Tutor/s

Dr. Joan Llorens Llacuna
Departament Enginyeria Química

Xavier Fragua Fernandez
Alucha Recycling Solutions

Grau en Enginyeria Química

Treball Final de Grau

Phenolic fraction recovery from pyrolysis oil obtained from paper sludge.

Obtención de la fracción fenólica de aceite pirolítico proveniente de lodos de papel.

Álvaro González Rivas

Enero del 2016

UNIVERSITAT DE BARCELONA

"Fortune favors the prepared mind."

Louis Pasteur

Me gustaría dedicar y agradecer este trabajo a todas las personas que lo han hecho posible y que me han ayudado durante estos meses:

En primer lugar, a Xavier Fragua e Ignacio Lopez; por darme consejos, indicaciones y pautas a seguir durante estos meses en Alucha y por dedicar gran parte de su tiempo a acabar de pulir este proyecto.

También me gustaría agradecer al resto de miembros de Alucha: Hans Cool, Gijs Jansen, Carlos Ludlow, Marina Torrens y Anton Bijl, por hacer que mi paso por Alucha haya sido una gran experiencia y por todos los momentos compartidos.

En último lugar, y no por ello menos importante, me gustaría agradecer a mi familia y amigos todo el apoyo que me han dado en los buenos ratos y, sobre todo, en los no tan buenos. Sin vosotros no habría llegado hasta aquí.

Gracias

REPORT

CONTENTS

1. SUMMARY

The energy of biomass can be obtained by various techniques, such as combustion or by upgrading it into a more valuable fuel, gas or oil. Biomass can also be transformed into a source of value-added products for the chemical industry by using different thermochemical technologies; one of them is fast pyrolysis, which has received extensive interest in recent years. Fast pyrolysis of biomass is a thermal decomposition process that occurs in the absence of oxidizing agents. Quick biomass decomposition followed by a rapid vapor condensation converts biomass into a liquid product known as bio-oil.

For the usage of bio-oil as fuel, its oxygen content must be reduced. On the other hand, if the intent is to only use it as a chemicals' source, then the oxygen removal step may not be necessary. Many oxygen-containing chemicals now are produced from fossil fuels via oxidation or hydration of olefins to introduce oxygen-containing functional groups. In contrast, these functional groups are already present in bio-oil.

The first step was to study different processes to obtain chemicals from bio-oil and to perform characterization analyses of a bio-oil from paper sludge feedstock in order to define its chemicals. Subsequently, some of the technologies to obtain these chemicals were tested to see if it was possible to obtain similar results when applying them to the bio-oil obtained from our pyrolysis process.

At the end of the project an initial approach to the investigation of two methods to recover the phenolic fraction present in pyrolysis oil was done. These methods are: solvent extraction using methanol and water and phase separation injecting sulfur dioxide, and both reported promising results, being able to obtain a final product which can be used as a substitute of traditional phenol.

Keywords: Pyrolysis oil, phenolic fraction, paper sludge, chemicals, bio-oil, lignin, solvent extraction, sulfur extraction, refining, bio-fuels.

2. RESUMEN

La biomasa contiene energía que puede ser obtenida a partir de diferentes métodos, como la combustión o refinando dicha biomasa en productos de más valor como combustibles líquidos, gas o aceite. También puede ser transformada en diversos productos de valor añadido para la industria química a través de diversos métodos termoquímicos; siendo uno de ellos la pirolisis rápida, método que ha recibido mucho interés en los últimos años. La pirolisis rápida de la biomasa es un proceso de descomposición química que se lleva a cabo en ausencia de agentes oxidantes. El proceso consiste en una rápida descomposición de la biomasa seguida de una condensación rápida de los gases producidos convierte la biomasa en un producto líquido conocido como “bio-oil”.

Para utilizar este aceite como combustible, debe reducirse su contenido de oxígeno. Como alternativa, si se enfoca su uso como fuente de productos químicos, eliminar dicho oxigeno puede no ser necesario. Muchos productos químicos que contienen oxigeno son producidos hoy en día a partir de combustibles fósiles a través de métodos que oxidan o hidratan olefinas para introducir grupos funcionales en los que el oxígeno está presente. En contraste, estos grupos funcionales ya están presentes en el aceite pirolítico.

El primer paso fue estudiar los diferentes procesos existentes basados en la obtención de productos químicos a partir de aceite pirolítico y caracterizar el aceite obtenido a partir de lodos de papel con la finalidad de definir sus propiedades químicas. Posteriormente se realizarón diversos experimentos para probar la viabilidad de los métodos estudiados e intentar obtener resultados similares al aplicar dichos métodos al proceso de pirolisis existente.

Dos métodos han sido estudiados (extracción líquido-líquido utilizando agua y metanol y separación de las fases orgánica y acuosa inyectando dióxido de azufre), dando resultados prometedores en la recuperación de la fracción fenólica del “bio-oil” y obteniendo un producto final que puede ser utilizado como substituto del fenol obtenido por procesos tradicionales.

Palabras clave: Pyrolysis oil, phenolic fraction, paper sludge, chemicals, bio-oil, lignin, solvent extraction, sulfur extraction, refining, bio-fuels,

3. INTRODUCTION

The use of renewable energy resources is becoming increasingly important in order to address the effects on climate change. With the increasing concern on fossil fuel storage and its associated environmental problems, the use of renewable lignocellulosic biomass resources, being a form of renewable energy that generates very low greenhouse emissions, is believed to play a crucial role in the future.

3.1. BIOMASS

When we talk about biomass, we mostly refer to agricultural and forestry biomass, which consists of (Athanasiadou et al. 2011):

- Cellulose, that constitutes about 40-45% of the cell wall. Chemically, is a complex polysaccharide $(C_6H_{10}O_5)_n$ with crystalline morphology. It is a glucose based polymer in which the glucose units are linked by β-1,4-glucosidic bonds.
- Hemicellulose, is mainly composed of pentosans and hexosans chains adding to about 20-25% of the cell wall.
- Lignin, which amounts 20-30% of the cell wall and is a natural aromatic polymer. The amount of lignin varies widely according to the kind of biomass. In the case of wood, it ranges from 19 to 30% and, in the case of non-wood fibers, it ranges from 8 to 22%.
- And at a minor extend: proteins, tannins, starch, free sugars and natural oils.

The energy of biomass can be obtained by various techniques, such as combustion or by upgrading it into a more valuable fuel, gas or bio-oil. Biomass can also be transformed into a source of value-added products for the chemical industry by using different thermal processes one of them being pyrolysis. Bio-oil itself can be used directly as a fuel oil type for recovery boilers and/or furnaces or upgraded by several methods to enhance its fuels properties.

3.2. PYROLYSIS PROCESS

Pyrolysis is the thermochemical decomposition of biomass into a range of useful products, either in the total absence of oxidizing agents or with limited supply that does not allow gasification[1] to an appreciable extent. During pyrolysis, large complex hydrocarbon molecules of biomass break down into relatively smaller and simpler molecules of gas, liquid and char.

Pyrolysis involves rapid heating of biomass (Only fast pyrolysis) in the absence of air or oxygen at a maximum temperature, known as pyrolysis temperature, and holding it there for a specific time in order to produce gases, which, upon cooling, decompose into condensables (bio-oil) and non-condensable gases at room temperature (mainly methane, hydrogen, carbon dioxide, carbon monoxide, ethane) and solid char.

The proportion of the different products obtained depends on several factors, being the most significant:

- Feedstock composition
- Pyrolysis temperature
- Heating rate
- Gas residence time

The last three factors determine the type of pyrolysis (**Table 1**). Based on the heating rate, pyrolysis can be broadly classified as slow or fast. It is considered slow if the time required to heat the fuel to the pyrolysis temperature is much longer than the characteristic pyrolysis reaction time, and vice versa. There are a few other variants depending on the medium at which the pyrolysis is carried out, like hydrous pyrolysis (in water), methanopyrolysis (in methane) or hydropyrolysis (in H_2). Normally these three types of pyrolysis are used for the production of chemical compounds (Prabir Basu, 2010).In slow pyrolysis, the residence time of vapor in the pyrolysis zone (vapor residence time) is of the order of minutes or longer. This process is not used for traditional pyrolysis, where the production of liquids is the main goal; it is primarily used

---

[1] Gasification: Biomass gasification is the conjunction of thermochemical reactions that are produced in an atmosphere low in oxygen and which results in the transformation of the solid biomass in a series of combustible gases that can be used in a combustion engine, a turbine or a motor, after being properly upgraded.

for char production and is broken down in two types: carbonization and torrefaction. Torrefaction takes place in a low and narrow temperature range (200-300ºC), while carbonization takes place at much higher and broad temperature range. In fast pyrolysis, the vapor residence time is in the order of seconds or milliseconds. This type of pyrolysis mainly used in the production of bio-oil and gas can be classified in three main types: fast, flash and ultra-rapid.

Pyrolysis process	Residence time	Heating rate	Final temperature (ºC)	Products
Carbonization	Days	Very low	>400	Charcoal
Torrefaction	10-60 min	Very small	280	Torrefied biomass
Fast	<2 s	Very high	~500	Bio-oil
Flash	<1 s	High	<650	Bio-oil, chemicals, gas
Ultra-rapid	<0,5 s	Very high	~1000	Chemicals, gas
Vacuum	2-30 s	Medium	400	Bio-oil
Hydropyrolysis	<10 s	High	<500	Bio-oil
Methanopyrolysis	<10 s	High	>700	Chemicals

Table 1: Characteristics of some thermal decomposition processes.
Font: Prabir Basu: Biomass, gasification and pyrolysis. Design and theory (2013).

Lately, biomass pyrolysis has been very focused in the generation of bio-oil and maximizing its liquid yield. To achieve good liquid yield, it is necessary to raise the heating rate, to work at temperatures of about 400 to 600ºC, to use a short residence time (in the order of seconds) and to induce a rapid cooling of the products in order to stop the secondary cracking reactions[2] of the oil. The properties of the resulting oil will depend in several factors, like the pyrolysis reactor design, the properties of the initial feedstock and the working conditions above mentioned.

3.3. PYROLYSIS OIL

Crude bio-oils, also referred to as biomass pyrolysis liquid, pyrolysis oils, or bio-crude oils, are dark brown, free flowing liquids with an acrid or smoky odor. Chemically, bio-oils are a complex mixture of water (15-30 wt%) and hundreds of organic compounds that belong to acids,

---

[2] Secondary cracking reactions may be present if the product gasses are not rapidly cooled, making a thermochemical process where the main products are char, carbon monoxide or methane.

aldehydes, ketones, alcohols, esters, anhydrosugars, furans, phenols, guaiacols, syringols, and nitrogen compounds, as well as large molecular oligomers (holocellulose-derived anhydrooligosaccharides and lignin-derived oligomers) (Balat et al. 2009).

The many different compounds in pyrolysis oil have their origin from the simultaneous degradation of cellulose, hemicellulose and lignin during pyrolysis. The pyrolysis oil is generally collected as one liquid, resulting in a very complex mixture of many different oxygenated compounds with different functional groups. This makes identification and quantification of compounds in pyrolysis oil a very difficult task (Garcia-Perez et al. 2007).

Typical physical properties (**Table 2**) and chemical composition (**Table 3**) of bio-oil obtained during fast pyrolysis of wood are shown in the tables below:

Pyrolysis oil properties	Value
Moisture content (wt%)	15-30
pH	2,5
Specific gravity	1,2
Elemental composition (wt%)	
C	54-58
H	5,5-7
O	35-40
N	0-0,2
Ash	0-0,2
HHV (MJ/Kg)	16-19
Solids (wt%)	0,2-1

Table 2: Typical properties of pyrolysis oil from wood.
Font: Catalytic vapor cracking for improvement of Bio-oil. Hyun Ju Park et al. (2011)

Major components	Value (wt%)
Water	20-30
Pyrolytic lignin[3]	15-30
Aldehydes	10-20
Carboxylic acids	10-15
Carbohydrates	5-10
Phenols (*)	2-5
Furfurals	1-4
Alcohols	2-5
Ketones	1-5

Table 3: Chemical composition of fast pyrolysis liquid from wood.
Font: Michael J. McCall “Production of chemicals from pyrolysis”. US8158842 (2012)
(*) Phenol is included in the pyrolytic lignin

The pyrolysis oil is neither a mixture of compounds at thermodynamic equilibrium nor a stable product at room temperature. The viscosity tends to increase during storage, especially

---

[3] Pyrolysis of lignin yields a range of products, being methoxy-substituted phenols the most characteristic ones but also including simple phenols and oligomeric polyphenols.

at higher temperatures, due to the reactions of certain reactive compounds thus forming larger molecules. This is referred to as ageing (Oasmaa et al. 1999)

Because of all the properties mentioned above, bio-oilcan not be a substitute to traditional petroleum based fuels or as sustainable feedstock for renewable liquids fuels. The main reason being its lower heating value due to its high oxygen content. In addition, its high polarity makes it immiscible with crude oil, making it unsuitable as co-feedstock in petroleum refineries. Moreover, upgrading of bio-oil in current fossil oil refineries is rather difficult due to its high tendency towards polymerization.

However, if we take bio-oil as a source of chemicals, where oxygen removal may not be necessary, different technical and commercial applications may then become possible. Many oxygen-containing chemical stocks are now produced from fossil fuels via oxidation or hydration of olefins to introduce oxygen-containing functional groups. In contrast, these functional groups are already present in bio-oil, but, although many chemical constituents in bio-oil are valuable, their contents are still low, making their recovery technically difficult and costly.

3.4. DIFFERENT APLICATIONS OF BIO-OIL

When studying possible uses to pyrolysis oil, different approaches can be taken (**Figure 1**). It can be seen as a possible feedstock for chemical products or as fuel for different uses. Mainly, their applications have been found in the chemicals production and heat/power generation rather than in the transportation sector.

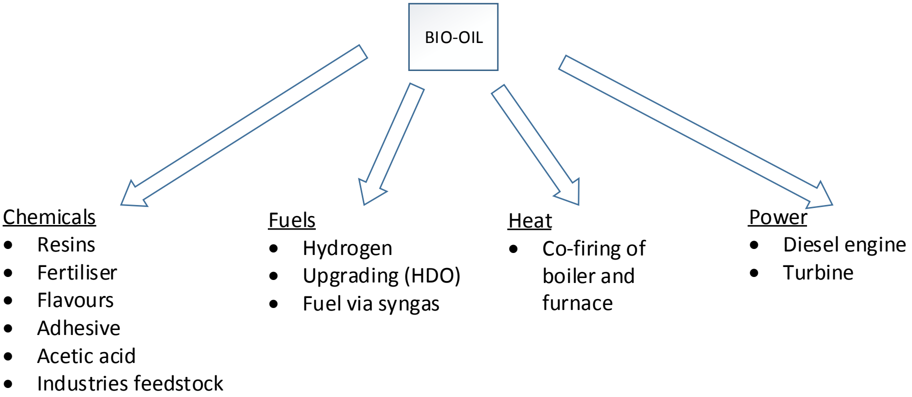


Figure 1: Various applications of bio-oil.
Font: Mohammad I. Jahirul et al. Biofuels production through biomass pyrolysis.

3.4.1. Energy valorization

Because bio-oils degrade with time, they cannot be used directly as a transportation fuel without upgrading or blending (Oasmaa et al. 1999). However, another limitation is that fuels derived from bio-oils have not been extensively investigated and the process of bio-oil upgrading is under steady development worldwide for enhanced efficiency and improved fuel properties. In addition, low cost processing technologies that could efficiently convert a large fraction of the lignocellulosic biomass into liquid or gaseous fuels do not yet exist (Elkasabi et al. 2015).

Pyrolysis oil can be used without further treatment in furnaces and boilers in co-generation plants as a source of energy. However, to cope with some of the properties and characteristics of the oil, these installations need to be modified to cope with the use of bio-oil instead of fossil fuels (Peters et al. 2015), (Ramirez et al. 2014). In a similar way, bio-oil can also be used as a fuel in conventional diesel engines (Prakash et al. 2013) or gas turbines (Kallenberg, 2013), which also need to be modified to cope with the properties of pyrolysis oil (varying chemical composition and low pH).

3.4.2. Chemicals from pyrolysis oil

As mentioned before, the main attractive of thinking of bio-oil as a source of chemicals is the enormous amount of value added chemical constituents that are present in it and the main disadvantage is that these components are often in low content, which makes it difficult to recover them. When facing this problem, the typical solution is to modify the pyrolysis working conditions and/or do a series of pretreatments of the biomass to modify its properties so that the resulting bio-oil has a higher yield of a specific chemical or group of chemicals and its further treatment to obtain this value added product has a reduced cost of recovery. This procedure, known as selective pyrolysis[4], has been tested with promising results achieving bio-oil with a high yield of components like furfural, hydroxyacetaldehyde or acetic acid amongst many others.

---

[4] Selective fast pyrolysis, differed from conventional fast pyrolysis which is usually aimed at the maximum bio-oil yield, is to drive the pyrolysis of biomass towards the products of interest, mostly by catalyst utilization, to maximize the yield of target product and obtain target products with high purity.

3.5. PAPER SLUDGE AS FEEDSTOCK FOR PYROLYSIS OIL

The topics described in this project will be developed within the frame of my scholarship at Alucha Recycling Solutions S.L.

Alucha Recycling Solutions develops technological solutions that enable waste recycling. Their focus is on used resources that are currently being landfilled or incinerated. Over the years, they have been zooming in on streams that contain both organic and non-organic matter. Examples are laminate materials (drink cartons, toothpaste tubes, pouches, etc.) and mixed plastics, but also biomass streams such as sludges, rice husk and other similar streams. With their technology, they are able to separate the organic from the inorganic matter, so recovering useable resources, typically oil and metals or minerals.

This project focuses in the biomass paper sludge stream waste being generated at the waste water treatment and deinking plants present in paper, tissue and board producing mills.

In the process of making paper, apart from the fibrous material and the chemicals that are added in order to increase its properties and quality, a great amount of water and energy in form of steam and electricity is needed. Consequently, nowadays paper producers face serious environmental problems regarding the water content in their paper sludge (5-10m^3/ton paper), energy consumption (2-5 ton steam/ton paper) and atmospheric emissions. Paper sludge is produced in paper, tissue and board recycling plants and it is a type of solid byproduct inherent to their pulping and papermaking operations. Normally it contains a high amount of water and fibers, but it is also rich in charges or minerals, which make paper sludge an important feedstock for the recovery of valuable products. Because of the operational problems of further treating paper sludge to recover paper, and the difficulty of separating the organic (fiber) and the inorganic (minerals) fractions, paper sludge is currently treated as a waste stream and it is commonly disposed in landfills (process that has some disposal costs attached) or co-incinerated (cement kilns), causing environmental problems through chemical leaching and greenhouse gas effect emissions production.

This project consists on pyrolyzing paper sludge for obtaining value added pyrolysis oil. This technology has already been tested by Alucha Recycling Solutions at laboratory scale and proven to be feasible, which led them to take the project to a further level and build a pilot plant at the University of Twente in Enschede, The Netherlands. This pilot plant works at closer conditions to fast pyrolysis than the multi-purpose laboratory scale reactor where these project tests have been undertaken. The results obtained so far seem to be promising, as a semi-commercial scale plant is now in development and will be commissioned by the end of 2016.

Until recently, the bio-oil was burnt in recovery boilers in order to obtain energy, this project now aims to identify and to start developing a process which can turn bio-oil into a feedstock to produce value-added chemicals.

Even though selective pyrolysis is a procedure that is giving promising results when it comes to the obtainment of chemicals from pyrolysis oil, this project focuses on developing a method to obtain fine chemicals from a bio-oil obtained from a defined feedstock (paper sludge) and through a pyrolysis process (pyrolysis temperature, type of reactor, etc.) already defined.

3.6. CHEMICALS FROM PAPER SLUDGE PYROLYSIS OIL

Pyrolysis oil has a huge potential as feedstock for several chemical products and Alucha Recycling Solution's next objective is to investigate which of these chemical compound scan be economically obtained through the simplest process possible. Having this in mind, the first step was to take a look at the gas chromatography analysis[5]of different bio-oil samples that had already been done in order to define its chemical composition.

The analysis where carried in a Mass spectroscopy thermo scientific LTQ 900, using an HP-5MS column of 30m x 0,25 mm of internal diameter x 0,25 µm p. diameter. The process used involved a temperature profile with a temperature of 35ºC passed the first minute and a slope of 4ºC/min with a temperature of 320ºC after 20 minutes of analysis.

The results of the GC:MS performed are shown in the graph below (**Figure 2 & Table 4**), where we can see pyrolysis oil samples of three different companies: Companies #1, #2 and #3.

---

[5] Gas chromatography is a chemical analysis which separates and identifies chemicals from a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas steam (carrier gas) at different rates depending on the various chemical and physical properties and their interaction with a specific column filing, called stationary phase. As chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at different time (retention time).

