acidic fuel and that is why we had expected it to cause some damage to the materials or, due to its "stickiness", we assumed that many of the samples would have been impossible to clean or, at the very least, quite difficult. It seems like these materials can be re-used in real-life applications after collecting or storing pyrolysis oil. NExBTL made the inner part of the storage bag clearer and slightly shiny, whereas it had a slightly "cloudy" and opaque appearance when other fuels were applied to it. However, it seems like no structural damage was caused to the sack.

7 CONCLUSION

There were generally clear and visible differences in the performance of the tested sorbents for various fuels. Nevertheless, it can be concretely stated that synthetic sorbents are much more efficient and re-usable for this task than the organic and inorganic sorbents. Many types of sorbents will work well fo the presented biofuels when sorbing off of a solid surface. However, the biggest challenge is that pyrolysis oil and E85 cannot be retrieved as easily from water (currently, these spills would not be mitigated at all) as the conventional fuels and some biofuels such as NExBTL and biodiesel. As described in Chapter 3, E85 does form a thin layer of mostly petroleum compunds on the top of the surface, but this would mix in with the rest of the water really quickly in natural conditions without providing us with enough time to extract it. There are methods, such as aeration, to make E85 biodegrade faster and to prevent anoxia. The possibility to extract NExBTL by sorbing is viable and economically feasible because the test results are very similar to those for diesel. My thesis demonstrates that there exists a large number of sorbents that are available on the market and their effectives for NExBTL can be easily measured the same way it is measured for conventional fuels.

The tested biofuels did not cause any damage (at least, judging from our basic tests developed for this task) to the sampled materials. However, more detailed and specialized tests such as tensile strength test, 3D-microscoping imaging of the surface might

be needed to establish the precise effect on materials if these biofuels are to become ubiquitously used. Other types of common materials compatabile with traditional fuels such as hoses and gaskets migh be susceptible to damage by the biofuels as well.

One of the most important and natural conclusions that the research done during this thesis leads to is the problem in legal matters when it comes to dealing with biofuel spills. There is very strict, standardized and widely applied legislature that has been used for preventing and dealing with conventional fuels' spills (The Senate of the United States of America 2009). As seen in Chapter 2, this can be extended to such fuels as biodiesel and NExBTL. In fact, NExBTL is probably the more likely candidate to fit into the existing framework of legislature for conventional diesel. On the other hand, bio-oil is a compex issue, differening immensely chemically from petroleum fuels and requiring new standards. Pyrolysis oil can differ in composition depending on the feed-stock, which complicates the matter. A very dense tarry layer emerging on the bottom could in theory be recovered by dragging a large net along the bottom of a water body that makes this substance stick to its surface (or using any other mechanical collection device), although this could only be possibly done in a shallow lake or river and would most likely cause much biological damage but this aassumption still need to be tested by chosing appropriate materials. Finally, if it is to become another well-established biofuel on the market, with large volumes of it being transported all over the globe on a daily basis, technologies that can help us mitigate the inevitable spills must be invested into and investigated. Perhaps, a possible solution to this problem could be developing strains of bacteria that could speed up the biodegradation of the spilled substance (Conversion and Resource Evaluation Ltd. 2006). Research on the toxicological effects of spilled pyrolysis oil must be one of the priorities in this regard as well. Large industrial producers of pyrolysis oil and its users must be mindful of the problems that using this "clean" energy source can create, simply due to our inability to deal with a big spill of this type of fuel for now, should it ever occur. A clean and safe fuel does not simply refer to the emission levels and energy efficiency as I'm confident my research on this topic has shown.

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Suitability of different sorbent materials according to the qualititative tests. Sorbing capacity (1 = worst, 3 = best). The grading is approximate. For the names of the materials refer to Picture 2.

	Diesel	Renewable NExBTL	Ethanol blended gasoline E85	Gasoline 95 E10	Pyrolysis oil
Light sorbent granules (a)	1	1	1	1/3	2
Brown sorbent granules (Imu Hirmu) (b)	1	1	2	1-2	2
Knorring OIL ONLY sorbent (c)	3	3	2	3	2*
Peat moss (d)	2	1	1	1-2	2*
Finnish peat (e)	2	2	2	2	1*
Knorring OIL ONLY-mat (f)	2-3/2	2/2-3	2/2-3	2-3	2*
Knorring UNIVERSAL-mat (g)	1/2-3	2	2/2-3	2	3
Knorring CHEM-mat (h)	2-3/2	2	2/2-3	2-3	3
Knorring beach protection mat (i)	3	3	3	3	1*
Wool mat (j)	1	2	3	3	2*
Syke sorbent mat (k)	3	3	3	3	3
White mat (l)	1	1	2	1	2
Brown pig-mat (OIL ONLY) (m)	2	2	3	3	1*
ORSORB Original-sorbent particulate (n)	3	2	3	2	2
Cotton-waste sorbent(o)	3	3	1-2	1	2*
GreenOil fiber glass (p)	3	3	2	3	2*
VAPO peat (q)	2	1	3	1	2

*The fuel flows off of the surface of the sorbent.

Some products were testedf twice. The table presents the sorbing capacity for both tests..

Test Result Form		
Product:		
Manufacturer:		
Distributor:		
Product Description:		
Recommendations for usage by the manufacturer:		
Instructions for disposal of the material:		
Fuel used in the test:		
Oil absorption capacity of the material:	Mass (g)	Absorption capacity (g/g) `
Dry mass of the material:		
Mass after submersion:		
1 min.		
2 min.		
3 min.		
4 min.		
5 min.		
15 min.		
30 min.		
Observations during the test:		
Product Properties:		

Is the product dusty:		Water absorbance:	
No		Yes	
Slightly		No	
Yes			
How difficult is it to collect the product (1 - easiest; 4 - hardest		Does the product float on top of water when soaked in the tested liquid:	
1		Yes	
2		No	
3			
4			

Absorbance on the surface of water:
Stable:

When stirred:

Test Result Form	
Product:	
Manufacturer:	
Distributor:	
Recommendations for usage by the manufacturer:	
Instructions for disposal of the material:	
Fuel used in the test:	
Before the damage tests:	

Mass (g)	Cross sectional area (m^2):	Tensile strength:

Detailed description of the material:

After the damage tests:

Mass (g)	Cross sectional area (m^2):	Tensile strength:

Detailed description of the material:

Despite the lack of a large numbers of complicated terms, in order to dispel any confusion about the terminology used in this text, some often-repeated and central to the topic words must be described:

Pyrolysis oil and bio-oil are used interchangeably.

Sorbent is any material that soaks up liquid by absorption, absorption or both. Sometimes the term absorbing is used to mean sorbing.

A sorbent mat is a compacted material that is not easily torn or broken into pieces. In contradistinction, particulate sorbent simply means that the sorbent consists of more or less loose material, be it fibers or grains, that are all interconnected but can be easily torn into small fragments without applying much force.

Uptake capacity and absorbence capacity are the same properties.

Retention is different from absorbence in the sense that a sorbent might be able to have a high uptake capacity at some point but the fuel could drip out of the sorbent due to the low retention capability or the ability to hold liquid inside.

Conventional, traditional and fossil fuels all mean the same thing, unless given some distinctive caveat in the text.