

**Integrated Master in Bioengineering**

***Structural Characterization of Heat Treated  
Poplar Wood***

**Master Thesis**

**Gonçalo de Bastos Monteiro**

**Developed within the course of Dissertation**

**In a partnership with**

**Laboratoire de Génie des Procédés et Matériaux, LGPM**

**CentraleSupélec**



**Supervisors in LGPM: Professor Patrick Perré**

**Dr. Pin Lu**

**Supervisor in FEUP: Professor Luís Melo**

**Department of Chemical Engineering**

**June of 2016**





“Even if there is only one possible unified theory, it is just a set of rules and equations. What is it that breathes fire into the equations and makes a universe for them to describe? The usual approach of science of constructing a mathematical model cannot answer the questions of why there should be a universe for the model to describe. Why does the universe go to all the bother of existing?”

Stephen Hawking, A Brief History of Time

---

## Acknowledgements

This work was conducted at CentraleSupélec in the Laboratoire de Génie des Procédés et Matériaux (LGPM) in a partnership with Faculdade de Engenharia da Universidade do Porto (FEUP) under the supervision of Professor Patrick Perré. I would like to express my sincere gratitude to Prof. Perré for believing in me and for the fruitful and interesting discussions we have had over the months. I never left his office without having learnt something new, and a great part of the engineer found in me is due to him. Once again, thanks Patrick!

I would also like to thank my co-supervisor, Dr. Pin Lu for his constant interest in my research and for always being ready to help. His positive energy has been contagious and inspiring. His knowledge and perseverance made me improve each and every day my skills as an engineer and as a team member.

To my co-supervisor in FEUP, Professor Luís Melo, I would like to thank for the valuable comments and suggestions to improve the quality of the present work.

I gratefully acknowledge the financial support provided by the French State.

I am indebted to many people who have contributed to the completion of this thesis. Ms. Mathilde Charters is thanked for helping with laboratory and equipment related issues. Ms. Barbara Malinowska is thanked for her support and help with the elemental analysis. Also, to Floran Pierre, Jean Trubuil and all people of LGPM who helped with their experience and good will.

My colleague and friend Shirley Duarte, at LGPM, is thanked for her help and encouragement to finish my studies.

Special thanks go to all my friends in Paris, so many different people from different nationalities but always kind and friendly, in Porto for the great times and experiences we have spent together during these last 5 years and in Espinho, where my heart and my true buddies are, waiting for me to give me a hug.

Finally, I would like to thank my parents, Luís and Cláudia, my little sister Matilde and all my relatives for their endless love, trust and support in everything I have ever attempted in life even when I am far. You have always been an amazing example to me.

And you, my loved Sofia, thank you for standing by me throughout the years, encouraging me during the downs and sharing with me the ups of this process. Let's continue this path together!

Paris, June 2016

Gonçalo Monteiro

---

## Resumo

A madeira é um recurso bastante útil para diversas áreas e aplicações, principalmente devido às suas várias propriedades excelentes. No entanto, este material apresenta também algumas características menos favoráveis, como uma elevada higroscopicidade e baixas eficiências de bioconversão. Neste contexto, o tratamento térmico de biomassa tem vindo a ser utilizado na melhoria destas propriedades menos favoráveis tornando os materiais linhocelulósicos uma alternativa ainda mais forte às fontes não renováveis para a produção de energia e outros produtos essenciais do dia-à-dia.

Assim sendo, este estudo incidiu sobre as alterações estruturais na madeira de álamo (*Populus*) após tratamento térmico sob diferentes condições de temperatura. O processo de adsorção de azoto, a distribuição do tamanho dos poros, a área superficial específica, a degradação térmica e as alterações na composição química foram as propriedades associadas à estrutura da madeira estudadas. Além disso, um estudo exploratório sobre as propriedades higroscópicas do material também é apresentado. Neste trabalho, o aumento da temperatura de tratamento conduziu a uma alteração nas características das isotérmicas de adsorção de azoto. O volume de poros na região dos microporos para as amostras tratadas a temperaturas mais altas é muito superior em comparação com o volume de poros para as amostras tratadas abaixo de 400 °C. Nas regiões dos meso e macroporos, especialmente para os poros com maiores dimensões, entre 400 e 500 Å, o volume de poros aumenta para a menor temperatura de tratamento e, em seguida, começa a diminuir. As áreas superficiais específicas obtidas através da aplicação da teoria do BET foram geralmente baixas para amostras produzidas a temperaturas até 400 °C, mas após essa temperatura ocorreu um grande aumento até aos 500 °C (413,06 m<sup>2</sup>/g). A degradação térmica das amostras ocorre principalmente em três fases. A maior parte do peso perdido devido ao tratamento térmico ocorre até os 350 °C, com uma perda de massa de cerca de 80%. A análise elementar realizada mostrou que o teor de carbono aumenta e os níveis de hidrogénio e oxigénio diminuem com o aumento da temperatura, atingindo, respectivamente, valores de 82,1%, 2,83% e 9,44% por peso seco para um tratamento a 500 °C. Por fim, um método inovador desenvolvido para actuar como uma alternativa valiosa aos métodos clássicos para a determinação das isotérmicas de sorção de vapor de água, como a sorção de vapor dinâmica, é apresentado.