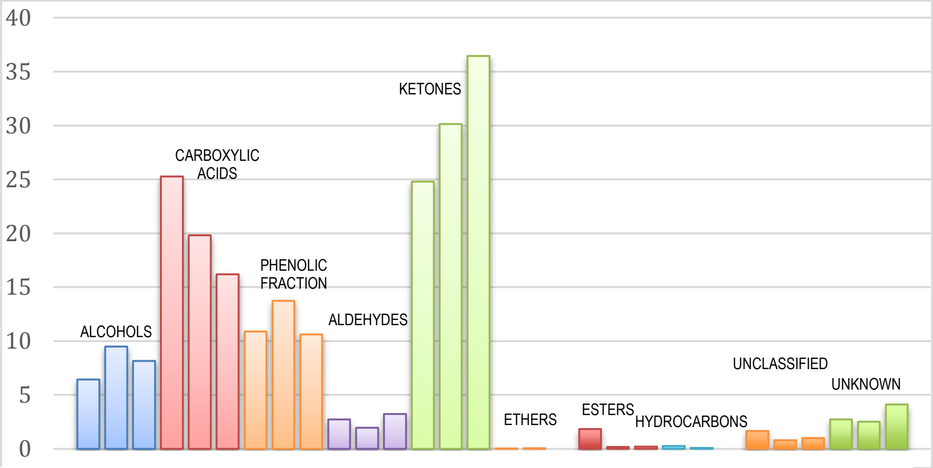


Figure 2: Composition of pyrolysis oil three different paper sludge providers.

Font: Author

Functional group	wt%
Water	20-30
Alcohols	6-9
Carboxylic acids	16-25
Phenolic fraction	11-14
Aldehydes	3-4
Ketones	24-36

Table 4: Chemical composition of samples from three diferent companies.
Font: Author

The three pyrolysis oils where produced under the same conditions at the laboratory scale multi-purpose pyrolysis reactor. This reactor did not operate at proper fast pyrolysis conditions, since the feedstockwas introduced in the reactor at the beginning of the experiment, and not when the temperature inside of the reactor is close to the pyrolysis temperature. Moreover, the residence time of gases is of the order of seconds. The methodology of these experiments will be further explained in the Section-6 of this report.

When we compare the chemical composition of the pyrolysis oil obtained from the samples from these companies with the bio-oil obtained from a wood-based feedstock (**Table 3**) we can appreciate how the composition of bio-oil changes significantly depending on the initial feedstock. The first observation we can do when looking at the results, is the lower amount of ethers, esters and hydrocarbons present in all three samples, and that the yield of hydrocarbons is almost inexistent due to the high amount of oxygen. When we remove from the picture the peaks corresponding to components which cannot be identified and the ones that belong to components too complex to be classified in of the categories listed, we are left with five big groups of chemicals whose presence is significant in bio-oil: alcohols, carboxylic acids, phenol and aromatic derivates, aldehydes and ketones.

Focusing on these five groups separately, it is possible to appreciate that the amount of alcohols obtained from the three oils is very similar and the difference of aldehydes and phenolic fraction is very small between the three samples. When it comes to acids and ketones, the situation is slightly different: the three samples yielded quite similar amounts of these groups of components, but the difference between experiments is bigger than compared with the other groups.

With three analyses we can have a general overview of the chemical composition of pyrolysis oil from paper sludge. Nevertheless, we have to take into consideration that a slight change in the pyrolysis conditions or the pretreatment of the biomass can change the yield of every functional group significantly, and more analysis would be advisable when the pyrolysis oil starts to be produced at the pilot plant instead than at the laboratory scale reactor.

4. OBJECTIVES

1. Investigating the current state of the art of the upgrading of bio-oil to its use as a sources of chemicals
2. Select the most promising methods that are already being used and try to obtain similar results using paper sludge as feedstock.
3. Determine the feasibility of said methods for its industrial application.
4. Depending on the results obtained from testing the different technologies, investigate and plan the next steps required to further investigate the process.

5. CHEMICALS FROM PYROLYSIS OIL

5.1. STATE OF THE ART

The first step of every project is to do a literature review. In our case, the obtainment of chemicals from pyrolytic oil is still a very recent research topic. That being said, a lot of improvement has been done in the last years and some processes are starting to prove to have some potential when it comes to its industrial application.

The next pages are a review of some of the processes that have shown promising results when it comes to obtaining chemicals through a feasible process and that are starting to be scaled industrially.

5.1.1. Acetic acid obtainment

Acetic acid is a high volume chemical utilized as a reactant, solvent, or catalyst in numerous processes. For example, acetic acid is converted according to known reaction pathways to vinyl acetate monomer, which is polymerized to form latex emulsion resins for paints and adhesives. Fibers and plastics as well are manufactured from acetic anhydride, which is another conversion product of acetic acid (Kocal, 2014).

Recently, methods for producing acetic acid from renewable carbon sources, in a manner that is generally less expensive than conventional routes based on fossil-derived carbon sources, have been investigated. These methods address the separation and recovery of acetic acid as a substantial product of biomass pyrolysis.

Amongst the enormous amount of chemicals that compose bio-oil, acetic and formic acid, and other organic acid components are present. Since these organic acids are responsible for corrosion of metals and storage instability of pyrolysis oil, removal of these components can be a useful approach both to isolate them and use them as feedstock for other processes or to reduce the corrosiveness of the pyrolysis oil in case we want to improve its properties for another use.

Removal of acetic and formic acid has been investigated by various authors. The water-soluble fraction of bio-oil contains various organic acids, aldehydes and simple phenolic components. A further distillation of this fraction was reported to give a distillate containing formic and acetic acid as well as some other volatile components, and treating this distillate with calcium oxide led to form calcium salts of organic acids that could be treated with a strong inorganic acid to recover the acids (Sukhbaatar et al. 2009). However, the precipitates also included high amounts of pyrolytic lignin and the distillation process proved to be costly. Development of lower cost separation methods would be desirable. Removal of acetic acid from bio-oil has also been investigated using an anion-exchange resin. These approach proved to be very effective when it comes to remove the organic acids of the oil, but the yields of recovered bio-oil where low (Sukhbaatar et al. 2009) due to adsorption of bio-oil components on resin particles and some improvement on this technology is needed for this purpose.

5.1.2. Hydrogen production

Hydrogen is considered to be a clean fuel and could have an important role in reducing environmental emissions in the future. Unlike fossil fuels, hydrogen burns cleanly, without emitting any environmental pollutants. In addition, hydrogen also possesses the highest energy content per unit of weight (about 120.7 MJ/kg) (Ye, T. et al. 2009). Hydrogen is also an important raw material for the chemical industry, which is mainly used for ammonia production or refining and methanol production. Currently, commercial hydrogen is primarily produced from methane and other hydrocarbon feedstocks, such as naphtha and heavy residues from petrochemical process, among others (Ye, T. et al. 2009). An alternative method of producing a H_2 rich gas is the catalytic steam reforming of the aqueous fraction of bio-oils. This method requires an initial separation of the bio-oil in two phases: the water-soluble fraction, containing the low molecular weight organics, and the insoluble fraction, enriched with lignin-derived compounds. The aqueous phase, being a complex mixture of different compounds such as acids, ketones, aldehydes, alcohols, sugars, phenols and more complex carbohydrates in water, can be catalytically reformed to produce a gas with a high H_2 content.

Probably, production of hydrogen from bio-oil reforming is one of the most promising options because it can achieve high hydrogen yield and high content of hydrogen. The main difficulty of this method relays on the use of a catalyst. The efficiency of the process is determined by the ability of the catalyst to catalyze the steam reforming reactions of the oxygenated organic compounds in bio-oil and the water-shift reaction.

Conventional steam reforming catalysts are 10-33 wt%NiO on a mineral support (alumina, magnesia, etc.), usually operating at T=600-700ºC. Recent investigation showed that Ni-Cu bimetallic catalyst supported on SiO_2, Al_2O_3, ZnO/Al_2O_3exhibited acceptable activity, stability and selectivity to hydrogen. In these systems, Cu is the active agent and promotes fast ethanol dehydrogenation to acetaldehyde, Ni promotes C-C bond rupture of acetaldehyde to produce CH_4 and CO and increases hydrogen selectivity (Ye, T. et al. 2009). Noble and precious metals (Pt, Ru, Rh) are generally more effective than the Ni-based catalyst and present less carbon depositing but are not very common because of their high cost. Another hindering is the deactivation of catalyst due to coke or oligomer deposition. Thus, it is very important to significantly reduce the carbon depositions during the bio-oil reforming process and lower the reforming temperature before this method can be applied at industrial scale (Sanna et al. 2005).

5.1.3. Bio-ethanol production

The main objective of this method is to convert the anhydrosugars in pyrolysis oils into ethanol. Pyrolytic sugars[6] are extracted from the bio-oil via phase separation and acid-hydrolyzed into glucose, which will be fermented into ethanol. Despite being a process to obtain chemicals (glucose that will be converted in ethanol), the final purpose of these processes is the obtainment of transportation fuels that can be a substitute for the traditional fossil fuels. When treating biomass under fast pyrolysis conditions, one of the primary degradation products of cellulose is levoglucosan (1,6-anhydro-b-D-glucopyranose) (Bennett et al. 2009). As an anhydrosugars, levoglucosan can be hydrolyzed to glucose, thereby providing a potentially rapid and efficient route to the production of bio-ethanol.

The initial step of this method is to separate bio-oil into aqueous and non-aqueous phase so the majority of anhydrosugars are in a different phase than the phenolic components. Once the separation is completed, these sugars are hydrolyzed into glucose using sulfuric acid as a catalyst. Sulfuric and carboxylic acids are then neutralized with $Ba(OH)_2$and the phase rich in sugars is further detoxified with activated carbon. The resulting aqueous phase rich in glucose is fermented to produce ethanol. Different yeasts have been tested (specially *S. cerevisiae*) (Luque, L. et al. 2014), (Lian, J. et al. 2010) giving promising results, but the main difficulties of these method relays on the initial phase separation and the subsequent removal of toxic compounds, like phenols or acids, that could inhibit the growth of the yeast. Therefore, proper phase separation needs to be developed before this process is industrially feasible.

---

[6] Pyrolytic sugars: name given to the mixture of sugars, aldehydes and ketones present in the pyrolysis oil.

5.1.4. Phenolic components

Because bio-oil contains lots of simple phenols and oligomeric polyphenols (or pyrolytic lignin), the application of bio-oil depends on which fraction is used. A very useful application way for phenolic compounds in bio-oil is to recover simple phenols from bio-oil, because they are valuable chemicals which are suitable for a broad range of applications. Despite that, due to the difficulty in separating simple phenols and the low yield of this component in bio-oil, this method has not been further investigated. In contrast, efforts have been made to apply pyrolytic lignin as a substitute for fossil phenols in phenolic resins. Phenolic resins are normally synthesized by acid or basic catalyzed reactions between phenols and aldehydes. Phenol-formaldedhyde (PF) resin, a representative phenolic resin, is obtained by the reaction of phenol or substituted phenol with formaldehyde, leading to the formation of novolacs (thermoplastic) or resoles (thermosetting), respectively. Phenolic resins are widely used in many industries, including electronic laminating and wood composite industries (Kim, J. S. 2015).

Several processes for the recovery of the phenolic fraction from pyrolysis oil from biomass have been investigated, using different procedures and methods having all in common that the ultimate product is a phenolic fraction, which is desired to be as pure as possible.

Although bio-oils containing a high content of phenolic compounds have a strong potential for the replacement of fossil phenol, they suffer from a relatively low reactivity in the phenolic resin synthesis, as typical bio-oil contains a low concentration of reactive phenol, and the mixture of phenolic compounds (primarily alkylated phenol and aromatic ethers) in bio-oils is less reactive than pure phenol. In addition to this, all processes for recovering the phenolic fraction involve an initial separation of the aqueous and non-aqueous phase that still hinder the feasibility of the process and its industrialization.

5.2. PHASE SEPARATION

Taking a closer look to all the processes stated above, it is possible to appreciate that they all have in common the need of an initial treatment to separate bio-oil in two phases (aqueous and non-aqueous) in order to simplify the complex mixture of components that bio-oil is made of and in an attempt to obtain two phases with similar chemical and physical properties. Although this initial separation may not seem complicated to perform is one of the main factors that hinders the obtainment of chemical products from pyrolysis oil.

Conventional separation technologies such as solvent extraction, column chromatography and distillation are amongst the most investigated.

5.2.1. Solvent extraction

Solvent extraction is a process which selectively dissolves target components of a mixture of components into a solvent for which those components have a greater affinity. Commonly used solvents for the extraction of specific compounds from bio-oil include water, alcohols, ethyl acetate, hydrocarbons such as toluene and n-hexane, ethers, ketones, dichloromethane, and alkaline solutions (Vecino Mantilla, S. et al. 2015).In solvent extraction procedures, large volumes of solvents are required, making the industrialization of some extractions unfeasible.

5.2.2. Column chromatography

The separation of bio-oil components through column chromatography commonly utilizes silica gel and aluminum oxide as the stationary phase, where the mobile phase is selected according to the polarity of bio-oil components which are to be extracted. The separation is based on the different adsorption capabilities of bio-oil components onto the stationary phase. Column chromatography can economically separate bio-oil, but its low throughput makes it only suitable for high value-added compounds (Zeng, F. et al. 1987).

5.2.3. Distillation

Distillation separates bio-oil components according to their different volatilities. Atmospheric pressure-, vacuum-, steam-, and molecular distillation can be applied to bio-oil separation. Boiling of bio-oil starts below 100ºC at atmospheric pressure, and stopping the distillation at 280ºC leaves 35–50 wt% of the starting material as a residue (Czernik et al. 2004). In contrast to atmospheric pressure distillation, vacuum distillation has a strong advantage, allowing to operate at much lower temperatures. The distilled organic fraction from vacuum distillation contains almost no water and fewer oxygenated compounds, although the method uses large amounts of energy. Steam distillation, which requires a relatively large initial capital investment, can be applied for the separation of bio-oil components, introducing steam into the distilling column to heat bio-oil and decrease its viscosity. With the addition of steam, the organic-water mixture (bio-oil) boils at a lower temperature (below 100ºC) (Czernik et al. 2004), allowing thermally sensitive compounds to be separated with reduced decomposition. Molecular distillation, which is widely applied in petrochemical, fine chemical, medicine, pharmaceutical, and food-processing industries, is also considered to be an appropriate process for the separation of thermally unstable bio-oils. Compared to other forms of distillation, molecular distillation has the advantages of lower operating temperatures, shorter heating time, higher separation efficiencies and minimal losses by thermal decomposition. In a study of the separation of bio-oil using molecular distillation, a maximum distillate yield of 85% was obtained without coking or polymerization (Wang, S. et al. 2009). The main disadvantage of molecular distillation lies in the high equipment costs.

5.3. SELECTION OF THE TARGET CHEMICALS TO BE RECOVERED

All the methods to obtain chemicals described above have in common an initial separation of the bio-oil in two phases: the aqueous phase, containing all the sugars, and the non-aqueous phase, composed by the pyrolytic lignin, even though some of the methods focus on obtaining chemicals from the aqueous phase and some from the organic phase.

The table below shows a comparison of the possible methods mentioned, with its benefits and withdraws, in order to serve as guide to decide which process is more interesting to be investigated.

From all the methods previously mentioned, the obtainment of the phenolic fraction from pyrolysis oil to use it as a substitute of phenol obtained from fossil resources will be studied. One of the main factors that influenced into taking this decision was the fact that after obtaining the phenolic fraction it is possible to stop the process right after the phase separation and use the obtained organic fraction as a partial substitute of phenol, unlike the other three processes mentioned, which need further treatment to obtain a final product that can be commercialized. Other important factors are the non-restrictive working conditions that this process needs to be carried out, or the possibility of developing a method which can obtain substitutes of phenol from a greener and cheaper process.

The table below (**Table 5**) shows a comparison of the possible methods mentioned, with its benefits and withdraws, in order to serve as guide to decide which process is more interesting to be investigated.

OBJECTIVE	DESCRIPTION	METHOD	PROS	CONS	PHASE SEPARATION
ORGANIC ACID OBTENTION	· Acids like acetic acid are used in numerous processes. · Alternative obtention of acids from the traditional fossil-derived carbon source. · Acetic and formic acid are known to be amongst the compounds with higher yield in bio-oil. · The removal of organic acids can improve the properties of oil for its use as fuel.	Distillation of the water soluble fraction of pyrolysis oil, followed by treating the distillate with CaO to form calcium salts from which, upon treating with a H_2SO_4, the acids are recovered.	· Simple method with no restrictive conditions. · The chemicals needed are do not hinder the feasibility of the process with its price or the amount needed.	· The precipitates include high amounts of pyrolytic lignin · Distillation cost prohibitive.	YES
		Anion-exchange resin.	· Very effective way to remove the organic acid from oil. · Effective way to improve the quality of oil removing certain components.	· Yield of recovered oil is low due to adsorption of bio-oil components on resin particles.	YES
HYDROGEN PRODUCTION	· Hydrogen has a huge potential as fuel. · Important raw material for the chemical industry · Alternative obtention of hydrogen from the traditional production from hydrocarbon feedstocks.	Catalytic steam reforming of the aqueous fraction of bio-oil.	· High content of gas with high yield of hydrogen. · Can be carried in two steps with less restrictive operation conditions.	· Process efficiency determined by catalyst. · Price and deactivation of catalyst.	YES
BIO-ETHANOL PRODUCTION	· Convert sugars in pyrolysis oil into ethanol. · Alternative obtention of ethanol that can be used as transportation fuel.	Hydrolysis of anhydrosugars of bio-oil into glucose using sulfuric acid as catalyst followed by fermentation.	· Rapid and efficient route to produce bio-ethanol. · Price and amount of chemicals needed and operation	· Sulfuric and carboxylic acid need to be neutralized. · Phase rich in sugars needs to be detoxified before fermentation.	YES

			conditions are not restrictive. · Several yeasts are able to ferment glucose into ethanol and the price and working conditions are not restrictive.	· Process conditions need to be strictly controlled to meet the needs of the microorganisms.	
OBTENTION OF THE PHENOLIC COMPONENTS	· Phenols are valuable chemicals with a broad range of applications.	Separating simple phenol present in bio-oil.	· Route to obtain phenol from a greener feedstock rather than the traditional method from fossil sources.	· Several steps needed to separate simple phenols. · Low yield of simple phenols in oil.	YES
	· Pyrolytic lignin can be a substitute for fossil phenols in phenolic resins. · Phenolic resins are widely used in the industry	Recovering pyrolytic lignin from bio-oil by liquid-liquid extraction	· After separating the oil in two phases little additional treatment is needed. · Resultant phenolic fraction can be used as a cheaper source of phenol in existent processes. · Operating conditions are not restrictive	· Low amount of reactive phenol. · Mixture of phenolic components is less reactive and include non-phenolic compounds.	YES

Table 5: Benefits and withdraws of the selected methods to obtain chemicals from bio-oil from paper sludge.

Font: Author

5.4. RECOVERY OF THE PHENOLIC FRACTION

As stated before, different methods for conducting the separation of bio-oil in two phases have been investigated. Most of them present important drawbacks that hinder its industrialization, but some also proved to be great alternatives although they require further investigation to cope with some difficulties. From the methods mentioned in the previous pages, solvent extraction is considered to be a potential method to carry this initial separation successfully and that is why some experiments will be carried on to test some of the latest methods that have given promising results.

After carrying out some more literature review about solvent extraction, two methods where found that successfully overcame one of the main problems of solvent extraction: the high amounts of solvent needed. These methods where tested using lignin rich biomass, obtaining promising results, and further experiments will be made to see if these technologies can give similar results when applied to a bio-oil obtained from paper sludge.

5.4.1. L-L extraction using methanol and water

This process is based on the work carried out by Sukhbaatar, B. et al. (2009), where they investigated the application of lignin separated from bio-oil in oriented strand board (OSB) binder phenol-formaldehyde resins. As stated before, it is almost indispensable to carry out the separation of bio-oil in two phases, and they came out with an alternative solvent extraction which reduced the amount of solvent needed, improving significantly the economy of the process in comparison with previous methods.

The separation of lignin has been investigated based on the lignin's good solubility in organic solvents and poor solubility in water (Chum, H. L. et al. 1992). An initial attempt of mixing the bio-oil with ethyl acetate and washing the resultant organic layer with water and sodium bicarbonate yielded up to 31% of pyrolytic lignin (Chum, H. L. et al. 1993). However, a commercialization effort of the technology was initiated but not continued due to the costly lignin separation procedure and variable yields of lignin due to the water and sodium bicarbonate washing procedures (Sukhbaatar, B. et al. 2009).

In their work, Sukhabaatar, B. et al. separated the lignin fraction from a woody feedstock bio-oil using only water and methanol with a 25 wt% of bio-oil. Despite the yield being lower than the previous method, the amount of solvent needed is much lower and the amount of steps required to conduct the separation is lower, which benefits the economy of the process. In their experiments, they did an initial test using only water and bio-oil was mixed with water in a 1:1 ratio. Despite they obtained two clearly separated phases, the phenolic fraction was found to contain certain non-lignin materials that made it unsuitable for its use as a phenol replacement. Therefore, this fraction was further treated with methanol in a 1:1 ratio and then the lignin fraction was precipitated adding about the same amount of water. After allowed to stand at room temperature and evaporating the remaining methanol pyrolytic lignin was obtained with a yield of 22 wt%, which means that 71% of the phenolic fraction present in the initial bio-oil was recovered.

5.4.2. Method of separating lignin derived compounds from pyrolysis oil

An alternative method to the most studied extraction with a polar hydrophilic solvent, capable of separating light oxygenates from lignin derived compounds was carried out by Wang et al. (2014)

It has been found that the separation of lignin derived compounds from bio oil by use of reversible α-hydroxysulfonic acid remarkably increase the extraction efficiency. Hydroxyl aldehydes and ketones present in bio oil are combined with SO_2 and water to generate α-hydroxysulfonic acid in situ. The presence of α-hydroxysulfonic acids in bio oil eliminates the surfactant properties of bio –oil, makes the water very acidic ($pH<1$), and drives the lignin and phenolic based species into a separate phase. Once the water is separated, the carbonyls can be regenerated by heating the mixture or reducing the pressure, allowing volatile SO_2 to depart the reaction zone.

The acid is generally formed by reacting at least one carbonyl compound with sulfur dioxide and water. This reaction is a true equilibrium, with in a facile reversibility of the acid. That is, when heated, the equilibrium shifts towards the starting carbonyl, sulfur dioxide, and water. If the volatile components are allowed to depart the reaction mixture via vaporization or other methods, the acid reaction completely reverses and the solution becomes effectively neutral.

These process not only reported good results in separating bio-oil in two phases, but also grants the possibility of using both phases to obtain chemicals (phenols from the apolar phase and glucose from the polar phase).

5.5. ANALYSIS TO DETERMINE THE AMOUNT OF PHENOLIC FRACTION PRESENT IN BIO-OIL

In order to determine the efficiency of each of the methods, an analysis technique that shows the amount of phenolic fraction in the samples needs to be selected. This analysis will be done to the initial bio-oil obtained after the pyrolysis test and to the sample recovered after treating it to separate it in two phases. This analysis should give a clear and representative value, which would allow to compare the percentage of phenolic fraction in the initial and the final product.

Due to the high amount of different components present in bio-oil, an analysis which identifies the entire chemical composition of pyrolytic oil is still not available, but different methodologies for where investigated, each of them with benefits and disadvantages when applied to bio-oil samples.

With all the considerations mentioned below (**Table 6**), GC:MS was considered to be the most suitable technique for this experiments, since not only identifies a board range of components (which will be useful to identify components which were not initially taken into consideration but that represent an important percentage of the pyrolysis oil), but also is the technique which suffers less interferences caused by the high number of components present in bio-oil. For each chromatography, the methodology will be identical to the one followed with the three initial samples of bio-oil analyzed: all the components identified will be classified into functional groups, allowing a quick comparison between samples.

Analysis	Description	Advantages	Disadvantages
PHENOL NUMBER	Colorimetric analysis which determines the quantity of phenolic components in a sample by using free phenol as referent. The sample needs to be previously distilled for removing all the non- phenolic components that may give color to the pyrolytic oil.	Once the sample is distilled the interference produced in the result by non-phenolic components is reduced. Obtainment of a single value which is indicative of the presence of phenolic components in the sample.	Difficult to know the efficiency of the distillation due to the high amount of components. It is possible that some phenolic components are distilled as well. These factors make it easy to obtain a result which is not accurate

GC:MS (Gas chromatography mass spectrum)	The sample is introduced in the chromatography column, which has a defined temperature slope. Each component leaves the column at a certain time (retention time) which is distinctive for each compound. Depending on the properties of the column, the components move at a velocity determined by its polarity	Allows to obtain a graphic in which each peak represents an identified component. A huge range of components can be identified with this method.	Because of the high amount of components, some of the peaks are mixtures of two or more chemicals. Certain components (like water or some alcohols) cannot be identified in the same column as phenolic components. Chemicals which have small yield in the sample are not identified.
HPLC (high performance liquid chromatography)	The sample is introduced in the column and its components are differentially delayed depending on the interactions which they suffer with the column. It works under the same principle as GC:MS	Obtains a graphic in which each peak is a chemical component (or mixture of similar chemicals). A huge range of components can be identified in the same column.	The obtained peaks are difficult to identify without a proper pattern. Due to the complex composition of bio-oil, several components are not identified and certain compounds can cause interferences.
NMR (Nuclear magnetic resonance)	Spectroscopic technique based on the interaction between atoms under the influence of a magnetic field and an electromagnetic field of a specific frequency used to obtain information about the properties of the chemical compounds present in the sample	Technique capable of identifying precisely the components of a sample by determining the atoms of each compound.	A high amount of chemicals present in the sample cause interferences in the identification of each component. Aromatic compounds without phenol might be identified as phenolic fraction as well and acid components are also difficult to differentiate

Table 6: Benefits and withdraws of different analysis used to determine the amount of phenolic fraction in bio-oil.

Font: Author

6. BIO-OIL UPGRADING FOR RECOVERING THE PHENOLIC FRACTION

The main objective of this project is to prove the feasibility of the methods explained before for recovering the phenolic fraction of bio-oil. In this section of the report, the process used to obtain pyrolysis oil from new samples from the same companies mentioned before and the treatment done to this oil to isolate the phenolic fraction are explained.

6.1. FEEDSTOCK

As stated before, paper sludge obtained at paper mills is a solid byproduct of pulping and papermaking operations which contains a high amount of water and fiber as well as minerals. Because of its composition, paper sludge needs to be treated before being used as feedstock for pyrolysis oil (**Figure 3**). This pretreatment generally consists on a drying step to remove the high amount of water present in the sample, and a shredding process to reduce the size of the sample and increase the contact surface of the particles.

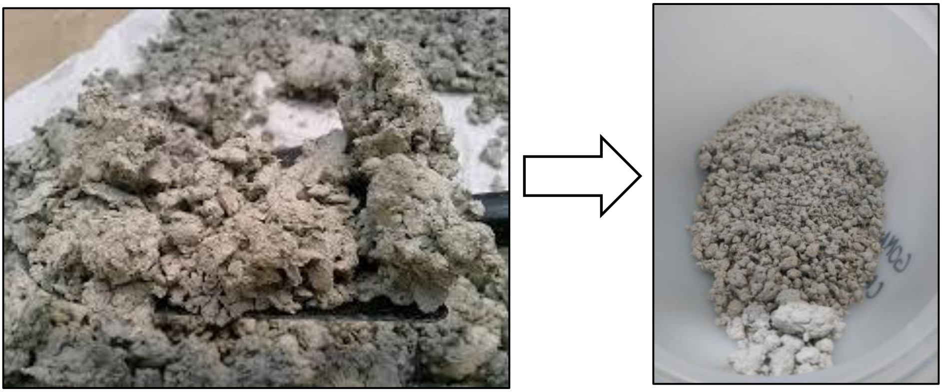


Figure 3: Paper sludge samples before and after drying and shredding the feedstock.

Font: Author.

6.2. REACTOR AND CONDENSATION SYSTEM

The lab pyrolysis tests are carried out in a stirred-tank reactor (**Figure 4**). The reactor is a stainless steel cylindrical vessel of 12 liters of capacity sealed to avoid the entrance of oxidant agents, with three thermo-couples on the side and four connections on top: one inlet for feeding the reactor and to introduce the flow of nitrogen, one outlet connected to a pressure relief safety valve which activates when the pressure in the reactor exceeds a fixed value, one for the stirrer and the last one as outlet for off-gases. The exit outlet is electrically traced in order to avoid condensation of the off- gases inside the outlet pipe. The reactor is contained by an electrical refractory lined oven so that its inner temperature can be maintained, monitored and controlled.

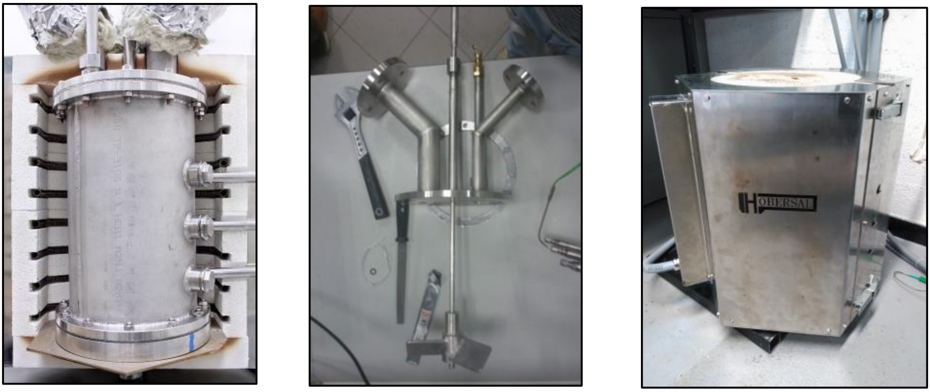


Figure 4: Detail of the reactor (a), the agitator and top orifices (b), and the closed oven (c).

Font: Author

Figure 5: Detail of the injector.

Font: Author

The reactor's material feed inlet consists of a screw injector (**Figure 5**) used to dose the sample in when the reactor has reached the desired pyrolysis temperature. Using the injector to feed the sample we reduce the residence time of gases (avoiding cracking reactions of vapors at high temperatures) and increase the heating velocity.

The condensation system (**Figure 6**) consists of two double tube condensers(one of 600 mm and one of 300 mL) connected in series, followed by a third condenser which consists of a cotton filled tube. The two double tube condensers have a vessel connected at the bottom in which the oil is collected. All the components are glass made and need to be manipulated with caution. When assembling, in order to keep the system gas tight, grease is applied at the joints.

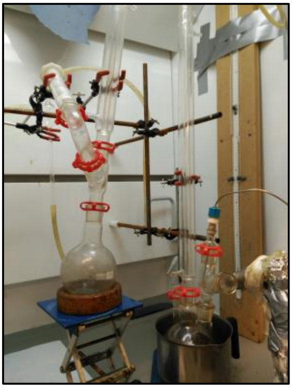


Figure 6: Detail of the condensation system.

Font: Author

6.3. EXPERIMENTAL PROCEDURE

The experiences are divided in two main parts: the pyrolysis tests, from which we will obtain the pyrolytic oil, and the phenolic fraction recovery, where the oil is treated to isolate this fraction conducting one of the methods described previously.

6.3.1. Pyrolysis test

The steps followed during the described experiences are listed below.

Reactor and the condensation system assembly

1. The stirrer is coupled in the reactor taking special attention to its mechanical alignment.

2. The body and the top of the reactor are joint by 12 screws previously coated with copper grease.
3. The injector is mounted on the reactor inlet and a connection is attached to the top of the injector to introduce the nitrogen. The nitrogen tube is connected to a rotameter in order to adjust its flow. Before sealing the adapter, the feedstock is placed in the injector's hopper.
4. The reactor is introduced in the oven and the axle of the stirrer is coupled to an electrical motor.
5. The reactor outlet consists of a flexible electrically traced pipe, which is connected to the condenser system described above. At the end of this flexible pipe there is a thermocouple that controls the off gas exit temperature (**Figure 7**).
6. A pressure indicator is connected at the first condenser outlet for controlling any possible pressure increase that may be produced in the condensation system (basically by fouling of the cotton). This manometer is also used to check if there are any pressure drops caused by leaks in the condensation system.
7. The second condenser is connected to the water system of the laboratory (around 15ºC) from its bottom and the top is connected to the top of the first condenser, providing counter flow in both condensers.
8. Dry ice is introduced mixed with acetone around the first vessel tank to ensure the condensation of the heavier fractions.
9. Once the whole installation is ready, a pressure drop test is done to check that there are no leakages in the system.

Figure 7: Detail of the reaction system.

Font: Author

<u>Experimental procedure</u>

1. The thermo-couples are connected to a thermo-couple data logger. This continuously registers the temperature variation from all three sensors. The program is set to record the temperatures every 30 seconds.

Note: The middle temperature transmitter gives the process value temperature to the oven temperature loop controller.

2. The electrical tracing is switched on, the water which feeds the condenser is connected and a nitrogen flow of 5 L/min is introduced to purge out the oxygen from the system.
3. The oven temperatures are increased (Set points 1 and 2) to the desired values and the temperature profiles are registered.
4. Once the temperature of the bottom of the reactor reaches the desired value (the pyrolysis temperature) the sample is injected. Depending on the amount of sample is advisable to introduce it in separate batches to avoid a drastic increase in the exit temperature of the reactor, which would hinder the proper condensation of the gasses.
5. Once the pyrolysis has ended, the oven, the stirrer and the water flow of the condensers are switched off.

Cleaning and sample collection

1. Once the reactor and the oven temperatures have decreased, the condensation system is disassembled inside the fume hood.
2. The liquid oil in the vessels is collected and every component of the condensation system is weighed before and after cleaning it with acetone.
3. The injector and the top cover of the reactor are removed and the stirrer is uncoupled from the motor.
4. The solids remaining in the reactor are collected and weighed.
5. A mass balance is conducted knowing the amount of solids and liquid collected and the initial quantity of sample to calculate the amount of gas generated.
6. Different types of analysis are done, depending on the objectives of the test. In our case, only gas chromatography of the liquid was performed.

Calculation of the amount of minerals

1. Approximately 5g of the solids collected from the reactor are placed on a ceramic plate and introduced in the oven, which is not completely closed and has an oxygen entrance.

2. The solids are left in the oven at a temperature of 450ºC (to avoid degradation of the minerals) for six hours. The sample is weighted every two hours in order to know when a complete oxidation has been achieved. The difference is the fraction of inorganic products.

Once the pyrolysis test has been completed, the oil obtained is further treated to recover the phenolic fraction. The methods previously explained where tested following the next steps.

6.3.2. Solvent extraction

The main idea of this procedure is to dilute the aqueous fraction further more by adding water and then decanting the mixture, obtaining the organic fraction (which is heavier) and decant it one last time after adding methanol for enhancing even more the separation of the polar and the apolar components (**Figure 8**).

1. The bio-oil obtained in the pyrolysis test is collected from the vessel tanks and placed in a 500ml capacity glass decanter.
2. Water is added in a 1 to 1 ratio to bio-oil and left at room temperature for 2h.
3. The water insoluble fraction is decanted giving a viscous and black product.
4. This organic fraction is further treated with methanol, also in a 1 to 1 ratio of bio-oil and methanol.
5. The lignin fraction is precipitated adding water incrementally while stirring until no further precipitation is observed.

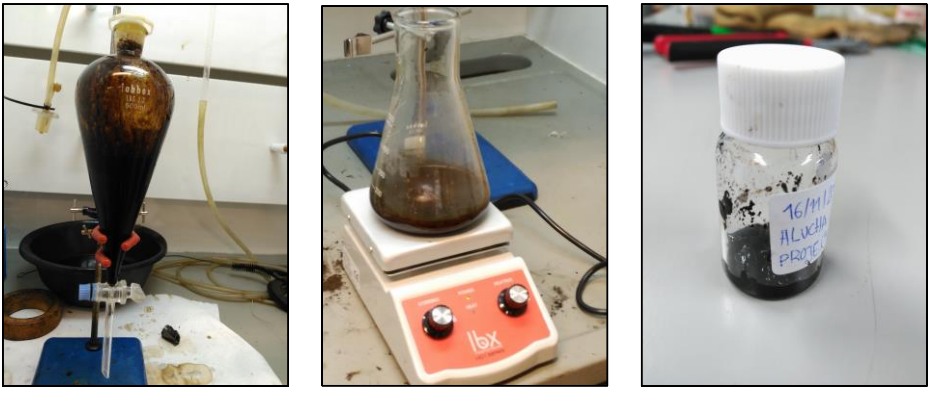


Figure 8: Detail of different parts of the solvent extraction method.

Font: Author

6. The mixture is then heated to evaporate the methanol and the remaining water and the dark viscous lignin material that is left in the bottom.
7. The collectable solids are sent for analysis

6.3.3. Sulfur extraction

The idea of this method is to substitute the traditional polar hydrophilic solvent used in solvent extraction. The bio-oil obtained during the pyrolysis experiment is collected and placed in a Kitasato flask (**Figure 9**).

1. Water is added in a 3:1 bio-oil to water ratio.
2. While stirring the mixture, sulfur dioxide is introduced in stoichiometric excess and allowed to react for one hour.

   Note: Sulfur dioxide is generated in situ by combusting sulfur in the presence of oxygen.
3. Once the reaction has taken place, the mixture is heated in order to reverse the equilibrium. The sulfur dioxide gasses are removed by introducing a reverse nitrogen flow.
4. The mixture is cooled down to room temperature by introducing a cooling air stream while the mixture is left to settle down for another hour.
5. The aqueous fraction is removed by decantation and the solids are collected and sent for analysis.

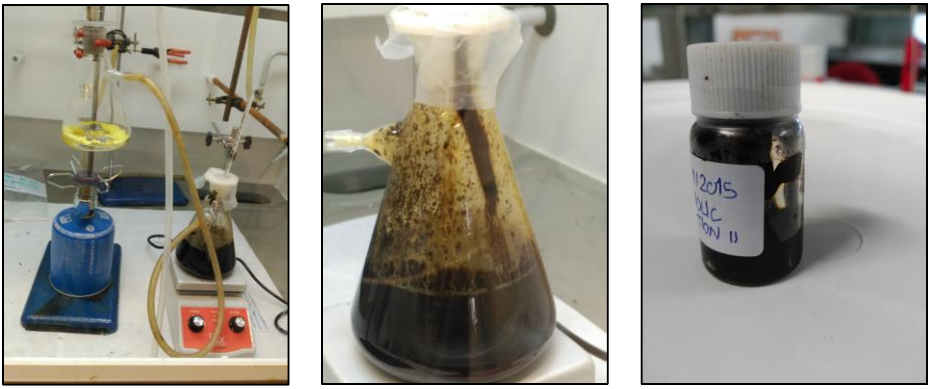


Figure 9: Detail of different parts of the sulfur extraction method.

Font: Author

6.4. RESULTS AND ANALYSIS

Two initial pyrolysis experiments where planned with the objective of obtaining enough oil to test the two methods described above. For each experiment we will use a different feedstock and the oil obtained will be analyzed via GC:MS before and after the extractions. Without taking into account the three weeks that the analyses take to be done, each experiment lasts for approximately three days, breaking down this time in the following operations:

Assembly of the reaction system	Pyrolysis experiment	Cooling and recovery of the sample	Separation experiment	Cleaning	Balances	Calcination
4 hours	2 hours	4 hours	3 hours	4 hours	2 hours	8 hours

Table 6: Amount of hours needed to do one complete experiment.
Font: Author.

These two initial experiments will serve as a starting point in order to test the efficiency of each of the methods described above and its advantages and disadvantages. If chromatographies from both methods report successful separation results, the next step would be to start introducing changes in certain parameters of the experiment, like the working conditions or the ratios of components used, with the objective of improving the yield and/or the purity of the phenolic fraction recovered. If the results prove one of the methods to not be feasible or to be significantly worse than the other, another experiment would be done using the same method but introducing major changes in the parameters mentioned before.

6.4.1. Pyrolysis test from company #1 followed by solvent extraction

Since the extraction tests are designed to be done with 100mL of oil, an initial approximation of the amount of paper sludge that will be needed to yield enough liquid was done. From previous experiments done at Alucha Recycling Solutions with this kind of feedstock we can approximate the amount of minerals of around 50% of the total of the paper sludge weight and the remaining fiber yields to about 30% of oil. Assuming that part of the pyrolysis oil generated will not be collected because it remains in the components of the condensation system (the amount of oil can be quantified because the whole condensation system is weighted, but it cannot be completely recovered because it is a batch system), we can calculate that for obtaining 100mL of oil we will need around 750g of paper sludge.

Phase	Weigh [g]	Percentage	Phase	Percentage
Sample mass	742	-	Regarding the organic	-
First liquid fraction	130,2	17,5%	Liquid	46,6%
Second liquid fraction	23,6	3,1%	Char	23,5%
Solids remaining in the reactor	489,7	66,0%	Gas	29,8%
Gas	98,4	13,2%	Inorganic	55,5%

Table 7: Mass balance of the pyrolysis test from company #1.
Font: Author

From the 153,8g of bio-oil produced (**Table 7**), 124,1g where collected in the first tank, from which about 5g where used as sample to analyze the oil. After decanting the obtained oil into the decanter, where the extraction will be done, a total of 105,3g from the initial 153,8g where mixed stoichiometrically with water. After doing the first extraction, the same amount of methanol (105g) was mixed with the organic phase and, after left to settle, solid lignin was precipitated and recovered.