Com este estudo, pretende-se demonstrar que as características obtidas após tratamento térmico da madeira de álamo podem ser muito úteis para a indústria dos produtos da madeira conduzindo à criação de novas e atrativas oportunidades

**Palavras-Chave:** Biomassa, Tratamento Térmico, Adsorção de Azoto, Porosidade, BET, Análise termogravimétrica, Análise Elementar, Sorção de Vapor de Água

---

## Abstract

Wood has been a very useful resource in many fields and applications, mainly because of its many excellent material properties. However, it also has some less attractive characteristics, like high hygroscopicity and low bioconversion efficiencies. Therefore, heat treatment of biomass has been proved to improve these less interesting properties making lignocellulosic materials a stronger alternative to non-renewable sources for the production of energy and other essential products.

This study focused on the structural changes of heat treated poplar (*Populus*) wood specimens treated under different temperature conditions. The nitrogen adsorption, the pore size distribution, the specific surface area, the thermal degradation and the chemical changes were the properties associated with the structure of heat treated wood studied. Furthermore, an exploratory study on the hygroscopic properties of the material is also presented. The increasing of the temperature treatment leads to a change on the characteristics of the nitrogen adsorption isotherms. The volume of pores on the micropores region for samples treated at higher temperatures is much greater compared with the volume of pores for samples below 400 °C and, in the meso and macropores regions, especially for pores with bigger dimensions, between 400 and 500 Å, the volume of pores increases for the lowest temperature treatment and then starts to decrease. The BET specific surface areas were generally low for samples produced at temperatures until 400 °C, but after this temperature there was a great increase while increasing the temperature up to 500 °C (413,06 m<sup>2</sup>/g). The thermal degradation of the heat treated samples occurs in mainly three steps. The major mass loss of the samples occurs until 350 °C with a weight loss of about 80%. The elemental analysis performed on the samples showed that the carbon content increases and the levels of hydrogen and oxygen decrease, reaching values of 82,1%, 2,83% and 9,44% per dry weight, respectively, for a 500 °C treatment. Finally, an innovative method developed to act as a valuable alternative to the classical methodologies for determination of vapor sorption isotherms, like the dynamic vapor sorption is presented.

With this study, it is intended to show that the improved characteristics of heat treated poplar wood that were verified during this project can be very useful for the timber product industry leading to the creation of many potential and attractive new opportunities.

**Keywords:** Biomass, Heat treatment, Nitrogen Adsorption, Porosity, BET, TGA, Elemental Analysis, Water Sorption

---

## Declaração

Declara, sob compromisso de honra, que este trabalho é original e que todas as contribuições não originais foram devidamente referenciadas com identificação da fonte.

*Assinar e datar*

# Table of Contents

Table of Contents .....	ii
List of Figures.....	iv
List of Tables.....	v
Nomenclature and Glossary.....	vi
<b>I. Introduction .....</b>	<b>1</b>
1. Framework of the Project .....	1
2. Objectives of the Project .....	2
3. Contributions .....	2
4. Structure of the Thesis .....	3
5. Using Wood: The Biorefinery Approach .....	4
6. The composition of lignocellulosic material.....	6
6.1. Cellulose .....	6
6.2. Hemicellulose.....	6
6.3. Lignin.....	7
6.4. Extractives .....	7
7. Value-Added Products from Wood: Examples.....	8
7.1. Methane production by anaerobic digestion .....	8
7.2. Ethanol production by fermentation.....	9
<b>II. State of the Art: Wood Treatment Methods .....</b>	<b>10</b>
1. Chemical Treatment of Lignocellulose .....	10
2. Thermal Treatment of Lignocellulose .....	10
2.1. Process description and Mode of action.....	11
2.1.1. Torrefaction .....	11
2.1.2. Pyrolysis .....	12
3. Physiochemical Changes in Wood due to Pretreatments .....	14
3.1. Effects on the Surface Characteristics of Wood .....	17
3.1.1. Torrefaction .....	17

3.1.2.	Pyrolysis .....	17
3.2.	The Wood-Water Relationship .....	18
3.2.1.	Moisture Sorption and Desorption .....	18
III.	Materials and Methods .....	20
IV.	Results and Discussion .....	22
1.	Adsorption Study: Surface Area and Porosity Distribution Analysis.....	22
2.	Thermogravimetric Analysis .....	27
3.	Elemental Analysis .....	30
4.	Perspectives and Future Work .....	33
V.	Conclusions .....	35
VI.	References .....	37
Annex 1	.....	47
I.	Feedstock preparation.....	48
II.	Surface structure characterization .....	49
III.	Thermogravimetric analysis .....	64
IV.	Elemental analysis .....	65
	Calibration Curves for Determination of Carbon, Hydrogen and Oxygen .....	66
V.	Water Sorption Study .....	68
Annex 2	.....	74