The amount of solid lignin obtained was too little (**Figure 10**) to do a representative mass balance. Since the apolar phase of the oil is more viscous it is easy to lose an important part of this fraction when decanting the oil or moving it from one equipment to another, and most of the solid lignin was left at the bottom of the glass equipment used rather than extracted with both water and methanol. This can be partially avoided by reducing the steps done and minimizing the amount of times that the pyrolytic oil was moved from one equipment to another, but still the solid lignin left unreacted would be too high in percentage to make a representative mass

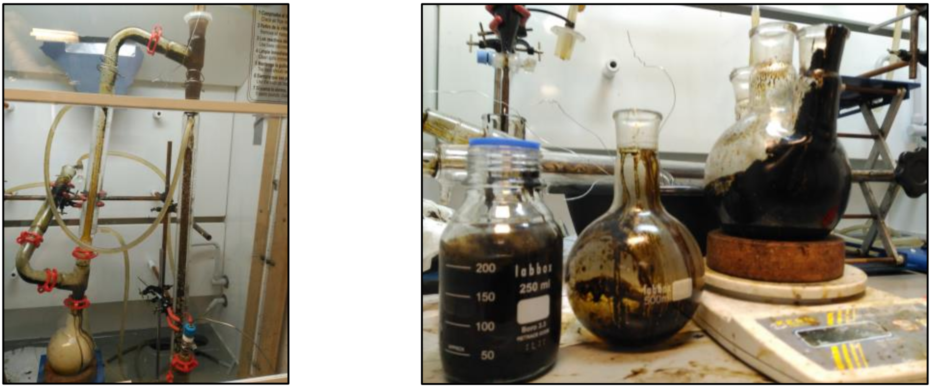


Figure 10: Detail of the condensation system (a) and the two tanks (the two balloons) after the pyrolysis test.

Font: Author

balance of the process. Despite this restriction, the solid lignin yielded was analyzed by GC:MS and compared with the initial oil to see if the percentage of phenolic fraction in the treated oil has increased after the extractions.

The results of both chromatographies (**Figure 11**) can be seen in detail in **Appendix-1**, but, as the table below shows (**Table 8**), the percentage of phenolic fraction in the initial and the treated oil increased from 8,6% to 70,2%, proving it to be a good method for obtaining a fraction of oil much richer in pyrolytic lignin than the initial bio-oil.

In order to simplify the comparison of the results obtained with the different methods a "concentration factor" will be introduced to quantify the increment or decrement of the yield of each functional group present in the bio-oil, a concentration factor <1 meaning that the yield of the correspondent functional group has decreased after the treatment and a value >1 meaning that it has increased.

Functional group	Before	After	Percentage	Concentration factor
Alcohols	20,1%	0,9%	4,5%	0,05
Acids	6,3%	16,9%	267,5%	2,68
Phenolic Fraction	8,6%	70,2%	810,8%	8,11
Aldehydes	12,5%	0,0%	0,0%	0,00
Ketones	5,3%	0,2%	4,8%	0,05
Ethers	2,3%	7,4%	255,2%	2,55
Esters	2,0%	2,7%	133,7%	1,34
Hydrocarbons	0,00%	0,0%	0,0%	0,00
Unclassified	22,1%	1,6%	7,5%	0,07

Table 8: Pyrolysis oil from company #1 treated with methanol extraction method.
Font: Author.

6.4.2. Pyrolysis test from company #2 followed by sulfur extraction

A second pyrolysis test was done, identical to the first one but with feedstock from company #2. In this case the amount of sludge introduced in the reactor was bigger and with less moisture content than the previous sample. These two factors result into increasing the yield of bio-oil and its properties:

The amount of oil which is difficult to recover due to fouling in the walls of the condensation system and the exit of the reactor reaches a maximum point at a certain moment during the pyrolysis test, and once this maximum is achieved the oil produced afterwards will be condensed more easily and the yield of both liquid fractions will increase. On the other hand, a reduced moisture content in the initial bio-oil will mean a decrease in the amount of pyrolytic oil produced, but the amount of water in this oil will be smaller, meaning that the properties of the oil will be better.

Phase	Weigh [g]	Percentage	Phase	Percentage
Sample mass	1000	-	Regarding the organic	
First liquid fraction	220,8	22,1%	Liquid	56,7%
Second liquid fraction	37,8	3,8%	Char	14,2%
Solids remaining in the reactor	608,5	60,8%	Gas	29,1%
Gas	132,9	13,3%	Inorganic	54,3%

Table 9: Mass balance of the pyrolysis test from company #2.
Font: Author.

From the 258,6g produced (**Table 9**), 204,1g where decanted into a Kitasato flask where 130g of water were added and where the sulfur dioxide was later introduced while stirring. For producing this sulfur dioxide 9g of sulfur where introduced in the second Kitasato where the reaction took place, generating 18g of sulfur dioxide. The amounts of sulfur dioxide and water needed were extrapolated from the experiments disclosed in the patent, in order to benefit from the previous experiences described and reduce the error in the initial experiments.

Despite that the amount of lignin left unreacted due to moving the oil fraction from one container to another is very small compared to the one from the previous experiment, it was considered that the quantity of solids left unreacted inside the condensation system would make a mass balance of this experiment not representative of the efficiency of the method.

Like in the solvent extraction, a gas chromatography of the initial and the final oil where compared to see how the amount of phenolic fraction increases after the process. The results show that amount of phenolic fraction in the samples analyzed has increased from 15,7% in the initial bio-oil to 55,8% (**Table 10**).

Functional group	Before	After	Percentage	Concentration factor
Alcohols	24,3%	7,4%	29,6%	0,30
Acids	0,9%	10,0%	1046,7%	10,47
Phenolic Fraction	15,7%	55,8%	355,9%	3,56
Aldehydes	1,4%	0,4%	26,9%	0,27
Ketones	16,1%	11,5%	71,5%	0,72
Ethers	0,6%	0,2%	38,4%	0,38
Esters	0,3%	7,1%	2366,9%	23,67
Hydrocarbons	0,5%	3,9%	799,9%	8,00
Unclassified	19,5%	3,6%	18,5%	0,18

Table 10: Pyrolysis oil from company #2 treated with SO_2 extraction method.
Font: Author.

6.4.3. Results of the two initial experiments

Looking into detail the table presented below (**Table 11**), it is possible to appreciate significant similarities between the two methods. Both not only increased the amount of pyrolytic lignin present in the sample, but also increased the amount of acids, ethers and esters and decreased the yield of alcohols, aldehydes, ketones and the percentage of chemicals grouped as “unclassified”.

	Concentration factor of test #1	Concentration factor of test #2
Alcohols	0,05	0,3
Acids	2,68	10,47
Phenolic fraction	8,11	3,56
Aldehydes	0	0,27
Ketones	0,05	0,72
Ethers	2,55	0,38
Esters	1,34	23,67
Hydrocarbons	0	8
Unclassified	0,07	0,18

Table 11: Comparison of the concentration factors of both methods.
Font: Author

Both methods proved to have a high efficiency when it comes to remove oxygenated compounds from pyrolysis oil, especially the solvent extraction using methanol, which decreased the yield of alcohols, aldehydes and ketones to almost zero. Eventhought both methods increased the percentage of organic acids, ethers and esters, this increment is significantly higher when using the extraction with sulfur dioxide. It is also noticeable that the decrease of the percentage of alcohols and ketones is significantly lower using this method, and the increase of the yield of the phenolic fraction is lower as well.

These factors are a proof of the feasibility of both methods, but the results obtained when comparing both separations may indicate that the working conditions used during the second experiment are probably not the best ones to obtain a good efficiency. In an attempt to obtain better results using the sulfur reaction method, another experiment was carried on, in which the bio-oil mixed with water and sulfur dioxide will be heated to 100ºC (in order to reverse the reaction of formation of acid) after the separation and not before.

6.4.4. Improvement of sulfur extraction

A third pyrolysis test was done, following the same procedure but using a feedstock from a different company (#3). Like in the previous test, the amount of paper sludge introduced in the injector is of 1000g in order to yield about 200mL of oil. With bigger amounts of oil, the error committed during the experiment is smaller, since the percentage of bio-oil which is lost due to fouling when moving the liquid from one flask to another is smaller.

Phase	Weigh [g]	Percentage	Phase	Percentage
Sample mass	1058,8	-	Regarding the organic	-
First liquid fraction	210,4	19,9%	Liquid	54,8%
Second liquid fraction	49,7	4,7%	Char	16,9%
Solids remaining in the reactor	664,2	62,7%	Gas	28,3%
Gas	134,5	12,7%	Inorganic	55,1%

Table 12: Mass balance of the pyrolysis test from company #3.
Font: Author

From the 260,1g produced (**Table 12**), 210,1g where decanted into a Kitasato flask and mixed with 140g of water were added and where the sulfur dioxide was later introduced while stirring.

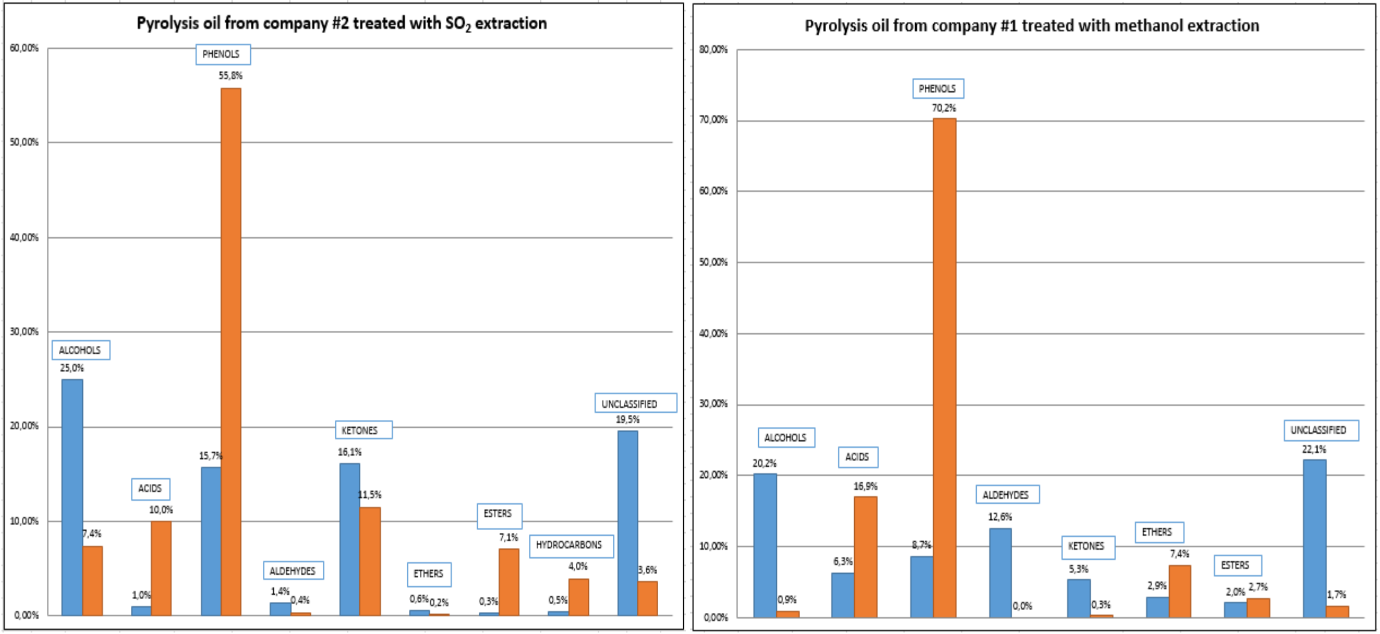


Figure 11: Chemical composition of bio-oil from companies #1 & #2 before (blue) and after (orange) treatment with two different methods to recover a fraction rich in pyrolytic lignin.

Font: Author.

For producing this sulfur dioxide 14,5g of sulfur where introduced in the second Kitasato where a “roasting” reaction took place, generating 29g of sulfur dioxide.

Like in the previous experiments, the amount of lignin left unreacted in the condensation system due to moving the oil fraction from one container to another would make a mass balance of this experiment not representative of the efficiency of the method.

In this experiment a GC:MS of the aqueous fraction was also done in order to obtain more information about the efficiency of the method and to know the chemical composition of the fraction of bio-oil which is not used to obtain pyrolytic lignin with the objective of finding another use for it. The results show that the amount of pyrolytic lignin in the organic fraction has increased from 6,5% in the initial bio-oil to 33,7%. The tables below (**Tables 13 & 14**) show a comparison between the two experiments done using the sulfur extraction method.

Functional group	Before	After	Percentage	Concentration factor
Alcohols	3,9%	9,0%	232,7%	2,33
Acids	0,1%	14,5%	8628,9%	86,29
Phenolic Fraction	6,5%	33,7%	516,4%	5,16
Aldehydes	2,1%	1,9%	94,1%	0,94
Ketones	14,5%	7,6%	52,6%	0,53
Ethers	4,0%	12,3%	309,4%	3,09
Esters	0,2%	0,2%	111,9%	1,12
Hydrocarbons	0,7%	19,1%	2790,4%	27,90
Unclassified	47,9%	1,3%	2,7%	0,03

Table 13: Pyrolysis oil from company #3 treated with SO_2 extraction method (organic fraction).
Font: Author

Functional group	Before	After	Percentage	Concentration factor
Alcohols	3,9%	7,5%	193,5%	1,94
Acids	0,2%	2,6%	1532,1%	15,32
Phenolic Fraction	6,5%	1,8%	27,7%	0,28
Aldehydes	2,1%	0,2%	11,6%	0,12
Ketones	14,5%	11,5%	79,4%	0,79
Ethers	4,0%	6,2%	154,7%	1,55
Esters	0,2%	0,0%	0,0%	0,00
Hydrocarbons	0,7%	1,1%	156,5%	1,57
Unclassified	47,9%	49,1%	102,4%	1,02

Table 14: Pyrolysis oil from company #3 treated with SO_2 extraction method (aqueous fraction).
Font: Author

6.4.5. Results of both sulfur extraction experiments

When comparing the results obtained after repeating the sulfur extraction method with the first experiment using the same technology, some changes can be appreciated (**Table 15**).

	Concentration factor of test #2	Concentration factor of test #3
Alcohols	0,3	2,33
Acids	10,47	86,29
Phenolic fraction	3,56	5,16
Aldehydes	0,27	0,94
Ketones	0,72	0,53
Ethers	0,38	3,09
Esters	23,67	1,12
Hydrocarbons	8	27,9
Unclassified	0,18	0,03

Table 15: Comparison of the concentration factor of both experiments using the sulfur extraction method.
Font: Author

It is clear that the amount of phenolic fraction present in the sample after the second experiment is bigger, but the amount of acids and hydrocarbons has drastically increased as well, so this new working conditions are far from being the optimal working conditions of the process. Focusing on the other functional groups, the percentage of aldehydes, ketones and unclassified components has followed a similar pattern in both experiments, but in the second experiment, the amount of ethers and alcohols (both oxygenated components) in the final product has increased. The amount of each functional group can be seen in detail when comparing the results obtained in both chromatographies (**Figure 12**). These results show that, even though the recovered product after the second experiment is richer in phenolic fraction than the product obtained with the first experience, the quality of the treated oil is worst in the second case, since it contains bigger amounts of oxygenated compounds and acids, which will hinder its utilization as substitute of phenol. One positive aspect of the second method is that, unlike in the first experiment, no presence of sulfur containing components where found in the final product nor the aqueous phase.

Both experiments done with the sulfur extraction method serve as an initial approach to studying and optimizing the method, but the results of the experiences indicate that further investigation needs to be done.

Since one of the advantages of this method is the possibility of recovering the aqueous fraction without any contaminants introduced during the separation process an analysis of this phase was also done. As shown in the graph below (**Figure 13**), pyrolytic oil of paper sludge from company #3 has an important amount of unclassified compounds. In detail results of this chromatography can be found in Appendix-1, but this “unclassified” group is mostly composed of anhydrosugars (specially D-Allose).

This result opens a new route of investigation, since, as mentioned in previous sections of this project, anhydrosugars present in bio-oil can be hydrolyzed into glucose, from which the obtainment of bio-oil is possible. Given the scenario that more pyrolytic oil from paper sludge from different feedstocks is found to contain similar amounts of anhydrosugars, further research of this method (or other technologies for obtaining chemicals from anhydrosugars present in bio-oil) should be considered.

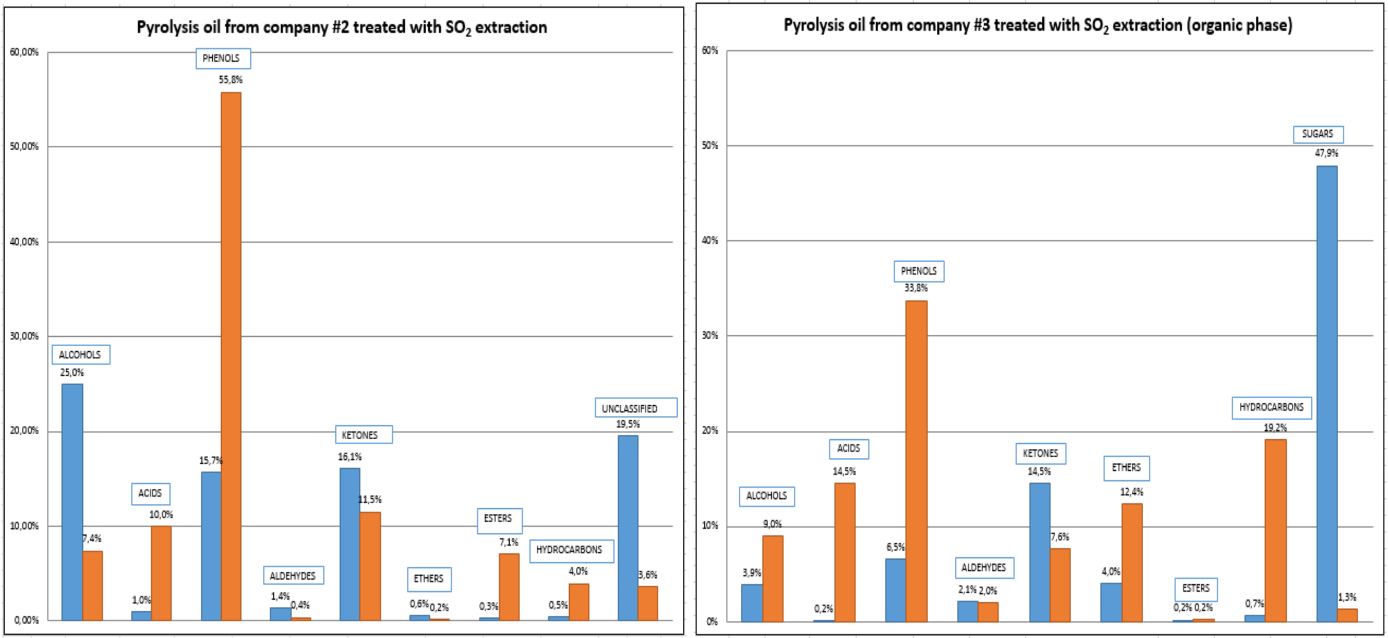


Figure 12: Chemical composition of bio-oil from companies #2 & #3 before (blue) and after (orange) treatment with the SO_2 extraction method to recover a fraction rich in pyrolytic lignin.

Font: Author.

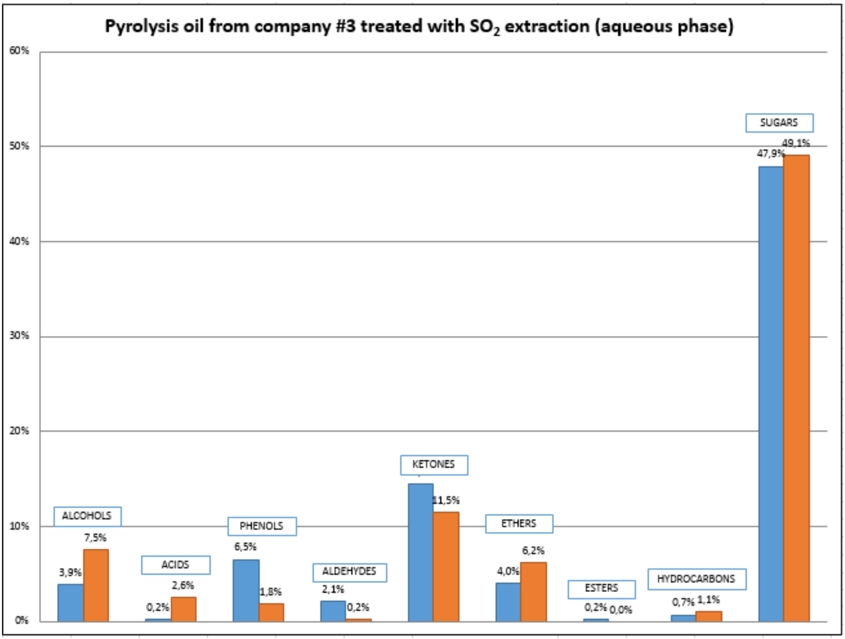


Figure 13: Chemical composition of the aqueous phase of bio-oil from company #3 after treatment with the SO_2 extraction method to recover a fraction rich in pyrolytic lignin.

Font: Author.

6.4.6. Solvent extraction using a centrifuge

As mentioned before, for deciding which of the two processes for separating bio-oil in two phases is better, a mass balance is needed in addition to the efficiency of each technology in recovering the phenolic fraction. Since the methodology that needs to be followed and the working conditions which optimize the sulfur extraction process are still unclear and need to be further investigated, an attempt of doing a proper mass balance of the solvent extraction with methanol and water will be done.

With the help of a centrifuge, it is possible to replicate the agitation and decantation steps that need to be done during the two step L-L extraction significantly faster than decanting by gravity. A series of experiments where designed in which the centrifuge was configured to work at a speed of 3000 rpm for a period of two minutes. This speed and time residence are believed (based on previous experiments done at Alucha Recycling Solutions) to be enough to ensure a proper separation of the two phases formed after mixing the bio-oil with water.

For these experiments, a series of centrifuge tubes will be filled with a certain amount of bio-oil (10 or 20 mL) and with water until the total amount of liquid in the tube is of 40 mL (**Table 16**). After stirring all the mixtures manually for a few seconds, all the samples were introduced in the centrifuge in batches of four. After this initial centrifugation the aqueous phase of each sample will be decanted and collected in a different tube. The organic phase remaining will be treated with methanol and water, according to the ratio selected to see how the amount of solvent affects to the organic fraction yielded. Following the same procedure, the tubes are centrifuged and the aqueous phase decanted. Each tube will be weighed at each step to do a mass balance, and the aqueous and the organic phase will be collected and send to analyze.

	Bio-oil [mL]	Water [mL]	First extraction	Ratio of MeOH and water	Second extraction
1A	10	30	Amount of lignin recovered after the first extraction	1:2	Amount of lignin recovered after the second extraction
1B	10	30		1:2	
1C	10	30		1:0	
1D	10	30		1:0	
2A	20	20		1:1	
2B	20	20		1:1	
2C	20	20		2:1	
2D	20	20		2:1	

Table 16: Experimental procedure of the centrifuge experiments.
Font: Author

Another pyrolysis test was done (**Table 17**) using paper sludge from company #3 (the remaining from the previous experiment) in order to obtain enough bio-oil to do the experiments.

Phase	Weigh [g]	Percentage	Phase	Percentage
Sample mass	1058,8	-	Regarding the organic	-
First liquid fraction	210,4	19,9%	Liquid	54,8%
Second liquid fraction	49,6	4,7%	Char	16,9%
Solids remaining in the reactor	664,2	62,7%	Gas	28,3%
Gas	134,5	12,7%	Inorganic	55,1%

Table 17: Mass balance from the second pyrolysis test with sample #3.
Font: Author

A total of 157,8g of oil were produced and 110,2g where decanted into different centrifuge tubes (**Figure 14**) in different quantitates (10 or 20mL).

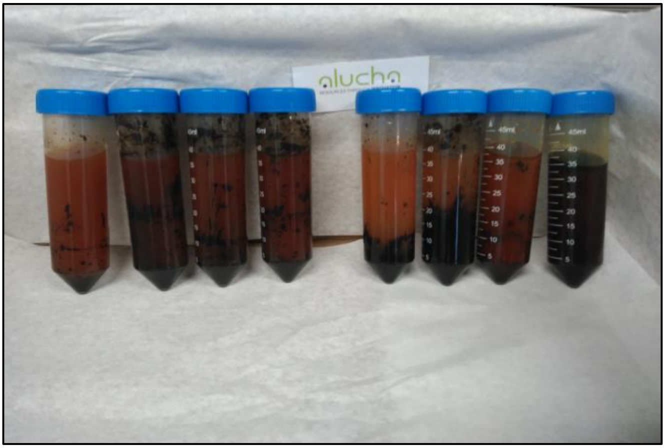


Figure 14: Detail of the eight samples of oil mixed with water before the first extraction.

Font: Author

After the first centrifugation, the organic phase of the pyrolysis oil was at the bottom of the tube as a compacted solid paste with a high content of water (**Figure 15**), and the aqueous phase was at the top of the tube. The next step was to remove this aqueous fraction by decantation and left the solid pyrolytic lignin in the bottom of the tube.

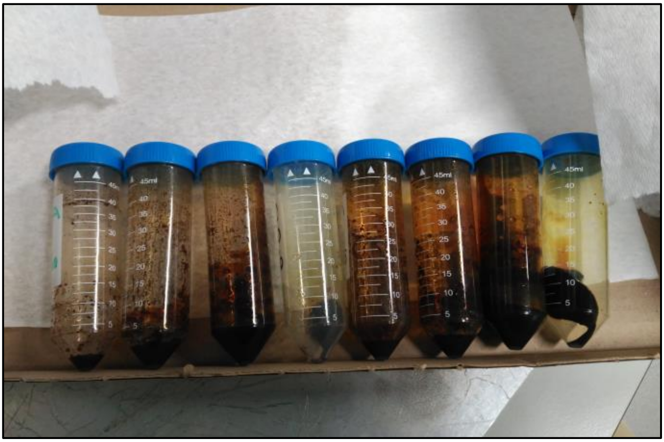


Figure 15: Detail of the eight samples of oil mixed with water after the first extraction.

Font: Author

The second extraction was done with a ratio of oil using different ratios of methanol and water to test the effect that these have on the efficiency of the method. The first experiment, were the whole pyrolysis oil was treated with this method, was done using the same amount of water, methanol and bio-oil, as stated in the literature. After weighing the amount of pyrolytic lignin present in each tube, solutions with different ratios were prepared, measuring the amount of solvent and water that needed to be added to each tube to fit the specifications.

These samples were treated following the same procedure as in the first extraction and the centrifuge specifications were also the same ones (3000rpm during 2 minutes). As in the previous experience, the aqueous phase was decanted, leaving the solid lignin in the bottom of the tube. A sample from the two decanted water phases (mixed proportionally) and a sample of the pyrolytic lignin were collected and sent to analyze.

The table below shows the amount of each component used during the different stages of these experiments and the final amount of lignin recovered, comparing it with the initial bio-oil introduced in the tube. From these results it is possible to do a mass balance of each experience and know the efficiency of each of the different ratios used to treat the pyrolytic oil.

In order to understand better the tendency of the results shown above two determinant factors need to be explained:

1. The pyrolysis oil obtained after the pyrolysis test is always very aqueous and, eventhought two phases are not always appreciated, the bottom fraction of the oil is always richer in pyrolytic lignin than the top fraction, which is more aqueous. It is because of this factor that the efficiency of the extractions is worst in the first samples (1A and 2A), slightly better in the second ones (1B and 2C) and significantly better in the last ones (1C and 2C).
2. The yield of pyrolysis oil obtained after the second pyrolysis test done with paper sludge from company #3 turned out to be insufficient to do all the centrifuge experiments planned. As a solution, bio-oil from another source, which had been stored for several months, was used to perform the two last experiments (1D and 2D). This aged bio-oil breaks the upward trend of the efficiency results and seems to have an amount of pyrolytic lignin similar to samples 1B and 2B respectively.

Once these two points have been clarified, the results can be discussed in detail.

	FIRST EXTRACTION (with water)					Efficiency of the first extraction	Ratio MeOH: water	SECOND EXTRACTION (with water and methanol)						Efficiency of the second extraction	Percentage of pyrolytic lignin left from the first extraction
	BEFORE			AFTER				BEFORE				AFTER			
	Oil	Water	TOTAL	Water	Lignin			Lignin	MeOH	Water	TOTAL	Water	Lignin		
1A	10,11	29,86	39,97	39,06	0,66	7%	1:02	0,66	0,78	1,29	2,73	2,34	0,39	4%	59%
1B	11,16	29,04	40,2	38,84	1,31	12%	1:02	1,31	1,34	2,7	5,35	4,11	1,24	11%	95%
1C	11,06	29,11	40,17	36	4,07	37%	1:00	4,07	4,15	0	8,22	4,63	3,59	32%	88%
1D	10,19	29,95	40,14	38,64	1,45	14%	1:00	1,45	1,55	0	3	2,31	0,69	7%	48%
2A	20,56	19,55	40,11	39,09	1,07	5%	1:01	1,07	0,98	0,98	3,03	2,12	0,91	4%	85%
2B	19,99	20,2	40,19	38,61	1,63	8%	1:01	1,63	1,49	1,49	4,61	3,18	1,43	7%	88%
2C	20,48	19,76	40,24	33,76	6,49	32%	2:01	6,49	13,12	6,5	26,11	20,79	5,32	26%	82%
2D	20,41	19,5	39,91	37,4	2,48	12%	2:01	2,48	4,98	2,81	10,27	8,23	2,04	10%	82%

Table 18: Mass balance and efficiency of the extractions of pyrolysis oil from company #3 done with methanol and water using a centrifuge

Font: Author

The results shown above (**Table** 18) are not as representative as it would be desired, but prove that the experiments done with the centrifuge are a good starting point for understanding the process of solvent extraction and how the ratios of solvent affect the final yield of pyrolytic lignin.

Regarding to the first extraction. When comparing tubes with different oil to water ratios (1A with 2A, 1B with 2B, etc.) it is clear that, as expected, when increasing the amount of water, the efficiency of the extraction is bigger since the separation of bio-oil in two phases will be better. Although increasing the amount of water used in the first extraction might seem only beneficial, this increment has operation costs implied (like the cost of evaporating this water for removing it from the final product), and so an optimal ratio should be obtained.

When looking into the results from the second extraction, regarding the difference of solids, it is noticeable that the amount of final product has decreased when comparing it with the solid yielded after the first extraction, but its amount of phenolic fraction will be higher, since the separation of oil in two phases has been done. Increasing the amount of water used during this second extraction does not seem to further separate the two phases, but the ratio of methanol, specially when mixed with water, makes the L-L extraction more efficient. From this initial approach it is possible to conclude that a ratio of methanol to oil of 1:1 is sufficient to conduct an efficient separation and a ratio of 2:1 (which would increase the economic cost of the process) is not needed.

Next step would be to perform GC:MS analysis of the organic and aqueous phase from samples 1C and 2C (the ones richer in lignin), to be able to compare which of the ratios used recovered more phenolic fraction.

7. CONCLUSIONS

- An initial approach to the investigation of two methods (solvent extraction using methanol and water and phase separation injecting sulfur dioxide) to recover the phenolic fraction present in pyrolysis oil was done. Both methods reported promising results, being able to obtain a final product rich in phenolic fraction. This phenolic fraction, as stated in the literature of the project, can be used as a substitute for traditional phenols in the synthesis of phenol-formaldehyde resins.
- Two step liquid-liquid extraction, using water in the first step and a mixture of water and methanol in the second step, reported promising results for obtaining a final product rich in phenolic fraction (from the initial 8,6% to 70,2%). An initial mass balance of the process was done using a centrifuge but further experiments need to be done.
- The sulfur dioxide extraction method succeeded into obtaining a final product richer in phenolic fraction than the initial bio-oil (from the initial 15,7% to 55,8%), which is a lower recovery ratio than in the first method, but it cannot be labeled as unsuccessful until a comparison of the mass balances of both methods is done.
- After repeating the sulfur extraction method in order to improve its efficiency, the amount of phenolic fraction recovered increased (from the initial 6,5% to 33,7%) with the new operation conditions, but these conditions are far from the optimal since the percentage of acid and oxygenated compounds increased as well.
- Results of the gas chromatography analysis of the aqueous fraction of bio-oil from paper sludge from company #3 showed an important amount (around 50%) of anhydrosugars present in the sample. This high yield should encourage the investigation of possible methods to use this phase as feedstock for chemicals (like bio-ethanol obtainment through hydrolysis of anhydrosugars).

- The experiments done with the centrifuge are a good starting point for understanding the process of solvent extraction and how the ratios of solvent affect the final yield of pyrolytic lignin.
- A feasibility study of each method for its industrial application could not be done since both processes need to be further investigated in order to fully define the obtained products and the mass balance of each method.

8. NEXT STEPS AND RECOMMENDATIONS

- Realization of more experiments using both separation methods in order to define an accurate mass balance of each process.
- Would be advisable to do more analysis of the obtained pyrolysis oil once the bio-oil starts being produced at the pilot plant instead than at the laboratory scale reactor.
- Improvement of the operation conditions and ratios used in the sulfur extraction technology.
- Further investigation of how the ratio of methanol and water used during the solvent extraction method affect the final yield pyrolytic lignin and the amount of phenolic fraction present in it.
- Doing an approximate mass balance of the complete process in order to know the amount of pyrolysis lignin and aqueous fraction that could be obtained regarding a ton of paper sludge.
- Perform an initial study of the economic feasibility of each process, taking into consideration how the amount of components used at each step affect the cost of the process.
- Start a market study targeting companies that use phenol-formaldehyde resins as reactant or as product for offering them an alternative and greener phenol source.

9. REFERENCES AND NOTES

1. Anders Kallenberg. Liquid bio fuels for gas turbines. Master thesis at Lund University, 2013.
2. Athanasiadou, E. &Papadopoulou, H. “Non-food Crops-to-Industry schemes in EU27” WP1. Non-food crops, 2011, CHIMAR Hellas SA.
3. Balat, M. et al. Main routes for the thermo-conversion of biomass into fuels. Part 1: pyrolysis systems, 2009
4. Bennett, N. M. et al. Extraction and hydrolysis of levoglucosan from pyrolysis oil. *Bioresource technology,* (2009) 100: 6059-6063.
5. Chum, H. L et al. (1993). Phenolic compounds containing neutral fractions extract and product derived therefrom from fractionated fast pyrolysis oil, U.S. Patent 5.223.601.
6. Chum, H. L., and Kreibich R. E. (1992). Process for preparing phenol-formaldehyde resin products derived from fractionated fast-pyrolysis oil, U.S. Patent 5.091.499.
7. Czernik, S., Bridgewater, A.V. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels (2004)* 18 (2): 590–598.
8. Elkasabi et al. Characterization of fast-pyrolysis bio-oil distillation residues and their potential Applications. *Journal of analytical and applied pyrolysis* (2015) 114: 179-186
9. Garcia-Perez, M; Chaala, A.; Pakdel, H.; Kretschmer, D.; Roy, C., Characterization of bio-oils in chemical families. Biomass and Bioenergy 2007, 31 (4), 222-242.
10. Jens F. Peters; Diego Iribarren; Javier Dufour. Life cycle assessment of pyrolysis oil applications. *Biomass Conv. Bioref,* (2015) 5:1-19.
11. Joseph Anthony Kocal. *Acetic acid production from biomass pyrolysis.* US Patent 8.716.522 B2 (2014).
12. Kim, J. S. Production, separation and applications of phenolic-rich bio-oil. *Bioresource Technology (2015)* 178: 90-98.
13. Lian, J. et al. Separation, hydrolysis and fermentation of pyrolytic sugars to produce ethanol and lipids. *Bioresource Technology* (2010) 101: 9688-9699.
14. Luque, L. et al. Pyrolysis based bio-refinery for the production of bioethanol from demineralized lingo-cellulosic biomass. *Bioresource Technology (2014) 161: 20-28.*
15. Oasmaa, A.; Czernik, S. Fuel oil quality of biomass pyrolysis oils – state of the art for the end users. Energy & fuels 1999, 13, 914-921.
16. Prabir Basu, Biomss gasification and pyrolysis. Practical Design and theory (2010) ISBN: 978-0-12-374988-8.
17. Prakash, R.; Singh, R. K.; Murugan, S. Use of biodiesel and bio-oil emulsions as an alternative fuel for direct injection diesel engine. *Waste Biomass Valor*, (2013) 4:475-484.

18. Ramirez Corredores et al. *Renewable heating oil*. US Patent 8.628.589 B2 (2014).
19. Sanna, A. et al. Hydrodeoxygenation of the aqueous fraction of bio-oil with Ru/C and Pt/C catalysts. *Applied Catalysis B,* (2015) Enviromental 165: 446-456.
20. Sukhbaatar, B. et al. Removal of acids from bio-oil. *BioResources,* (2009) 4: 1319-1329.
21. Sukhbaatar, B. et al. Use of lignin separated from bio-oil in oriented strand board binder phenol-formaldehyde resins. *BioResources,* (2009) 4(2): 789-804.
22. Vecino Mantilla, S. et al. Methodology for the extraction of phenolic compounds of bio-oil from agricultural wastes. *Waste Biomass Valor (2015)* 6:371-383.
23. Wang, P. C., Weider, P. R., and Blackbourn, R. L. (2014). Method of separating lignin derived compounds from pyrolysis oil, U.S. Patent 2014/0259888 A1
24. Wang, S., Gu, Y., Liu, Q., Yao, Y., Guo, Z., Luo, Z., Cen, K., 2009. Separation of bio-oil bymolecular distillation. *Fuel Process. Technol. (2009)* 90 (5): 738–745.
25. Ye, T. et al. High efficiency production of hydrogen. *Catal Lett* (2009) 127: 323-333.
26. Zeng, F., Liu, W., Jiang, H., Yu, H.-Q., Zeng, R.J., Guo, Q. Separation of phthalate esters from bio-oil derived from rice husk by a basification-acidification process and column chromatography. *Bioresource Technology (2011)* 102 (2): 1982–1987.

10. ACRONYMS

1. Gasification: Biomass gasification is the conjunction of thermochemical reactions that are produced in an atmosphere low in oxygen and which results in the transformation of the solid biomass in a series of combustible gases that can be used in a combustion engine, a turbine or a motor, after being properly upgraded.
2. Secondary cracking reactions may be present if the product gasses are not rapidly cooled, making a thermochemical process where the main products are char, carbon monoxide or methane.
3. Pyrolysis of lignin yields a range of products, being methoxy-substituted phenols the most characteristic ones but also including simple phenols and oligomeric polyphenols
4. Selective fast pyrolysis, differed from conventional fast pyrolysis which is usually aimed at the maximum bio-oil yield, is to drive the pyrolysis of biomass towards the products of interest, mostly by catalyst utilization, to maximize the yield of target product and obtain target products with high purity.
5. Gas chromatography is a chemical analysis which separates and identifies chemicals from a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas steam (carrier gas) at different rates depending on the various chemical and physical properties and their interaction with a specific column filing, called stationary phase. As chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at different time (retention time).