## List of Figures

<i>Figure 1- The composition of lignocellulosic materials. Adapted from Tomme et al., 1995 .....</i>	<i>8</i>
<i>Figure 2- Process of Production of Bioethanol .....</i>	<i>9</i>
<i>Figure 3- Simplified Impact of Pretreatment on Biomass. Adapted from Mosier et al. 2005. ....</i>	<i>15</i>
<i>Figure 4 - A sorption and desorption isotherm, showing hysteresis. Adapted from Hill, 2006.....</i>	<i>19</i>
<i>Figure 5 - N<sub>2</sub> adsorption isotherms at -196,15 °C of Untreated and Heat Treated Poplar samples. ....</i>	<i>22</i>
<i>Figure 6 - DFT (Density Functional Theory) pore size distribution for Untreated and Heat Treated Poplar Samples.....</i>	<i>24</i>
<i>Figure 7 - DFT (Density Functional Theory) pore size distribution for Untreated and Heat Treated Poplar Samples until 400 °C. ....</i>	<i>24</i>
<i>Figure 8 - DFT (Density Functional Theory) pore size distribution for Untreated and Heat Treated Poplar Samples.....</i>	<i>25</i>
<i>Figure 9 - Comparison between specific surface area and temperature of treatment. ....</i>	<i>26</i>
<i>Figure 10 - Measured anhydrous weight and its derivate for poplar samples in function of time .....</i>	<i>27</i>
<i>Figure 11 - Comparison between specific surface area and anhydrous weight loss. ....</i>	<i>28</i>
<i>Figure 12 - Photos of the original poplar wood; untreated poplar powder and heat treated poplar samples after 2h of heat treatment. ....</i>	<i>29</i>
<i>Figure 13 - The spectrum of the combustion product continuum as a result of the chemical-thermal conversion of biomass. Adapted from Spokas, 2010 .....</i>	<i>31</i>
<i>Figure 14 - Van krevelen plot for all experiments measured in elemental analyzer. ....</i>	<i>31</i>
<i>Figure 15 - Measured anhydrous weight for an untreated sample and at different temperatures of treatment after 2h and its change in percentage. ....</i>	<i>32</i>
<i>Figure 16 - Comparison between anhydrous weight loss and composition in terms of H/C and O/C ratio.....</i>	<i>32</i>
<i>Figure 17 - Vapor sorption isotherms at 30 °C of Untreated and Heat Treated Poplar sample at 500 °C. ....</i>	<i>34</i>

## List of Tables

*Table 1 - Specific Surface areas of Untreated and Heat Treated Poplar Samples..... 26*

*Table 2 - Elemental composition of poplar after different heat treatments and untreated. Also H/C and O/C ratios. .... 30*

## Nomenclature and Glossary

AW	Anhydrous weight	%
AWL	Anhydrous weight loss	%
dAW	First derivative of the Anhydrous weight curve	%/min
EMC	Equilibrium moisture content	%
MC	Moisture Content	%
P	Pressure	mmHg
P <sub>0</sub>	Atmospheric Pressure	mmHg
RH	Relative Humidity	%
S <sub>BET</sub>	Specific Surface Area using BET theory	m <sup>2</sup> /g
V	Volume of Adsorbed Nitrogen per sample mass	cm <sup>3</sup> /g
W	Pore Width	Å
wt %	weight-weight percentage	%

### *List of Elements, Molecules and Compounds*

BBOT	2,5-(Bis(5-tert-butyl-2-benzo-oxazol-2-yl) thiophene
CH <sub>4</sub>	Methane
CHNS	Carbon, Hydrogen, Nitrogen and Sulfur
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
H	Hydrogen
N <sub>2</sub>	Nitrogen
N <sub>2</sub> O	Nitrous Oxide
O	Oxygen
OH	Hydroxyl
V <sub>2</sub> O <sub>5</sub>	Vanadium oxide

### *List of Abbreviations*

BET	Brunauer, Emmett and Teller
CrI	Crystallinity Index
DFT	Density Functional Theory
DTA	Differential thermal analysis
GHG	Greenhouse Gases
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
MC	Monte Carlo
MD	Molecular Dynamics
TG	Thermogravimetric

# I. Introduction

## 1. Framework of the Project

As wood continues to be very useful for many fields and applications, mainly because of its many excellent material properties (such as an incredible strength to weight ratio, appearance, etc.), it also has some disadvantages. High hygroscopicity, low efficiencies of bioconversion and susceptibility to biological attack are examples of this. (Green *et al.*, 1999) The genesis of the wood properties can be better understood by studying its structural characteristics at macroscopic, microscopic and molecular levels.

Wood is a natural material, and because of that it exhibits a great range of variation in its properties. Variations occur between tree species, between trees of the same species and within the tree itself. This can lead to problems for any study of the material, making it difficult to obtain comparable results. In the great majority of reviews related with wood sciences (or indeed any other kind of science), it is easily detected that, sometimes, disagreements appear between different studies, and it is not always possible to reach a consensus.

Since a great number of properties of wood are defined by its chemical constituents, wood treatment often tries to promote changes at this level, in order to produce a material with improved properties. In contrast, some other wood treatments are applied that do not alter the chemical structure of the material. Wood treatment works as a mean of changing the material to overcome or improve one or more of its disadvantages. (Rowell, 2006)(Esteves and Pereira, 2009)

The objective of a treatment may focus on the dimensional stability or decay resistance, to reduce water sorption and so on. The term ‘wood treatment’ can be applied when using a process that changes the properties of the material such that during its lifetime, there is no loss of the enhanced properties.

Particularly, heat treatments on wood result in degradation associated with chemical changes in the material. However, if carefully controlled, the properties that are obtained due to thermal treatment can be valuable for certain fields. There has been a major research and commercial activity in this sector, mainly in France. (Vernois, 2001)

The main studies on heat treatment of wood focus mainly on the dimensional stability, equilibrium moisture, durability and mechanical properties. Although, wettability, mass loss, wood color and chemical transformations have also been extensively studied, while more recent works try to highlight the quality control, modeling and investigate the reasons for the improvements. (Esteves and Pereira, 2009)

## 2. Objectives of the Project

The objective of this project was to investigate the structural changes that occur during heat treatment of poplar wood, and to evaluate their effects on the characteristics of the material. Understanding the effects of such treatments may provide a good basis for defining the best conditions to improve the mechanical properties of wood.

The particular aims of this project were:

- To investigate the effects of heat treatment on the adsorption mechanisms on poplar wood.
- To investigate the effects of heat treatment on the pore structure of poplar and, consequently, the effects on the specific surface area of this material.
- To investigate the thermal degradation of poplar wood by performing thermogravimetric studies.
- To evaluate the chemical changes during the process of heat treatment of poplar by performing an elemental analysis.
- To develop an exploratory study on the water sorption of heat treated poplar wood using a volumetric system.

## 3. Contributions

During the time spent in France, the author worked as a team member of Laboratoire de Génie des Procédés et Matériaux, LGPM in CentraleSupélec, not only developing this master thesis, but also working as the team specialist on surface characterization and mechanisms of adsorption developing several protocols for the Micromeritics 3FLEX accelerated surface area and porosimetry system, presented in annex 1.

The development of these protocols was essential for the development of this master thesis, but also for the laboratory, allowing several team members to perform adsorption studies on their samples.

Furthermore, as a result of this work on surface characterization and mechanisms of adsorption, the author participated in the publication (presented in annex 2):

**“Thermogravimetric analysis, composition and pore development during pyrolysis of coconut core”** presented on the *21<sup>st</sup> International Symposium on Analytical and Applied Pyrolysis*

This study, despite not being on poplar wood, followed the same guidelines and focused on the same topics of this thesis being a very valuable complement to the development of this study.

## 4. Structure of the Thesis

This thesis comprises a work developed during the last 6 months and apart from the results the intention has also been to review areas of interest up to date through literature studies.

For guidance, while reading this work, the following description will hopefully make reading easier:

The introduction section opens with a perspicuous discussion about the concept of biorefinery and the importance of using sustainable energy sources. Thereafter follows a brief introduction to the major constituents of solid wood together with an introduction of some examples of value-added products from wood.

On the state of the art section, this work starts giving attention to the different types of wood treatment focusing after on the thermal treatments, where it makes a review of different kinds of thermal treatments as well as their effects on the physiochemical structure of wood.

After these introductory parts, the different studies are presented continuously with a background to each subject followed by results and contribution from current thesis conducted by the author. In some cases, an up-to-date literature review of the topic is added.

The first study presented is focused on the effect of heat treatment on the adsorption mechanisms on poplar wood, as well as the changes on the pore structure of poplar and, consequently, the effects on the specific surface area of this material.

The second part presents a thermogravimetric study on the thermal degradation of poplar wood allowing to draw conclusions on the conditions for degradation of each component of the material.

The third study presented is focused on the chemical changes during the process of heat treatment of poplar by performing an elemental analysis, a rigorous method to assess the quantities of Carbon, Nitrogen, Hydrogen, Sulfur and Oxygen on the samples.

Finally, some initial perspectives on the water sorption of heat treated poplar wood by using a volumetric system are presented, in order to allow the evaluation of the hygroscopicity of different samples treated at different temperatures.

In the end of this work, the main conclusions of the developed studies are presented, as well as the most interesting points to highlight.

## 5. Using Wood: The Biorefinery Approach

The mankind's strong dependence on fossil fuels comes from the intensive use and consumption of petroleum derivatives which, combined with diminishing petroleum resources, leads to environmental and political concerns. Emissions of greenhouse gases (GHG), such as carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O), arising from fossil fuel combustion and land-use change as a result of human activities, have been scientifically proven to be responsible for perturbations on the Earth's climate. (Cherubini, 2010)

It is increasingly acknowledged globally that plant-based raw materials (i.e. biomass) have the potential to act as substitutes of a large fraction of fossil resources as feedstock for industrial productions, addressing both the energy and non-energy (i.e. chemicals and materials) sectors. Recently, society started to acknowledge alternatives given by a future sustainable economy based on renewable sources and has been starting to finance R&D activities for its implementation. The production of liquid biofuels from biorenewable feedstock has been regarded as a promising alternative for the future. (Demirbas, 2009)

Currently, fuels obtained from biomass (i.e. biofuels) are identified as 1<sup>st</sup> and 2<sup>nd</sup> generation biofuels. (Jansen, 2013) First generation biofuels usually refer to biofuels produced from raw materials that compete with food and feed industries. Because of this competition, these biofuels give rise to ethical, political and environmental concerns. In order to overcome these issues, production of second generation biofuels, from raw materials based essentially on waste, residues or non-food crop biomass, gained an increasing global interest in the last few years as a possible "greener" alternative to fossil fuels and conventional biofuels. As a way to improve the 2<sup>nd</sup> generation biofuel production, using biomass within a biorefinery concept is expected to guarantee additional environmental benefits and implement national energy security, thanks to the co-production of both bioenergy and high value chemicals. (Naik *et al.*, 2010)