APPENDICES

APPENDIX 1: CHROMATOGRAPHY RESULTS AND FUNCTIONAL GROUP CLASSIFICATION

Comapany #1	**Test 1**				**Test 2**					
	Apex RT	**Area**	**%Area**			**Apex RT**	**Area**	**%Area**		
Ethanol	4,53	148464345	0,13			4,54	260546867	0,28		
Allyl alcohol	6,07	262139799	0,22			6,07	578112116	0,61		
1-butanol	8,41	1994496282	1,7			8,41	4071300113	4,33		
Furfuryl alcohol	13,63	5229415227	4,46	5,208		13,62	4087922919	4,35	7,656	6,432
Formic acid	6,72	1240018032	1,06			6,69	1299629751	1,38		
Acetic acid	7,72	3,2469E+10	27,66			7,66	1,9678E+10	20,93		
Propionic acid	9,86	3579125482	3,05			9,82	2727830089	2,9		
butyric acid	11,91	988908666	0,84			11,88	497579414	0,53		
2-methyl butyric acid	13,38	380187371	0,32			13,37	247823592	0,26		
2-pentenoic acid	14,12	223614994	0,19			14,11	174622990	0,19		
2-pentenoic acid?	15,3	1416670717	1,21			15,28	1375783221	1,46		
trans-2-methyl-2-pentenoic acid	16,98	711018978	0,61	27,952		16,97	571752181	0,61	22,608	25,28
pyrazine	9,96	477511829	0,41			9,96	568039848	0,6		
pyridine	10,43	1024947931	0,87			10,41	280672637	0,3		
methyl pyrazine?	12,17	865715712	0,74			12,15	969513839	1,03		
Furfural	13,06	4583857166	3,91			13,06	6696346693	7,12		
2-ethylfurane	13,88	102949606	0,09			13,88	238423821	0,25		
4,6-dimethylpyrimidine	14,2	199805902	0,17			14,2	550742208	0,59		
Ethylpyrazine	14,31	336496156	0,29			14,29	308763991	0,33		
2,3-dimethylpyrazine	14,35	127950818	0,11			14,35	90846388,2	0,1		
phenol	17,41	1155063505	0,98			17,41	667729343	0,71		
2-methylphenol (o-cresol)	18,7	677630649	0,58			18,7	379598058	0,4		
2-methoxyphenol	18,93	2297691678	1,96			18,93	1320299651	1,4		
3-methylpenol (m-cresol)	19,26	717269637	0,61			19,26	409346107	0,44		
2,5-xylenol	19,55	225690494	0,19			19,54	135858462	0,14		
2,4-xylenol	20,47	320984642	0,27			20,47	178472571	0,19		
2-methoxy-p-cresol	21	1228122594	1,05			21	672565361	0,72		
p-Ethylguaiacol	22,64	400496671	0,34			22,65	190537093	0,2		
3-Allyl-6-methoxyphenol	24,31	55332453	0,05	10,096		24,31	36730583,5	0,04	11,648	10,872
Acetaldehyde	3,77	549320748	0,47			3,78	290308226	0,31		
Acrolein	4,89	4755108,04	0			4,88	26481739,1	0,03		
Propionaldehyde	4,93	84425682,9	0,07			4,93	30810913	0,03		
Isobutyraldehyde	5,96	68241625,9	0,06			5,96	7509780,83	0,01		
Crotonaldehyde	8,22	121211008	0,1			8,22	218064544	0,23		
o-methyloxime butanal ?	11,14	856267916	0,73			11,12	848553530	0,9		
3-furaldehyde	12,38	193808991	0,17			12,38	475896101	0,51		
5-methyl-2-furan-carboxaldehyde	16,21	1710217701	1,46	2,448		16,21	1654237499	1,76	3,024	2,736
Acetone	5,02	398149182	0,34			5,02	745340299	0,79		
2-butanone	6,81	179681594	0,15			6,83	328334021	0,35		
1-penten-3-one	8,8	70501945,2	0,06			8,8	28981335,3	0,03		
2-pentanone	8,83	24016853,6	0,02			8,85	39184253,8	0,04		
1-hydroxy-2-propanone	9,14	1,4254E+10	12,14			9,09	1,1265E+10	11,98		
3-hydroxy-2-butanone	10,11	1264292465	1,08			10,09	1081674404	1,15		
3-pentan-2-one	10,34	516715318	0,44			10,34	584876024	0,62		
1-hydroxy-3-butanone	11,54	2009907676	1,71			11,52	1577134803	1,68		
cyclopentanone	11,86	343839098	0,29			11,84	798209061	0,85		
1-hydroxy-2-butanone	13,5	61962300,8	0,05			13,49	73223546,6	0,08		
1-acetyloxy-2-propanone	13,79	3361653512	2,86			13,79	2329261322	2,48		
6,10-dimethyl-5,9-dodecandien-2-one	14,01	682770423	0,58			14,01	673734449	0,72		
Dihydro-2H-pyran-3(4H)one	14,21	162911406	0,14							
cyclohexanone	14,53	42560456,3	0,04			14,53	99581632,4	0,11		
2-methyl -cyclopentenone	14,7	1477882618	1,26			14,7	1770216196	1,88		
1-(2-furanyl-ethanone)	14,85	1361094228	1,16			14,85	1200925190	1,28		
2,5-hexanedione	15,54	382014456	0,33			15,54	211844756	0,23		
2-cyclohexen-1-one	15,65	268377474	0,23			15,65	301507629	0,32		
2,3-pentanedione	15,9	1595875127	1,36			15,9	1170910237	1,25		
1-acetyloxy-2-butanone	15,96	1259535262	1,07			15,95	897014891	0,95		
butyrolactone	16,09	685002702	0,58			16,09	433064073	0,46		
2(5H)furanone	16,16	625821679	0,53			16,15	373315322	0,4		
1-methyl-cyclopenten-3-one	16,62	1339390580	1,14			16,62	860042050	0,91		
3,4-dimethyl-2-cyclopenten-1-one	17,05	241032076	0,21			17,05	190875696	0,2		
3-methyl-1,2-cyclopentanedione	17,7	1907691984	1,63			17,7	1147313210	1,22		
2,3-dimethyl-2-cyclopenten-1-one	18,01	785824264	0,67			18,01	558126575	0,59		
2,3,4-trimethyl-2-cyclopenten-1-one	18,3	191622799	0,16			18,3	113500649	0,12		
Acetophenone	18,5	360345586	0,31			18,5	227927562	0,24		
3-ethyl-2-hydroxy-2-cyclopenten-1-one	19,64	135513119	0,12			19,64	123710759	0,13		
(4E)-6-Ethyl-7-hydroxy-4-octen-3-one	19,69	101497585	0,09			19,69	87290126,5	0,09		
1-Indanone	23,36	93802159,8	0,08	24,664		23,36	36976356,3	0,04	24,952	24,808
Methyl formiate	4,06	12885438,2	0,01	0,008		4,07	27695068,5	0,03	0,024	0,016
Acetic acid vinil ester	6,64	2030777439	1,73			6,64	2044598285	2,17		
Glycolic acid methyl ester	9,59	139972794	0,12			9,57	106372822	0,11		
Pyruvic acid methyl ester	12,05	117959871	0,1			12,06	170510858	0,18		
2-hydroxy-butyric acid methyl ester	12,56	84758668,6	0,07	1,616		12,56	95854044,7	0,1	2,048	1,832
3,3,4,4-tetramethylhexane	12,7	357491268	0,3	0,24		12,7	321969473	0,34	0,272	0,256
Propanenitrile	6,92	13324282,8	0,01			6,92	50372998,2	0,05		
Ethylene glycol monoacetate	11,28	913246668	0,78			11,26	1164487187	1,24		
N-(3-hydroxypropyl)guanidine	11,98	425752697	0,36			11,99	349241267	0,37		
isobutyric anhydride	12,76	750672749	0,64	1,432		12,76	637683389	0,68	1,872	1,652
?	7,21	87060571,9	0,07			7,18	125411651	0,13		
?	12,27	191253457	0,16			12,27	161434811	0,17		
?	12,81	367370288	0,31							
?	13,68	1119024434	0,95							
?	14,78	404222866	0,34			14,78	302753516	0,32		
?	15,04	187043359	0,16			15,03	289182010	0,31		
?	15,12	201606870	0,17			15,11	241736042	0,26		
?	15,73	231116289	0,2							
?	16,81	1950197687	1,66			16,81	1182224930	1,26		
?	18,13	222625972	0,19	3,368		18,13	157872825	0,17	2,096	2,732
			96,29					95,25		76,616

Company #2	**Test 3**				**Test 4**				
	Apex RT	**Area**	**%Area**			**Area**	**%Area**		
Ethanol	4,53	156768321	0,19			753938002	0,89		
allylic alcohol	6,07	674267600	0,82			3427494764	4,07		
1-butanol	8,41	929954718	1,14			6015570131	7,14		
2-buten-1-ol	8,54	12316373,7	0,02			131909412	0,16		
furfuryl alcohol	13,62	4000222244	4,89			2517847608	2,99		
2,5-dimethylcyclohexanol	14,78	163282888	0,2			188556505	0,22		
4-methyl-4-hepten-3-ol	15,54	212686476	0,26			239058119	0,28		
2-ethyl-1-hexanol	16,94	167442956	0,2	6,176		204607780	0,24	12,792	9,484
Formic acid	6,74	198254273	0,24						
Acetic acid	7,67	2,1402E+10	26,14			1,024E+10	12,15		
Propionic acid	9,85	4097928235	5			2393029271	2,84		
butyric acid	11,9	1004293853	1,23			286462078	0,34		
3-butenoic acid	12	644002724	0,79			398034304	0,47		
2-methyl hexanoic acid	13,36	190530247	0,23	26,904		103743099	0,12	12,736	19,82
2-methoxytetrahidrofuran	9,97	516858685	0,63			958558982	1,14		
pyridine	10,38					240515101	0,29		
toluene	10,42	312108415	0,38			208583730	0,25		
methyl pyrazine	12,15	550138386	0,67			314930276	0,37		
Ethylbenzene	12,82					588052116	0,7		
furfural	13,06	3650138759	4,46			4489012077	5,33		
styrene	13,71					1094843494	1,3		
cumene	14,2	228333417	0,28			319015423	0,38		
alfa-methylstyrene	15,74	64283986,5	0,08			507758461	0,6		
2-propyltetrahydrofuran	16,8	1740028399	2,13			1465086542	1,74		
Phenol	17,41	1501836252	1,83			1355173043	1,61		
Indene	17,62	117908447	0,14			219138600	0,26		
o-cresol	18,69	950011529	1,16			920923106	1,09		
o-methylphenol	18,93	500477288	0,61			352987084	0,42		
m-cresol	19,26	634639276	0,78			600307661	0,71		
2,6-xylenol	19,55	367305515	0,45			288826473	0,34		
2-methyl-1H-indene	19,8	63680480,3	0,08			154094937	0,18		
1,4-dihydronaphtalene	20,01	122899872	0,15			155045411	0,18		
o-ethylphenol	20,29	75725528,4	0,09			100563151	0,12		
3,4-xylenol	20,47	367326398	0,45			347259174	0,41		
Naphtalene	20,9	122062135	0,15			188992702	0,22		
2,5-xylenol	21,35	76502741,7	0,09			98715861,2	0,12		
6-ethyl-m-cresol	22,15	111063239	0,14			181222697	0,22		
biphenyl	24,72	140639902	0,17	12,152		343250318	0,41	15,304	13,728
Acetaldehyde	3,77	131384817	0,16			302073478	0,36		
Acrolein	4,88	41837848	0,05			168701767	0,2		
3-furaldehyde	12,38	202215045	0,25			555231368	0,66		
2-ethylbutanal	14	166616007	0,2			169049868	0,2		
5-methylfuraldehyde	16,21	1218810299	1,49	**1,72**		1121191164	1,33	**2,2**	1,96
acetone	5,02	159028399	0,19			1499999903	1,78		
2,3-butanedione	6,65	1215203660	1,48			3646498827	4,33		
2-butanone	6,82	40163841,7	0,05			566214547	0,67		
1-penten-3-one	8,8	67728881,9	0,08			197734472	0,23		
2-pentanone						101686351	0,12		
2,3-pentanedione	9,02	1729967328	2,11			356764308	0,42		
1-hydroxy-2-propanone	9,09	6995995480	8,54			5919729815	7,02		
3-hydroxy-2-butanone	10,09	1526587746	1,86			1049419805	1,25		
3-penten-2-one	10,34	500083169	0,61			1494725316	1,77		
1-hydroxy-2-butanone	11,52	2031714942	2,48			1028088748	1,22		
cyclopentanone	11,85	941688498	1,15			3749537100	4,45		
2-hexen-4-one	12,56	113192528	0,14			252667240	0,3		
2-methyl-cyclopentanone	12,99	249533494	0,3			472600185	0,56		
2-cyclopenten-1-one	13,18	3249600756	3,97			3182240991	3,78		
3-methyl-cyclopenten-1-one	13,25					75746787,5	0,09		
1-acetyl-oxy-2-propanone	13,79	2220838373	2,71			1287648329	1,53		
3-methyl-2-cyclopenten-1-one	13,87	179754828	0,22			440646480	0,52		
cyclohexanone	14,53	132466574	0,16			265227000	0,31		
2-methyl-cyclopentanone	14,7	1967931025	2,4			2436665590	2,89		
2-furyl-methylketone	14,85	966900687	1,18			1133046367	1,34		
n-propylbenzene	15,03	41484118,8	0,05			142062884	0,17		
3,4-dimethyl-2-cyclopenten-1-one	15,25	289535801	0,35			322828066	0,38		
cyclohexen-2-en-1-one	15,65	495479716	0,61			429145111	0,51		
2,3-pentanedione	15,89	624912237	0,76			411670475	0,49		
1-methyl-cyclopenten-3-one	16,61	879571136	1,07			735958919	0,87		
3,4-dimethyl-2-cyclopenten-1-one	17,05	276491053	0,34			261993429	0,31		
3-methyl-1,2-cyclopentanedione	17,7	722452133	0,88			682419950	0,81		
2,3-dimethyl-cyclopenten-1 one	18	742974263	0,91			637094897	0,76		
2,3,4-trimethyl-2-cyclopenten-1-one	18,29	141645281	0,17			150055655	0,18		
acetophenone	18,5	358857845	0,44			352990538	0,42		
2,3,4-trimethyl-2-cyclopenten-1-one	19,07	290966846	0,36	28,456		247252900	0,29	31,816	30,136
1,4-dioxane				0		139305308	0,17	0,136	0,068
glycolic acid methyl ester	9,57	148976711	0,18			89986397	0,11		
piruvic acid methyl ester?	10,19			**0,144**		143167893	0,17	**0,224**	0,184
1-phenyl-cyclopentene	22,63	68701627,8	0,08			139598546	0,17		
1-methylnaphtalene	23,08	41864485,1	0,05			145360488	0,17		
2-methylnaphtalene	23,49	112307793	0,14			306074184	0,36		
1,7-dimethylnaphtalene	25,96	30764320,6	0,04			69744147,4	0,08		
2,6-dimethylnaphtalene	26,08	15668594,1	0,02			36972393	0,04		
1,2-dimethylnaphtalene	26,57	19501762,5	0,02	0,064		76606536,9	0,09	0,136	0,1
acetic acid hydrazide	5,32	47589177	0,06			518546933	0,62		
Ethylene glycol monoacetate	11,26	341243541	0,42			298573950	0,35		
tertbutylhydroperoxide	12,27	257961783	0,32	0,64		199231491	0,24	0,968	0,804
?	8	122058828	0,15						
?	8,23	67671516,6	0,08			512634764	0,61		
?	10,79	310863411	0,38			293030571	0,35		
?	12,44	208269545	0,25			108316203	0,13		
?	14,17	193507560	0,24			160283873	0,19		
?	14,29	50006398,9	0,06			378056160	0,45		
?	15,11	83681551,2	0,1			78398481,6	0,09		
?	15,94	374816666	0,46			218132630	0,26		
?	16,08	523980815	0,64			570726212	0,68		
?	16,31	112190662	0,14			75154824	0,09		
?	16,89	96077522,2	0,12			114802690	0,14		
?	17,17	55355522,4	0,07			64705515,3	0,08		
?	18,13	128702088	0,16			101237326	0,12		
?	25,33	57126719,3	0,07	2,336		154687946	0,18	2,696	2,516
			98,24				98,76		

Company #3	**Test 5**				**Test 6**					
	Apex RT	**Area**	**%Area**			**Apex RT**	**Area**	**%Area**		
Ethanol	4,53	99260163,8	0,11			4,53	375854500	0,45		
Allylic alcohol	6,07	421143876	0,47			6,07	1360501269	1,64		
1-butanol	8,4	412799658	0,46			8,4	1514348866	1,82		
2-methyl-3-pentanol	12,27	225044070	0,25			12,26	246964963	0,3		
furfuryl alcohol	13,62	5826461710	6,51			13,62	4774644759	5,75		
4-methyl-4-hepten-3-ol	15,54	309034006	0,35			15,54	271078700	0,33		
(4E)-2-methyl-4-hexan-3-ol	16,8	870056583	0,97	7,296		16,8	812399587	0,98	9,016	8,156
Acetic acid	7,65	1,5866E+10	17,73			7,61	9875454562	11,89		
propionic acid	9,85	4308097826	4,81			9,82	3088564352	3,72		
butanoic acid	11,92	1097341820	1,23	19,016		11,9	927358076	1,12	13,384	16,2
2-methoxytetrahydrofuran	9,97	269522767	0,3			9,97	323543553	0,39		
Furfural	13,07	7968558171	8,91			13,07	7709059310	9,28		
Phenol	17,41	1072420981	1,2			17,41	805527985	0,97		
o-cresol	18,7	684539730	0,77			18,69	527110426	0,63		
2-methoxyphenol	18,93	579738807	0,65			18,93	386715734	0,47		
m-cresol	19,27	519673849	0,58			19,27	410498761	0,49		
o-ethylphenol	20,29	61947056,8	0,07			20,29	53177720,1	0,06		
2,4-xylenol	20,47	282503956	0,32			20,47	219428854	0,26		
oxypurinol	20,86					20,86	61827606	0,07		
2-methoxy-p-cresol	21	342881668	0,38			21	254497371	0,31		
3,4,5-trimethylphenol	22,15	86316739,7	0,1			22,15	66551458,8	0,08		
p-ethylguaiacol	22,64	100453848	0,11			22,63	73619571,1	0,09		
Biphenil	24,72	50508234,4	0,06	10,76		24,72	27365231	0,03	10,504	10,632
Acetaldehyde	3,78	194338763	0,22			3,78	468151997	0,56		
Crotonaldehyde	8,22	170312355	0,19			8,22	593211794	0,71		
3-furaldehyde	12,38	565735300	0,63			12,38	851977453	1,03		
5-methyl--2-furaldehyde	16,21	1912549876	2,14			16,21	1854545910	2,23		
5,5-dimethylhexanal	17,9	173656510	0,19	**2,696**		17,89	124774882	0,15	**3,744**	3,22
Acetone	5,02	513997226	0,57			5,01	2024912428	2,44		
2,3-butanedione	6,67	2373300163	2,65			6,64	3187873388	3,84		
2-butanone	6,82	235383655	0,26			6,82	926186098	1,11		
1-hydroxy-2-propanone	9,09	1,189E+10	13,29			9,08	8950736196	10,77		
3-hydroxy-2-butanone	10,09	1350711952	1,51			10,08	1205625994	1,45		
3-penten-2-one	10,34	472913373	0,53			10,34	977420210	1,18		
2-pentanone	11,12	987304287	1,1			11,12	932286185	1,12		
1-hydroxy-2-butanone	11,53	2570248063	2,87			11,51	1661597083	2		
cyclopentanone	11,84	1157748086	1,29			11,84	2467854159	2,97		
cyclopenten-1-one	13,18	3078061451	3,44			13,18	4071013790	4,9		
1-acetyloxy-2-propanone	13,79	2517748039	2,81			13,79	1998844425	2,41		
1-methyl-1-cyclopenten-3-one	13,88	249619326	0,28			13,88	232380092	0,28		
Dihydro-2H-pyran-3(4H)-one	14,29	203093470	0,23			14,29	319983006	0,39		
2-methyl-2-cyclopentenone	14,7	2286656016	2,56			14,7	2721113719	3,27		
2-furylmethylketone	14,85	1322295045	1,48			14,85	1563290032	1,88		
3,4-dimethyl-2-cyclopenten-1-one	15,25	431967133	0,48			15,25	422107823	0,51		
2-cyclohexen-1-one	15,65	358673048	0,4			15,65	333363504	0,4		
2,3-pentanedione	15,9	1104832481	1,23			15,89	1114322398	1,34		
1-acetyloxy-2-butanone	15,95	780959051	0,87			15,95	711305577	0,86		
1-methyl-1-cyclopenten-3-one	16,61	944664503	1,06			16,61	885858288	1,07		
2,3-dimethyl-2-cyclopenten-1-one	16,77	244505986	0,27			16,77	274163767	0,33		
3-cyclohexen-1-one-3 methyl	16,89	140929661	0,16			16,89	127410448	0,15		
4,4-Dimethyl-2-cyclopenten-1-one	17,05	258106873	0,29			17,05	299632812	0,36		
3-methyl-1,2-cyclopentanedione	17,7	1103969232	1,23			17,7	821321560	0,99		
2,3-dimethyl-2-cyclopenten-1-one	18,01	834596650	0,93			18	790914170	0,95		
2,3,4-trimethyl-2-cyclopenten-1-one	18,29	188946045	0,21			18,29	150669755	0,18		
3-ethyl-2-hydroxy-2-cyclopenten-1-one	19	200437018	0,22			19	212882535	0,26		
2,3,4-trimethyl-2-cyclopenten-1-one	19,07	296521326	0,33			19,07	263474577	0,32		
3-ethyl-2-hydroxy-2-cyclopenten-1-one	19,64	116292857	0,13			19,64	65702147	0,08		
4-ethyl-2-hydroxy-2-cyclopenten-1-one	19,69	145621097	0,16			19,69	141391006	0,17		
2,3,4-trimethyl-2-cyclopenten-1-one	20,01	87907831,6	0,1			20,01	79014632,5	0,1		
1-Indanone	23,36	55427963,6	0,06	34,4		23,36	59532651,8	0,07	38,52	36,46
glycolic acid methyl ester	9,57	103361697	0,12			9,56	82101972,8	0,1		
L-Alanine-N-2-furoyl-propyl ester?	18,43	114185002	0,13	**0,2**		18,43	115803493	0,14	**0,192**	0,196
Acetylhydrazide	5,32	70985105,6	0,08			5,31	182242421	0,22		
Ethyleneglycol monoacetate	11,26	1221430911	1,37			11,26	633795997	0,76		
(z)-11-tetradecen-1-ol acetate	21,25	21231635,2	0,02	1,176		21,24	50278939,7	0,06	0,832	1,004
?	10,47					10,47	45881826,3	0,06		
?	11,99	351056557	0,39			11,99	327198746	0,39		
?	12,17	916948188	1,02			12,17	554604687	0,67		
?	12,56	166763413	0,19			12,56	174308323	0,21		
?	12,7	204735920	0,23			12,7	241510548	0,29		
?	12,76	601954812	0,67			12,76	490394991	0,59		
?	14	660959624	0,74			14	466440059	0,56		
?	14,53	210607090	0,24			14,53	287169985	0,35		
?	15,73	205944405	0,23			15,73	176207197	0,21		
?	16,08	497264234	0,56			16,08	302688577	0,36		
?	16,98	174758792	0,2			16,97	133319415	0,16		
?	17,62	128168549	0,14			17,62	87224213,8	0,1		
?	18,13	260108199	0,29			18,13	217004570	0,26		
?	18,23	66435810,9	0,07			18,23	36237791,9	0,04		
?	18,5	210058455	0,23			18,5	172052482	0,21		
?	18,87	40469918,2	0,05			18,87	34861149,1	0,04		
?	19,54	276690529	0,31	4,448		19,54	226203593	0,27	3,816	4,132
			99,99					100,01		