Among several definitions of biorefinery, the most exhaustive was recently performed by the IEA (Kamm, 2008): "Biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy". The biorefinery concept is capable of embracing a wide range of technologies able to separate biomass resources (wood, grasses, corn) into their building blocks (carbohydrates, proteins, triglycerides) which can be converted to value-added products, biofuels and chemicals. A biorefinery works as a facility (or network of facilities) that promotes the integration of biomass conversion processes and equipment to produce biofuels, power, and chemicals from biomass. This concept is analogous to today's petroleum refinery, which produces multiple fuels and products from petroleum. (Cherubini, 2010)

The most important biobased products are today obtained from conversion of biomass to basic products like starch, oil, and cellulose. In addition, chemicals like lactic acid and amino acids are produced and used in the food industry. Other already commercially available biobased products include detergents, cleaning compounds, dielectric fluids, dyes, inks, lubricants, packaging materials, paints and coatings, plastic fillers, polymers, solvents, and sorbents. Some examples of biorefinery and non-conventional biomass industries which are already competitive in the market are listed in Cherubini *et al.*, along with some existing pilot and demo plants.(Cherubini *et al.*, 2012) The majority of the existing biofuels and biochemicals are currently being produced by single production chains and not within a biorefinery concept, and usually require raw materials competing with the food and feed industries. Their interest is thereby limited. By contrast, lignocellulosic crops can reduce the competition for fertile land, since they can be grown on land which is not suitable for agricultural crops. Moreover, in comparison with conventional crops that can only give a small contribution to the above standing biomass, biorefineries based on lignocellulosic feedstocks can have access to larger quantities of biomass per hectare yields, since the whole crop is available as feedstock.(Kamm and Gruber, 2006)

The development of biorefinery industries as industrial complexes is expected to occur over next few years. In contrast with oil refinery, which almost invariably requires plants with great dimensions, biorefineries will most probably be able to work on a wide range of installations with different sizes. In this context, several bio-industries promote the combination of material flows in order to guarantee a complete utilization of all biomass components: the residue from one bio-industry becomes an input for other industries, leading to an integrated bio-industrial system.(Naik *et al.*, 2010)

Although the applications of biobased products are raising rapidly, there are yet some limitations on their success and efficiency, mostly due to high non-competitive costs, poor technology reliability and limited resource availability.(Chen *et al.*, 2015)

Among these products and alternative fuels being developed, the produced energy from biomass is one of the most attractive resources to fill the requirements of a substitute of fossil energy.

Contrarily to fossil fuels, biomass is considered a renewable resource because it requires a reduced period of time to replace what is used as an energy resource. If this resource is used in a sustainable way, the net carbon emissions over the time frame of a cycle of biomass production should be reduced close to zero.(Sriram and Shahidehpour, 2005) However, some studies had shown an increase in greenhouse gas (GHG) emissions for some cases of biomass utilization for biofuels, due to GHG emissions resulted by use of fossil energy during several steps of the operation involved in supply-chain logistics, these conclusions show that, there is a long way yet until reaching the desired success and efficiency on these processes.(Jin *et*

*al.*, 2013) Apart from the process, there are also several less attractive characteristics that limit its application like high moisture content, low calorific value, hygroscopic nature and low bulk density, which leads to a low conversion efficiency as well as difficulties in its collection, grinding, storage and transportation. (Chen *et al.*, 2015) Therefore, its use as raw material is not viable, by which is necessary a treatment before its utilization.

Since last century, there has been done a lot of studies in order to improve the digestibility of lignocellulosic biomass, mainly promoting an increase on the efficiency of conversion of its components to ethanol, methane and, in the last years, also to hydrogen. However, it is not perfectly clear yet, which are the most important characteristics of the lignocellulosic biomass to determine a successful pretreatment. Additional problems, like production of recalcitrant or inhibitory products, are yet to be studied. (Hendriks and Zeeman, 2009)

A lot of literature is written about different pretreatment methods to enhance the digestibility of lignocellulosic material. The objective of this thesis is to study the structural changes of poplar wood after thermal treatment, in order to assess the effect of different temperature conditions on the characteristics of the lignocellulosic biomass studied.

## **6. The composition of lignocellulosic material**

The constitution of lignocellulosic material is based mainly in three different types of polymers, namely cellulose, hemicellulose and lignin, which are associated with each other and a group of components called extractives. (Fengel and Wegener, 1983)

### **6.1. Cellulose**

Cellulose is formed by D-glucose subunits, linked by  $\beta$ -1,4 glycosidic bonds. (Fengel and Wegener, 1983) The cellulose in a lignocellulosic material consists of portions with a crystalline (organized) structure, and parts with a, not well-organized, amorphous structure. The cellulose strains are structurally together and form so called cellulose fibrils or cellulose bundles. These cellulose fibrils are mostly independent and their bound through hydrogen bonding is generally weak. (Laureano-Perez *et al.*, 2005)

### **6.2. Hemicellulose**

Hemicellulose is a complex carbohydrate structure that consists of a group of different polymers like hexoses (like mannose, glucose and galactose), pentoses (xylose and arabinose, for example), and sugar acids. For hardwoods and plants used in agriculture (straw and grasses), the major component of hemicellulose is xylan; in the case of softwoods the major component is glucomannan. (Fengel and Wegener, 1983)(Saha, 2003)

Having a lower molecular weight than cellulose, and lateral chains with a reduced size consisting of various sugars, hemicellulose is a component that can be easily hydrolyzed. (Fengel and Wegener, 1983) Hemicellulose works as a link between the lignin and the cellulose fibers and increases the stiffness of the whole cellulose-hemicellulose-lignin network. (Laureano-Perez *et al.*, 2005) Different hemicellulose compounds have different solubility, here they are presented in descending order according with its solubility: mannose, xylose, glucose, arabinose, and galactose. These compounds become more soluble with the increase of temperature. For more complex polymers, the solubility could not be predicted yet, mainly due to unknown melting points. (Gray *et al.*, 2003) Inside water, the solubilization of hemicellulose components begins close to 180 °C. (Ortwin and Bobleter, 1994) However, other studies consider that already at 150 °C parts of the hemicellulose solubilize. (Garrote *et al.*, 1999) The solubility of lignocellulose constituents is dependent on temperature and other properties of the environment like moisture content and pH. (Fengel and Wegener, 1983)

The extraction of xylan of hemicellulose can be performed in either an acid or alkaline environment, in contrast extracting glucomannan is very difficult in an acid environment and needs a stronger alkaline environment than xylan to be extracted. Xylan seems to be the part that can be extracted the most easily. (Fengel and Wegener, 1983) (Lawther *et al.*, 1996b)

Between the three polymers that constitute lignocellulosic materials, hemicelluloses are the most sensitive to thermal and chemical treatments. (LeVan *et al.*, 1990) (Winandy, 1995) During these treatments, the side groups of hemicellulose react, followed by the hemicellulose backbone. (Sweet and Winandy, 1999)

### 6.3. Lignin

Lignin is, after cellulose and hemicellulose, one of the most abundant polymers in nature and is present in the cellular wall. It is an amorphous heteropolymeric compound formed by three main phenylpropane units (p-coumaryl, coniferyl and sinapyl alcohol) that are linked together by different kind of bonds. The main role of lignin is to give the plant structural support, impermeability, and increase its resistance against microbial attack and oxidative stress. Lignin also shows optical inactivity and insolubility in water; all these factors contribute to make the degradation of lignin very difficult. (Fengel and Wegener, 1983)

The solubility of the lignin in different environments depends on its constitution. (Grabber, 2005) (Ortwin and Bobleter, 1994)

### 6.4. Extractives

Extractives correspond to all components that can be extracted from wood without affecting the wood structure. The most important extractives are terpenes, fats/waxes,

phenolic components, sugars and salts. These extractives have a major importance because they offer protection to the tree as well as serving as backup nutrition. (Cole, 2013)

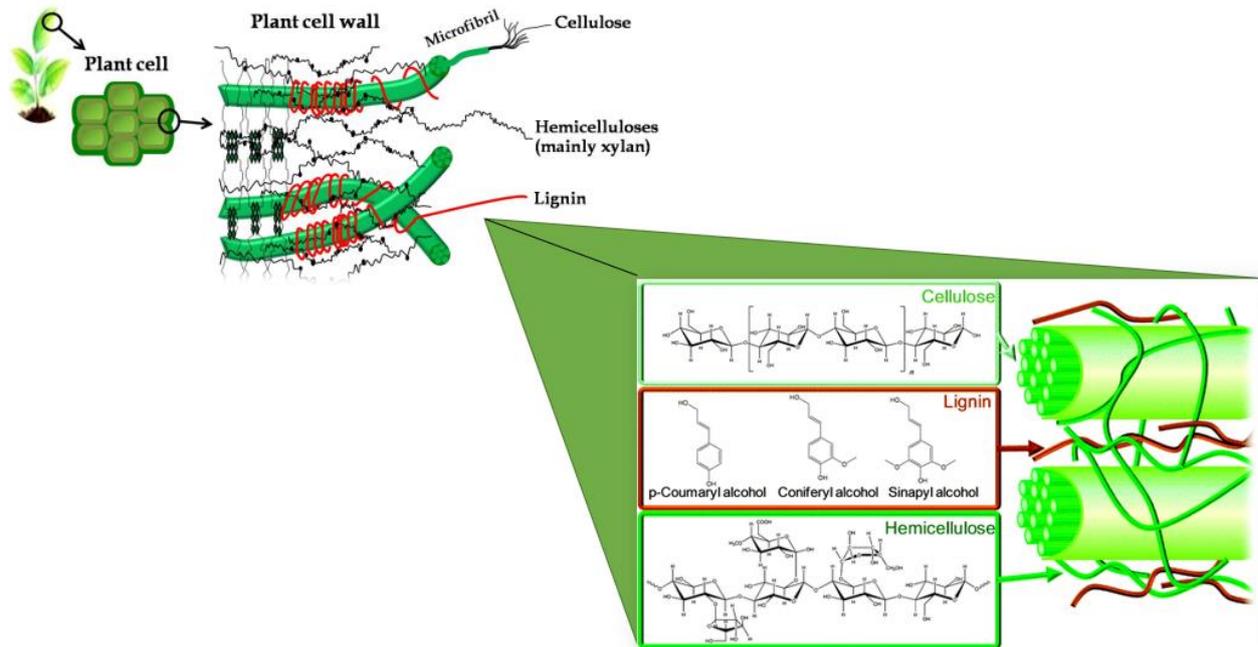


Figure 1- The composition of lignocellulosic materials. Adapted from Tomme *et al.*, 1995

## 7. Value-Added Products from Wood: Examples

### 7.1. Methane production by anaerobic digestion

The production of methane from lignocellulosic material normally occurs in a three-step process, namely pretreatment of the biomass, anaerobic hydrolysis resulting in methane production, and a treatment of the liquid part. The process of separation for this product is not required, because, under normal conditions, methane is in gaseous state and will be released from the liquid fraction.