Alucha project I (12/11/2015)

oil from paper sludge from company #1 **before treatment**

Peak	R.Time	Area	Percentage	Component		
9	8,166	1778907	1,551%	2-octen-1-ol		
11	8,457	166700	0,145%	4-methyl-cis-cyclohexanol		
18	9,265	5371462	4,684%	1,10-decanendiol		
21	9,992	933272	0,814%	cis-1,2-cyclododecanendiol		
22	10,171	156073	0,136%	2,2-dimethyl-1-pentanol		
27	10,789	1489227	1,299%	cyclodecanol		
29	11,134	210202	0,183%	5-methyl-pyrimidine-4,6-diol		water content of 20%
31	11,394	1275688	1,112%	2,6-dimethyl-7-octen-3-ol		
41	13,793	14551512	12,690%	1,2-benzendiol		
53	17,121	2951278	2,574%	7-hexadeyn-1-ol	25,189%	20,15%
3	6,182	3315	0,003%	octanoic acid		
4	6,224	4002	0,003%	7-oxo-octanoic acid		
5	6,384	225518	0,197%	2-noneonic acid		
6	6,503	11208	0,010%	2-methylcyclopropanecarboxylic acid		
16	8,91	184486	0,161%	1,2-Dimethylcyclopropanecarboxylic acid		
39	13,172	1328597	1,159%	3-heptenoic acid		
54	17,418	853096	0,744%	cyclohexanepropanoic acid		
56	17,963	6448231	5,623%	3-ethyl-2-butenoic acid	7,900%	6,32%
12	8,549	109395	0,095%	decahydropyrazine		
17	9,007	55222	0,048%	2,4-dimethil furan		
19	9,648	3620687	3,157%	3-methyl-phenol		
23	10,317	151346	0,132%	3-methyl-phenol		
45	14,493	768127	0,670%	octahydro-44,5-dimethyl-2(1H)-Naphtalenone		
49	15,382	246507	0,215%	hexahydro-3-methylene-2(3H)-benzofuranone		
51	15,89	189920	0,166%	2-piperidinemethanol		
52	15,999	7267576	6,338%	3,5-dimethyl-2-furylmethylketone	10,821%	8,66%
13	8,59	9727	0,008%	O-methyloximedecanal		
26	10,681	1112990	0,971%	8-octandecanal		
30	11,21	291573	0,254%	3-methyl-dimethylhydrazone-2-butenal		
57	18,526	189507	0,165%	(z)-9-octadecenal		
58	19,647	1371465	1,196%	(E)-2-tridecenal		
59	20,35	15019465	13,098%	14-methyl-(z)-8-hexadecenal	15,693%	12,55%
1	4,633	7683	0,007%	2-cyclopenten-1-one		
14	8,716	805778	0,703%	3-ethenyl-3-methylcyclopentanone		
20	9,861	549750	0,479%	1-(1H-pyrrol-2-yl)-Ethanone		
33	11,755	1872967	1,633%	tetrahydro-4-(2-methyl-1-propen-3-yl)-2H-pyran-2-one		
34	11,825	119313	0,104%	2,6-dimethyl-1-(methyl-1-piperazinyl-4(1H)-pyridinone		
37	12,73	469914	0,410%	2-ethyl--cycloexanone		
42	13,97	592683	0,517%	Hydroquinone		
44	14,123	859882	0,750%	Dihydro-3-methyl-2,4(1H-3H)-pyrimidendione		
46	14,858	365320	0,319%	Benzencyclohectanone		
47	14,93	337800	0,295%	decahydro-3-2H-cyclopentacyclocteno-2-one		
48	15,168	280876	0,245%	1,3-benzodioxin-4-one		
61	26,612	1285541	1,121%	2-hydroxy-3,5,5-trimethyl-cyclohexe-2-one	6,582%	5,27%
10	8,231	12155	0,011%	octamethyl-cyclotetrasyloxane		
32	11,573	1386131	1,209%	2-(1-methylpropyl)-bicyclo(2,2,1)heptane		
36	12,353	1649912	1,439%	dodecyl-oxirane		
38	12,992	41746	0,036%	(1,1-dimethylbutyl)-oxirane		
60	25,179	1044276	0,911%	1,2-dipropyl-cyclopentane	3,605%	2,88%
50	15,788	2911094	2,539%	4-noneonic acid methyl ester	2,539%	2,03%
2	4,676	13358	0,012%	3-(1-methylethoxy)-propanennitrile		
7	7,669	15415516	13,443%	1,3-dihydroxy-2-cycloheptano(d)imidazolidine		
8	8,038	5581	0,005%	2,3,6-tri-O-methyl-glucose		
24	10,538	3132138	2,731%	1-ethyl-2-methyl-1H-imidazole		
25	10,643	703168	0,613%	1-methyl-2,5-pyrrolidinedione		
28	10,902	90776	0,079%	3-ethyl-1,3-dimethyl-2,5-pyrrolidinedione		
35	11,965	5171076	4,510%	1-(3-oxobutyl)-3,3-pentanebuthyl enediaziridine		
40	13,383	3319153	2,895%	2-methoxy-1,3-benzodiozole		
43	14,064	1075014	0,937%	Anydro-d-mannosam		
55	17,704	2805268	2,446%	D-allose	27,672%	22,14%
		114670150	100,0%			

Alucha project II (13/11/2015)
oil from paper sludge from **company #2 before treatment**

Peak	R.Time	Area	Percentage	Component		
1	4,277	5475421	1,412%	4-cyclohexane-1,2-diol		
3	4,61	1570245	0,405%	2-methyl-4-hexen-3-ol		
7	6,175	2273821	0,586%	1,2,3-cyclopentanetriol		
12	6,692	1517264	0,391%	2-methyleneciclopentanol		
14	7,011	696473	0,180%	5-octen-1-ol		
16	7,186	338038	0,087%	3-decen-1-ol		
20	7,675	10957745	2,825%	2-ethylcyclohexanol		
21	7,725	613265	0,158%	1-nonen-3-ol		
25	8,493	901631	0,232%	5-octen-1-ol		
27	8,726	1029452	0,265%	3-methylcyclopentanol		
28	8,908	3173167	0,818%	cis-4-methyl-cyclohexanol		
38	10,817	977485	0,252%	2-(1-methylethyl)-cyclohexanol		
40	11,14	4001423	1,032%	1-none-3-ol		
43	11,873	5634208	1,453%	2-methyl-2-octen-4-ol		
44	12,292	3415252	0,881%	4-isopropulidene-cyclohexanol		
46	13,252	5231410	1,349%	2,3,6-dimethylhept-6-en-1-ol		
48	13,754	47804449	12,326%	1,2-benzendiol		water content of 20%
49	13,967	15206621	3,921%	2,7-dimethyl-4,5-octanediol		
56	17,014	3392559	0,875%	2-methyl-1,4-benzenediol		
58	17,825	6850860	1,766%	4-ethyl-1,2-benzendiol	31,216%	24,97%
5	4,808	532355	0,137%	cyclopentanedecanoic acid		
6	4,933	203636	0,053%	octanoic acid		
10	6,442	980774	0,253%	4-hydroxy-butanoic acid		
17	7,375	367190	0,095%	4-pentenoic acid		
19	7,476	340443	0,088%	7-oxo-octanoic acid		
30	9,2	620714	0,160%	octyl ester hexanoic acid		
62	28,601	1607684	0,415%	Hexadecanoic acid	1,200%	0,96%
2	4,483	380762	0,098%	4-hydroxyproline		
9	6,368	2065235	0,533%	1-(2-fuanyl)-ethanone		
11	6,5	6836000	1,763%	2-(5H)-furanone		
18	7,417	203474	0,052%	2-(3-butynyloxy)tetrahidro-2H-pyran		
22	8,025	3394567	0,875%	3-methyl-2,5(H)-furanone		
23	8,172	9127154	2,353%	Phenol		
26	8,592	2046795	0,528%	2,5-dihydro-3,5-dimethyl-2-furanone		
36	10,525	15884223	4,096%	3-methylphenol		
51	14,417	10816293	2,789%	5-hydroxymethyl-2-furane		
52	15,075	10846330	2,797%	2-ethoxy-4-methylphenol		
54	15,8	8591787	2,215%	4-methylphenol		
57	17,142	3315529	0,855%	2,3-dimethylhydroquinone		
61	23,225	2519453	0,650%	1,1'-(1,3-propanedyil(bis)benzene	19,604%	15,68%
13	6,783	4503471	1,161%	2-ethyl-2-butenal		
47	13,375	2225184	0,574%	3,4-dimethyl-3-cyclohexen-1-carboxaldehyde	1,735%	1,39%
8	6,242	6780210	1,748%	2-methyl-2-cyclopenten1-one		
29	9,075	2940795	0,758%	3-methylpiridazin-5-one		
31	9,411	48262779	12,445%	3-methyl-1,2-cyclopentanedione		
32	9,52	4130870	1,065%	2,3-dimethyl-2-cyclopentanedione		
34	10,075	3383625	0,872%	2,4-dimethyl-1-cyclopentanedione		
35	10,375	780157	0,201%	5,5-dimethyl-cyclohex-3-en-1-one		
37	10,692	1850183	0,477%	furylhydroxymethylketone		
42	11,633	9423494	2,430%	3-ethyl-2-hydroxy-2-cyclopenten-1-on		
45	12,817	608071	0,157%	5,9-dymethyl-5,8-decadien-2-one	20,154%	16,12%
15	7,075	1111930	0,287%	2,3-dimethyl-2-pentene		
33	9,7	1496925	0,386%	4-methyl-2-hexene		
53	15,683	109404	0,028%	1,2-dimethyl-cycloctene	0,701%	0,56%
24	8,392	1446717	0,373%	3,5-dimethylcyclohexil ester	0,373%	0,30%
55	16,214	2397159	0,618%	2-ethyldione-6-methyl-3,5-heptadienal	0,618%	0,49%
4	4,663	11643497	3,002%	4,5-dimethyl-1H-imidazole		
39	10,983	2281770	0,588%	3,4-anhydro-D-galactosan		
41	11,498	9308262	2,400%	Maltol		
50	14,291	62235920	16,048%	anhydro-D-mannosan		
59	22,217	3254200	0,839%	Glucopyranose		
60	22,858	5906497	1,523%	galactofuranose	24,400%	19,52%
		387822307	100,0%			

Alucha project III (16/11/2015)
oil from paper sludge from company #1 **after treatment**

Peak	**R.Time**	**Area**	**Percentage**	**Component**	
20	14,952	1795684	0,803%	3,5-dimethylbenzenemethanol	
28	16,417	251948	0,113%	alpha-1-propenyl-benzanemethanol	0,916%
1	7,002	933386	0,417%	trans-2-pentenoic acid	
3	9,092	2935325	1,313%	1,2-dimethylcyclopropane carboxylic acid	
47	28,042	8654461	3,871%	2,6-dihexadecanoate-1-(t)-ascorbic acid	
48	28,683	14589162	6,525%	1-hexadecanoicacid	
53	37,136	10699255	4,785%	1,2-benzenedicarboxilic acid	16,911%
2	8,17	2340293	1,047%	phenol	
5	9,65	157474	0,070%	3-phenyl-1-propine	
6	10,458	9359786	4,186%	3-methyl phenol	
7	11,217	614218	0,275%	2,6-dimethylphenol	
8	12,25	6104155	2,730%	2,5-dimethylphenol	
9	12,633	664309	0,297%	(1-methylene-2-propenyl)benzene	
10	12,733	3600300	1,610%	3-ethylphenol	
11	13,108	2425276	1,085%	Azulene	
14	13,975	661930	0,296%	(Ethenyloxy)benzene	
15	14,175	1109544	0,496%	2-ethyl-6-methyl-phenol	
17	14,433	2268826	1,015%	2-ethyl-5-methylphenol	
18	14,508	1655895	0,741%	hexahydronaphtalene	
22	15,3	738435	0,330%	1,2-dihydro-3-methylnaphtalene	
23	15,7	11082069	4,956%	chlorophenil silane	
29	16,492	493023	0,220%	3-methyl-6-propylphenol	
31	16,808	466678	0,209%	4-(2-propenyl)-phenol	
32	17,65	9378469	4,194%	Biphenil	
33	17,792	7649003	3,421%	3,4-dihydroisoquinoline	
34	18,033	994561	0,445%	2,3-dimethylphtalene	
35	18,458	4896360	2,190%	2-methylphenol	
36	18,925	1731544	0,774%	(1-Ethynyl-2-methyl-1-propenyl-benzene	
37	19,9	8450811	3,779%	4-methyl-1,1'-biphenol	
38	20,642	2495875	1,116%	bibenzyl	
39	21,742	2196532	0,982%	7-phenylbiciclo-(3,2,1)octa-2,6-diene	
43	23,225	36201803	16,191%	1,1'-(1,3-propanediyl bis)benzene	
45	24,742	6130853	2,742%	1,2-diphenylcyclopropane	
46	25,133	4308841	1,927%	bis(1,4-butanediyl)-1,1'-benzene	
49	28,833	7483416	3,347%	2-phenylnaphtalene	
50	31,192	5485344	2,453%	octahydro-1,2'-binaphtalene	
51	31,622	9457370	4,230%	p-terphenyl	
52	32,642	6344324	2,837%	2-isopropyl-10-methylphenanthrene	70,192%
12	13,367	563675	0,252%	5,9-dimethyl-5,8-decadien-2-one	0
4	9,317	634264	0,284%	2,4-dimethyl-1-decene	0,252%
16	14,205	759146	0,340%	1,5,5-trimethyl-6-methylenecyclohexane	
21	15,158	283196	0,127%	1-methylenebut-2-ethylbenzene	
24	15,825	1279645	0,572%	1-phenyl-2,3-diazabyciclo(2,2,1)hept-2-ene	
25	15,942	379915	0,170%	5-methylene	
26	16,108	5986893	2,678%	benzocycloheptatriene	
27	16,292	1112447	0,498%	1-phenylbiciclo(2,11)hexane	
40	21,833	2391060	1,069%	1,2-dimethyl-cyclopentene	
42	22,767	3633467	1,625%	2-phenyl-bicyclo(3,2,1)octa-2,6-diene	7,361%
41	22,023	2755922	1,233%	chloroaceticacid-hexadecil ester	
44	23,95	3314545	1,482%	pentadecyl ester chloroacetic acid	2,715%
13	13,558	1435390	0,642%	2-methoxy-1,3-benzodioxol	
19	14,742	257439	0,115%	oxacyclotetradeca-4,11-diine	
30	16,667	2003206	0,896%	benzenebutanenitrile	1,653%
		223596748	100,000%		

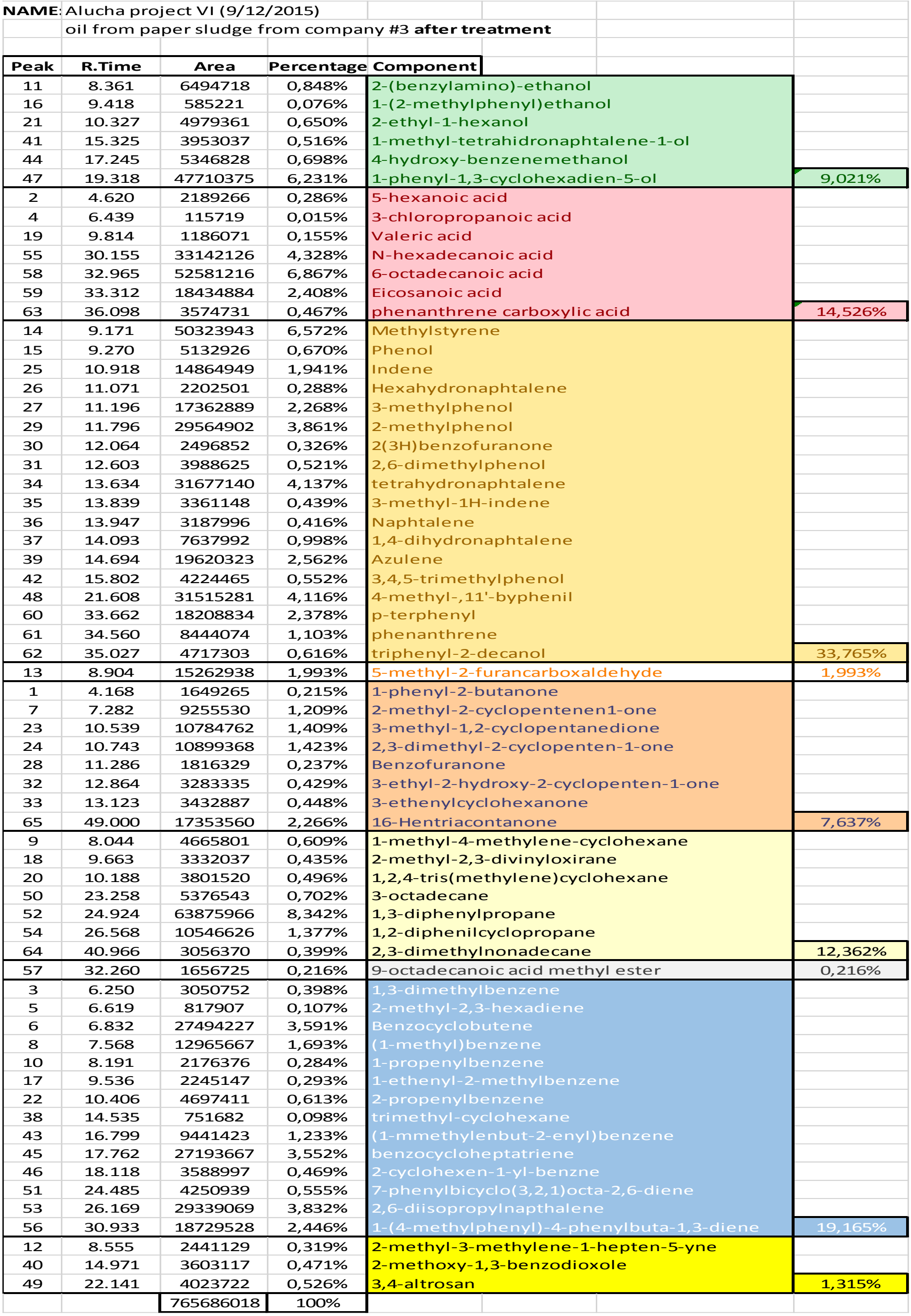
Alucha project IV (17/11/2015)
oil from paper sludge from company #2 **after treatment**

Peak	R.Time	Area	Percentage	Component	
6	6,364	2126014	0,485%	3,3-dimethyl-cyclohexanol	
8	6,843	489522	0,112%	1,6-diol-hexene	
9	7,008	929434	0,212%	5-octen-1-ol	
16	8,725	240874	0,055%	3-methyl-hepta-1,6-dien-3-ol	
17	8,996	233073	0,053%	propenylciclopropylmethanol	
41	13,567	14725681	3,360%	1,2-benzendiol	
46	15,025	5498330	1,255%	3-hydroxi-benzenmethanol	
53	17,8	8176153	1,866%	4-ethyl-2-benzendiol	7,398%
1	4,074	3011042	0,687%	butanoic acid	
4	6,117	83484	0,019%	8-chlorocapric acid	
47	15,427	7818354	1,784%	Benzoic acid	
56	19,742	3131660	0,715%	cyclopropanecarboxylicacid	
64	28,658	17509933	3,996%	1-hexadecanoic acid	
70	31,789	8569174	1,955%	octadecanoic acid	
73	36,217	3902857	0,891%	diphenolic acid	10,046%
3	4,634	6489961	1,481%	1,4-dimethyl-pyrazole	
10	7,633	9314617	2,125%	Furan	
12	8,107	11452822	2,613%	Phenol	
15	8,583	757252	0,173%	2,5-dihydro-3,5-dimethyl-2-furanone	
20	9,633	2641063	0,603%	3-phenyl-1-propyne	
21	9,944	14142084	3,227%	3-methylphenol	
23	10,2	1757197	0,401%	acetophenone	
25	10,475	16111366	3,676%	3-methylphenol	
28	11,217	4018475	0,917%	2,6-dimethylphenol	
32	12,02	3919968	0,894%	2,3-dimethylphenol	
33	12,156	1499122	0,342%	hexahydro-2,5-methano-furopyran	
34	12,292	14510582	3,311%	2,5-dimethylphenol	
35	12,617	1379116	0,315%	(1-methylene-2-propenyl)benzene	
37	12,775	3310168	0,755%	2,3-dimethylphenol	
38	12,913	2845726	0,649%	2,6-dimethylphenol	
39	13,1	3854429	0,880%	Azulene	
40	13,35	6584698	1,503%	2,3-dimethylhidroquinone	
42	14,175	3449051	0,787%	4-(1-methylethyl)phenol	
44	14,433	2603087	0,594%	2-ethyl-5-methylphenol	
48	15,7	15712390	3,585%	2-ethoxy-4-methylphenol	
49	16,225	16293771	3,718%	dihydromethyl-indanone	
51	17,098	1354600	0,309%	2,3-dimethylhydroquinone	
52	17,642	8032920	1,833%	byphenil	
54	18,364	1577345	0,360%	7-methyl-indanone	
55	19,187	7063989	1,612%	3-allyl-2-methoxyphenol	
57	19,917	7885658	1,799%	4-methyl-1,1'byphenil	
59	23,242	24567250	5,606%	1,3-diphenil-propane	
60	23,808	9467692	2,160%	2,6-diisopropyl-naphtalene	
61	24,642	15419564	3,519%	1,2-diphenilciclopropane	
63	25,952	2968002	0,677%	1,3-diphenil-butene	
65	28,842	4088918	0,933%	2-phenilnaphtalene	
66	29,592	2404585	0,549%	4-methylbenzene	
69	31,617	5999704	1,369%	p-terphenyl	
71	32,017	5590841	1,276%	4,4'-(1-methylethyldiene)bis-phenol	
72	32,642	3076111	0,702%	2-isopropyl-10-methylphenantrene	
74	37,125	2466160	0,563%	diisooctilpthalate	55,817%
7	6,443	1638471	0,374%	3,7-dimethyl-2,6-nonadienal	0,374%
5	6,223	2612083	0,596%	2-methyl-2-cyclopenten-1-one	
11	8,017	944779	0,216%	1-cyclopentene-3-one	
14	8,483	1224742	0,279%	2,3-dimethyl-2-cyclopenten-1-one	
19	9,285	26247523	5,989%	3-methyl-1,2-cyclopentanedione	
22	10,525	1482266	0,338%	2-cyclopenten-1-one	
26	10,792	4948922	1,129%	trymethylcyclopentenone	
27	11,125	2489875	0,568%	3-ethenylcyclohexanone	
30	11,567	6267740	1,430%	2-cyclopenten-1-one	
36	12,7	2709913	0,618%	dimethyl-decadienone	
75	47,433	1591875	0,363%	dipentanedecyl ketone	11,528%
18	9,048	942806	0,215%	2-methyl-2,3-divinyloxirane	0,215%
58	22,033	3096568	0,707%	chloroacetic acid hexadecil ester	
76	49,542	27859485	6,357%	octadecanoic acid ethenyl ester	7,064%
13	8,358	1294466	0,295%	2,3-dimethyl-2,4-hexadiene	
24	10,358	805570	0,184%	2-ethyl-2-pentenal	
31	11,853	1438637	0,328%	(1-methylethyldiene)cyclohexane	
43	14,27	5920009	1,351%	trimethylcyclohexene	
45	14,942	2480821	0,566%	trymethylcyclopropane	
62	25,767	5396324	1,231%	10-heneicosene	3,956%
2	4,226	73031	0,017%	6-deoxy-L-manose	
29	11,402	4194381	0,957%	Maltol	
67	29,825	11520403	2,629%	cyclooctasulfur	3,603%
		438236559	100,00%		

NAME: Alucha project V (9/12/2015)

oil from paper sludge from company #3 **before treatment**

Peak	**R.Time**	**Area**	**Percentage**	**Component**		
4	4.645	3472437	1,251%	1,2-ciclopentanediol		
6	6.082	6420089	2,312%	2-furanmethanol		
7	6.247	679915	0,245%	3-tertbutyl-4-methoxycyclohexanol		
12	8.072	1605611	0,578%	Hex-3-ene-1,6-diol		water content of 20%
20	10.333	393025	0,142%	2-Nonen-1-ol		
24	11.718	538852	0,194%	4,4-dimethyl-cyclohex-2-en-1-ol		
26	12.521	339629	0,122%	cyclodecanol	4,844%	3,876%
13	8.298	261818	0,094%	cyclopentaneundecanoic acid		
14	8.564	322388	0,116%	2-Nonenoic acid	0,210%	0,168%
8	6.385	2701337	0,973%	3-butylhydro-2(3H)-furanone		
9	6.860	8217885	2,960%	Styrene		
11	7.705	3782416	1,362%	Tetrahydropyran		
17	9.180	2843291	1,024%	3,3-dimethyl-(3H)-Indazole		
25	12.052	247157	0,089%	2(1H)-Naphtalenone		
29	13.637	710181	0,256%	3-methyl-1H-indene		
34	17.427	4187014	1,508%	2-ethoxy-4-methylphenol	8,173%	6,538%
23	11.177	2244497	0,808%	cyclohexanecarboxaldehyde		
27	12.901	1897453	0,683%	3,3-dimethyl-5-oxo-cyclohexacarboxaldehyde		
33	16.141	2720186	0,980%	5-Hydroxymethyl-2-furancarboxaldehyde		
35	19.050	488308	0,176%	2-formyl-3-methyl-cyclopentaneacetaldehyde	2,648%	2,118%
2	4.272	17999768	6,483%	1-hydroxy-2-butanone		
10	7.316	8381050	3,019%	2-methyl-2-cyclopenten-1-one		
18	9.680	405430	0,146%	Iridomyrmelin		
19	9.863	902462	0,325%	2-hydroxyhexadecilbutanone		
21	10.556	21894895	7,886%	3-methyl-1,2-pentanedione		
22	10.757	809794	0,292%	2(1H)-pyrimidinone	18,151%	14,521%
3	4.576	792200	0,285%	1-butoxy-2-methyl-butane		
15	8.742	473087	0,170%	1-Isobutoxy-2-ethylhexane		
16	8.965	2054170	0,740%	2-methyl-2,3-divinyloxirane		
31	15.591	10546999	3,799%	(1,1-dimethylbutyl)oxirane	4,995%	3,996%
28	13.427	670632	0,242%	4-pentadecyl ester valiric acid	0,242%	0,193%
38	25.029	2383473	0,859%	1,1'-(1,3-propanediyl)bis-benzene	0,859%	0,687%
1	4.054	3744	0,001%	3-O-Benzyl-d-glucose		
5	4.837	324742	0,117%	L-mannose		
30	15.121	21468160	7,733%	2-methoxy-1,3-benzodioxale		
32	15.895	6749562	2,431%	Anhydro-D-annosan		
36	22.776	1,35E+08	48,796%	D-Allose		
37	24.618	2222284	0,800%	1,5-Anhydro-D-mannitol	59,879%	47,903%
		2,78E+08	100%			



NAME: Alucha project VI (9/12/2015)
oil from paper sludge from company #3 **after treatment**

Peak	R.Time	Area	Percentage	Component	
11	8.361	6494718	0,848%	2-(benzylamino)-ethanol	
16	9.418	585221	0,076%	1-(2-methylphenyl)ethanol	
21	10.327	4979361	0,650%	2-ethyl-1-hexanol	
41	15.325	3953037	0,516%	1-methyl-tetrahidronaphtalene-1-ol	
44	17.245	5346828	0,698%	4-hydroxy-benzenemethanol	
47	19.318	47710375	6,231%	1-phenyl-1,3-cyclohexadien-5-ol	9,021%
2	4.620	2189266	0,286%	5-hexanoic acid	
4	6.439	115719	0,015%	3-chloropropanoic acid	
19	9.814	1186071	0,155%	Valeric acid	
55	30.155	33142126	4,328%	N-hexadecanoic acid	
58	32.965	52581216	6,867%	6-octadecanoic acid	
59	33.312	18434884	2,408%	Eicosanoic acid	
63	36.098	3574731	0,467%	phenanthrene carboxylic acid	14,526%
14	9.171	50323943	6,572%	Methylstyrene	
15	9.270	5132926	0,670%	Phenol	
25	10.918	14864949	1,941%	Indene	
26	11.071	2202501	0,288%	Hexahydronaphtalene	
27	11.196	17362889	2,268%	3-methylphenol	
29	11.796	29564902	3,861%	2-methylphenol	
30	12.064	2496852	0,326%	2(3H)benzofuranone	
31	12.603	3988625	0,521%	2,6-dimethylphenol	
34	13.634	31677140	4,137%	tetrahydronaphtalene	
35	13.839	3361148	0,439%	3-methyl-1H-indene	
36	13.947	3187996	0,416%	Naphtalene	
37	14.093	7637992	0,998%	1,4-dihydronaphtalene	
39	14.694	19620323	2,562%	Azulene	
42	15.802	4224465	0,552%	3,4,5-trimethylphenol	
48	21.608	31515281	4,116%	4-methyl-,11'-byphenil	
60	33.662	18208834	2,378%	p-terphenyl	
61	34.560	8444074	1,103%	phenanthrene	
62	35.027	4717303	0,616%	triphenyl-2-decanol	33,765%
13	8.904	15262938	1,993%	5-methyl-2-furancarboxaldehyde	1,993%
1	4.168	1649265	0,215%	1-phenyl-2-butanone	
7	7.282	9255530	1,209%	2-methyl-2-cyclopentenen1-one	
23	10.539	10784762	1,409%	3-methyl-1,2-cyclopentanedione	
24	10.743	10899368	1,423%	2,3-dimethyl-2-cyclopenten-1-one	
28	11.286	1816329	0,237%	Benzofuranone	
32	12.864	3283335	0,429%	3-ethyl-2-hydroxy-2-cyclopenten-1-one	
33	13.123	3432887	0,448%	3-ethenylcyclohexanone	
65	49.000	17353560	2,266%	16-Hentriacontanone	7,637%
9	8.044	4665801	0,609%	1-methyl-4-methylene-cyclohexane	
18	9.663	3332037	0,435%	2-methyl-2,3-divinyloxirane	
20	10.188	3801520	0,496%	1,2,4-tris(methylene)cyclohexane	
50	23.258	5376543	0,702%	3-octadecane	
52	24.924	63875966	8,342%	1,3-diphenylpropane	
54	26.568	10546626	1,377%	1,2-diphenilcyclopropane	
64	40.966	3056370	0,399%	2,3-dimethylnonadecane	12,362%
57	32.260	1656725	0,216%	9-octadecanoic acid methyl ester	0,216%
3	6.250	3050752	0,398%	1,3-dimethylbenzene	
5	6.619	817907	0,107%	2-methyl-2,3-hexadiene	
6	6.832	27494227	3,591%	Benzocyclobutene	
8	7.568	12965667	1,693%	(1-methyl)benzene	
10	8.191	2176376	0,284%	1-propenylbenzene	
17	9.536	2245147	0,293%	1-ethenyl-2-methylbenzene	
22	10.406	4697411	0,613%	2-propenylbenzene	
38	14.535	751682	0,098%	trimethyl-cyclohexane	
43	16.799	9441423	1,233%	(1-mmethylenbut-2-enyl)benzene	
45	17.762	27193667	3,552%	benzocycloheptatriene	
46	18.118	3588997	0,469%	2-cyclohexen-1-yl-benzne	
51	24.485	4250939	0,555%	7-phenylbicyclo(3,2,1)octa-2,6-diene	
53	26.169	29339069	3,832%	2,6-diisopropylnapthalene	
56	30.933	18729528	2,446%	1-(4-methylphenyl)-4-phenylbuta-1,3-diene	19,165%
12	8.555	2441129	0,319%	2-methyl-3-methylene-1-hepten-5-yne	
40	14.971	3603117	0,471%	2-methoxy-1,3-benzodioxole	
49	22.141	4023722	0,526%	3,4-altrosan	1,315%
		765686018	100%		

NAME: Alucha project VII (14/12/2015)

aqueous phase of oil from paper sludge from company #3 **after treatment**

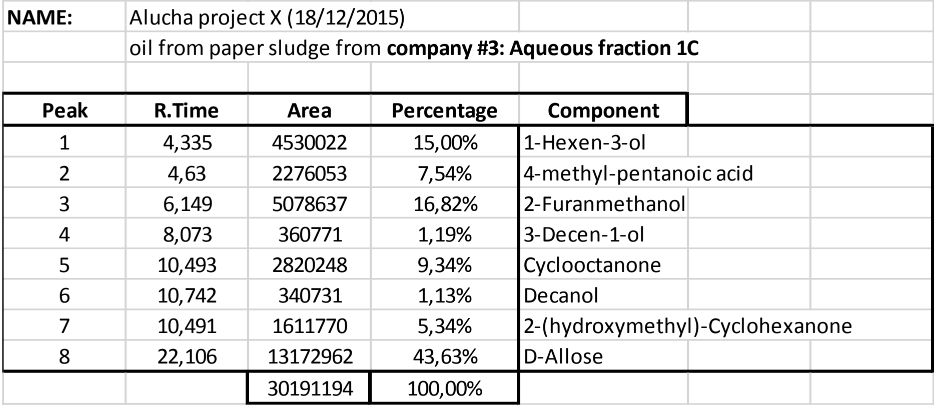
Peak	**R.Time**	**Area**	**Percentage**	**Component**		
7	6,385	725541	0,337%	cyclohexanetetrol		
8	6,92	386698	0,180%	cyclopentanetetrol		
10	7,366	1294290	0,602%	1,2,4-cyclopentanetriol		
12	7,7	3934140	1,830%	2-(3-Methylguanidino)ethanol		water content of 20%
14	9,018	1438047	0,669%	5-octen-1-ol		
21	13,507	2104366	0,979%	2-ethyl-2-hexen-1-ol		
23	15,541	10270960	4,777%	2,7-dimethyl-4,5-octanediol	9,374%	7,499%
11	7,573	257858	0,120%	7-oxo-octanoicacid		
13	8,081	472969	0,220%	2-nonenoic acid		
15	9,384	4642865	2,160%	2-chlorohexanoic acid		
18	11,229	920378	0,428%	octyl ester pentanoic acid		
19	11,694	637319	0,296%	4,4-dimethylcyclo-hex-2-en-2-ol	3,224%	2,579%
27	17,501	4872940	2,267%	2-ethoxy-4-methylphenol	2,267%	1,813%
17	11,151	663684	0,309%	3,3-dimethyl-5-oxo-cyclohexane carboxaldehyde	0,309%	0,247%
1	4,274	11414896	5,309%	1-Hydroxy-2-butanone		
16	10,51	19007619	8,841%	3-methylcyclopentanedione		
20	12,51	308454	0,143%	6-hydroxyhexahydropenta(b)furan-2-one		
24	15,772	247430	0,115%	2-hydroxymethylcyclohexanone	14,409%	11,527%
2	4,557	1160619	0,540%	1-butoxy-2-methylbutane		
6	6,254	151311	0,070%	1,3-dimethoxyciclopentane		
22	15,1	15304273	7,119%	2-methoxy-1,3-benzodioxole	7,729%	6,183%
26	16,238	2408926	1,120%	3-ethyl-4,4-dimethyl-2-pentene	0	0
28	17,714	479845	0,223%	hexahydro-3-methylene-2(3H)benzofuranone	1,344%	1,075%
3	4,797	2027709	0,943%	6-deoxy-L-mannose		
4	4,85	991762	0,461%	Digitoxose		
5	6,136	2473263	1,150%	3,4-Anhydrogalactosan		
9	7,194	245473	0,114%	2-Deoxy-D-galactose		
25	15,845	6831116	3,177%	Anhydro-D-mannosan		
29	22,665	116798525	54,327%	D-Allose		
30	24,601	2519458	1,172%	Heptose	61,345%	49,076%
		214992734	100%			

NAME: Alucha project VIII (17/12/2015)
oil from paper sludge from **company #3: Organic fraction 1C**

Peak	R.Time	Area	Percentage	Component
1	6	14602162	17,93%	Ethylbenzene
2	6,869	15261795	18,74%	Styrene
3	7,567	997278	1,22%	2-phenyloxetane
4	11,229	3423103	4,20%	3-cyclohexenil-1-phenyl-propane
5	11,328	6933512	8,52%	6-heptinyl-benzene
6	11,585	1716659	2,11%	8-phenyl-3-octen-2-one
7	11,871	495375	0,61%	methyl ester 2,5-octadecanoic acid
8	12,015	4277981	5,25%	?
9	12,766	2450578	3,01%	stigmastan-3,5-diene
10	13,466	2061149	2,53%	1-chlorooctadecane
11	15,06	7859024	9,65%	16-Hentriacontanone
12	16,341	673868	0,83%	?
13	16,816	1307119	1,61%	2,3,5,8-tetramethyldecane
14	18,691	1719526	2,11%	Palmitic acid vinyl ester
15	20,626	1034418	1,27%	1-chloroheptacosane
16	22,525	15953078	19,59%	ethyl ester octadecanoic acid
17	24,633	659076	0,81%	behenylchloride
		81425701	100,00%	

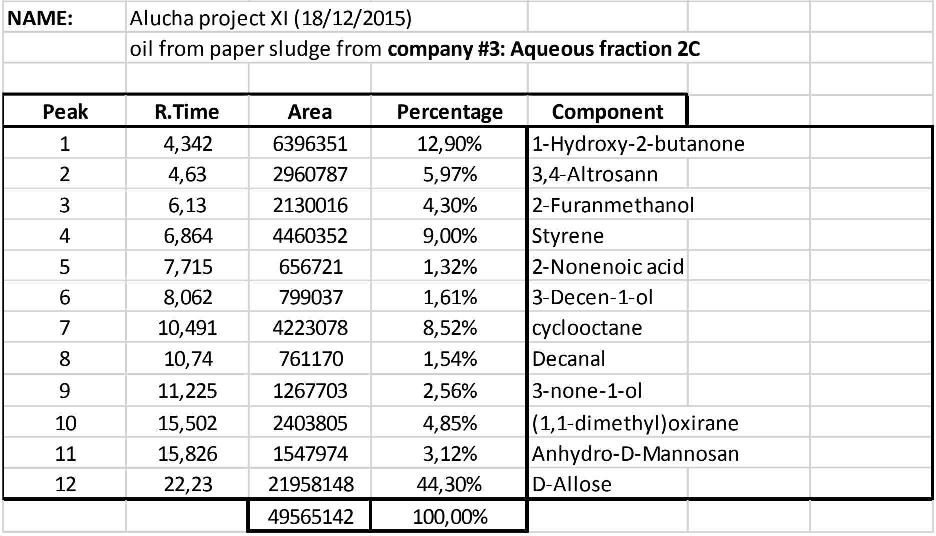
NAME: Alucha project IX (17/12/2015)
oil from paper sludge from **company #3: Organic fraction 2C**

Peak	R.Time	Area	Percentage	Component
1	6	23089262	13,65%	Ethylbenzene
2	6,933	20332980	12,02%	Styrene
3	7,567	2299494	1,36%	Benzamethylamino
4	10,703	567358	0,34%	Behenylchloride
5	11,3	14801144	8,75%	4-methylene-cyclooctane
6	11,966	6760325	4,00%	1-chlorooctadecane
7	12,75	7617278	4,50%	?
8	13,454	7602877	4,50%	phenylmethyl ester octoacetic acid
9	15,017	18914915	11,19%	16-hemtriacontanone
10	16,798	3305578	1,95%	1-chlorooctadecane
11	16,644	32626809	19,30%	palmitic acid vinyl ester
12	20,607	1840882	1,09%	Behenylchloride
13	22,64	26299351	15,55%	ethenyl ester octadecanoic acid
14	24,719	1117399	0,66%	?
15	25,886	841536	0,50%	?
16	26,885	1074292	0,64%	?
		169091480	100,00%	



NAME: Alucha project X (18/12/2015)
oil from paper sludge from **company #3: Aqueous fraction 1C**

Peak	R.Time	Area	Percentage	Component
1	4,335	4530022	15,00%	1-Hexen-3-ol
2	4,63	2276053	7,54%	4-methyl-pentanoic acid
3	6,149	5078637	16,82%	2-Furanmethanol
4	8,073	360771	1,19%	3-Decen-1-ol
5	10,493	2820248	9,34%	Cyclooctanone
6	10,742	340731	1,13%	Decanol
7	10,491	1611770	5,34%	2-(hydroxymethyl)-Cyclohexanone
8	22,106	13172962	43,63%	D-Allose
		30191194	100,00%	



NAME: Alucha project XI (18/12/2015)
oil from paper sludge from **company #3: Aqueous fraction 2C**

Peak	R.Time	Area	Percentage	Component
1	4,342	6396351	12,90%	1-Hydroxy-2-butanone
2	4,63	2960787	5,97%	3,4-Altrosann
3	6,13	2130016	4,30%	2-Furanmethanol
4	6,864	4460352	9,00%	Styrene
5	7,715	656721	1,32%	2-Nonenoic acid
6	8,062	799037	1,61%	3-Decen-1-ol
7	10,491	4223078	8,52%	cyclooctane
8	10,74	761170	1,54%	Decanal
9	11,225	1267703	2,56%	3-none-1-ol
10	15,502	2403805	4,85%	(1,1-dimethyl)oxirane
11	15,826	1547974	3,12%	Anhydro-D-Mannosan
12	22,23	21958148	44,30%	D-Allose
		49565142	100,00%	