Pretreatment acts as a tool to improve the efficiency of hydrolysis and, consequently, the total methane yield. A consortium of microorganisms is responsible for hydrolyzing the lignocellulose and converting it to methane. This is done in one reactor for energy production and recovery.

Using a group of different microorganisms can be very beneficial because the majority of components, like monosaccharides, volatile products and even compounds that promote inhibition like furfural and soluble lignin compounds can be converted to methane. (Benjamin *et al.*, 1984)(Fox *et al.*, 2003)

## 7.2. Ethanol production by fermentation

The production of ethanol from lignocellulosic material is based on five processes, namely pretreatment, (enzymatic) hydrolysis, fermentative process, product separation, and treatment of the liquid part. For the improvement of the efficiency of production and the total yield of the hydrolysis step the pretreatment is necessary. Converting (hemi) cellulose to monomeric sugars can occur using a chemical method with acids or an enzymatic method with addition of cellulases (enzymes responsible for the hydrolysis of cellulose). The fermentation of the produced monomeric hexoses to ethanol can occur quite easily. In contrast, for pentoses, the fermentation is only possible using a few strains. Volatile products are also not easily fermented to ethanol. During the fermentation, the biggest problem is that the formed product ethanol inhibits yeasts/bacteria responsible for the fermentation. Due to this, there is a limit to the concentration of fermentable sugars. For methane production, this problem does not appear as methane separates from the liquid phase. The ethanol, in opposition, has to be separated from the fermentation broth by distillation (Mosier *et al.*, 2005).

Furfural and other inhibitors like soluble lignin compounds also can be problematic for the fermentation step, because such compounds can interfere, inhibit, or even stop the fermentation. (Laser *et al.*, 2002)

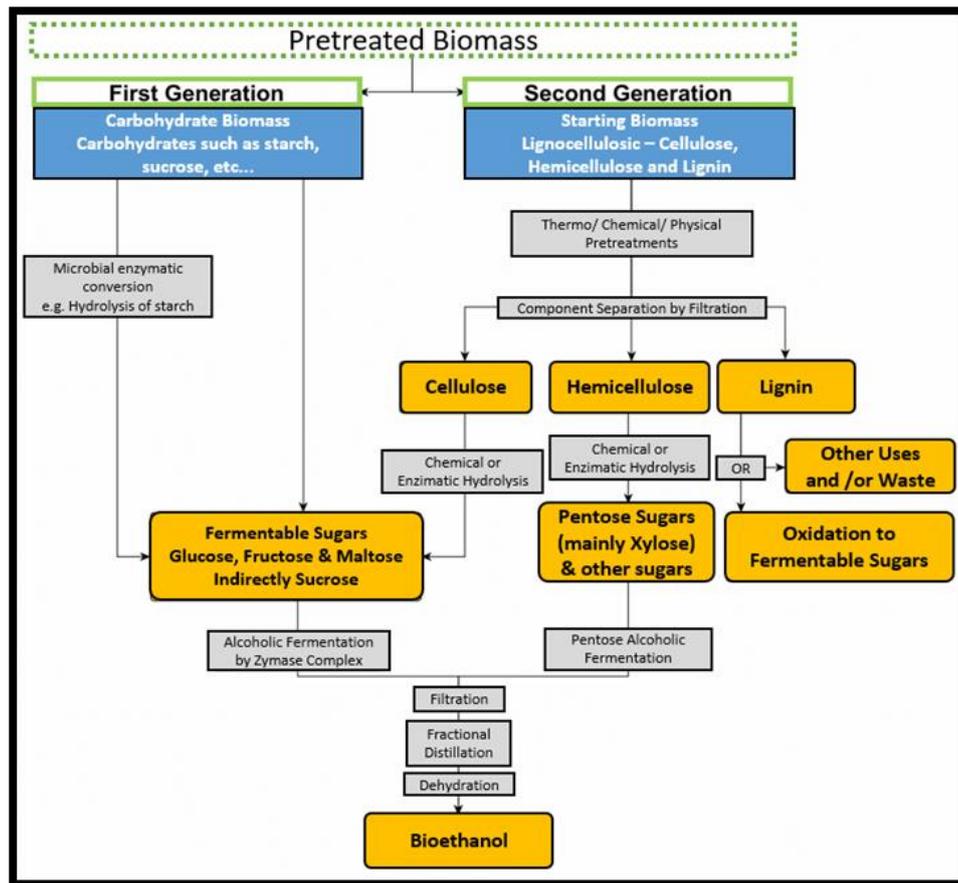


Figure 2- Process of Production of Bioethanol

## II. State of the Art: Wood Treatment Methods

The treatment of wood can lead to active modifications, which promote a change to the chemical nature of the material, or passive modifications, where despite occurring a change in properties, there is no alteration of the chemistry of the material. The classification of some modifications has been based on the resulting changes that occur at the cell wall level. (Norimoto and Gril, 1993). The different wood treatment methods are described below. Since during this work only thermal pretreatments were used, this state of the art will focus on this particular kind of treatments.

### 1. Chemical Treatment of Lignocellulose

The majority of the chemical treatment methods performed to date have involved the utilization of compounds capable of promoting a chemical reaction with the cell wall polymer hydroxyl groups. This reaction promotes the formation of a single chemical bond with one hydroxyl group, or cross-linking between two or more OH groups. The chemical nature and constitution of the cell wall polymers is thus altered, which can lead to new properties. Chemical modification of wood has been the subject of a number of reviews. (Kennedy *et al.*, 1995)(Kumar, 2007)(Birkinshaw, 1998)

### 2. Thermal Treatment of Lignocellulose

During treatment, the lignocellulosic biomass is heated. With the increasing of temperature between 150 °C and 180 °C, components of the material, initially the hemicelluloses after celluloses will start to solubilize.(Ortwin and Bobleter, 1994)(Garrote *et al.*, 1999) As written before, the composition of the hemicellulose backbone and the lateral groups can define the stability of the hemicellulose. Looking at the two dominant components of this compound (xylan and glucomannan), the xylans are, thermally, the least stable. Above 180 °C, an exothermic reaction of the hemicellulose starts.(Beall and Eickner, 1969) This temperature of 180 °C is most likely to be just an indication of the temperature at which the degradation of hemicellulose begins, due to the relation between the thermal reactivity of these materials and their constitution.(Fengel and Wegener, 1983)(Hon and Shiraishi, 2000)

As the treatment starts, a part of the hemicellulose begins to hydrolyze and leads to the formation of acids. These acids can be able to catalyze the remaining hydrolysis of the hemicellulose.(Gregg and Saddler, 1996) Some studies concluded that other parameters than the catalyzing effect of formed acids can take a major role in the reaction of hemicellulose.(Liu and Wyman, 2003)(Zhu *et al.*, 2004)(Zhu *et al.*, 2005)

However, heat treatments lead frequently to the formation of soluble compounds, promoting the production of phenolic and heterocyclic compounds, being vanillin and others an example of that, especially in acidic environments.(Ramos, 2003) These formed compounds can affect the process by acting as inhibitors on bacteria, yeast and methanogens/archae.(Gossett *et al.*, 1982)(Brownell *et al.*, 1986)

Furthermore, if not removed, these compounds can rapidly suffer condensation and precipitation on the biomass due to their reactivity.(Liu and Wyman, 2003) Especially pretreatments at harder conditions lead these compounds to condensate and precipitate, sometimes even with soluble compounds.(Bobleter and Concin, 1979)(Lora and Wayman, 1978)(Negro *et al.*, 2003)

Other studies suggest that thermal pretreatment can also cause an increase of the Crystallinity Index (Crl) of cellulose, however there was not detected any increase when the Crl was already high.(Weimer *et al.*, 1995)

## **2.1. Process description and Mode of action**

### **2.1.1. Torrefaction**

In order to improve the properties and characteristics of wood, heat treatments have been studied for a very long time. Studies from the beginning and middle of the 20<sup>th</sup> century showed that high temperature treatments lead to a decrease of the equilibrium moisture. (Esteves and Pereira, 2009)

Torrefaction is one of the most important strategies to treat biomass and its benefits include: higher heating value; lower atomic O/C and H/C ratios, lower moisture content, higher hydrophobicity, improved grindability and reactivity and more uniform properties of biomass.(Koppejan *et al.*, 2012) Torrefaction is one of the processes used to treat renewable materials that are most capable of competing with nonrenewable fossil fuel resources.(Spokas, 2010) During this treatment, a continuous supply of nitrogen is typically used to create the needed inert state. However, due to constant changes on the price of natural gas, using nitrogen can present some problems, however this can be avoided using air for this treatment.(Uemura *et al.*, 2015)

Thermal modification is invariably performed at temperatures higher than 180 °C. Temperatures lower than 140 °C only result in slight changes in material properties. Thermal treatments of wood above 300 °C lead to major changes on the structure of the material, as well as a great change in the degradation kinetics.(Hill, 2006)

The properties of thermally modified wood are highly dependent upon the thermal treatment employed, and taking these into account when comparing the various treatment methods is essential.

There are a variety of thermal modification methods that can be applied to wood. Important process variables include the following (Hill, 2006):

- time and temperature of treatment;
- treatment atmosphere;
- closed versus open systems;
- wood species;
- wet and dry systems;
- sample dimensions;
- use of catalysts.

### 2.1.2. Pyrolysis

Pyrolysis is the process of decomposition of materials applying a heat treatment in an atmosphere without oxygen or with a quantity of oxygen much lower than necessary for complete combustion. Differentiating pyrolysis from gasification is essential. Gasification is the process of decomposition of biomass to syngas by defining in a very restricted way the amount of oxygen present. Pyrolysis is a concept difficult to define in a very accurate way, especially when applied to biomass. Usually, older studies associate pyrolysis to carbonization, where the main product is a solid char. However, more recently, the term pyrolysis has been related with processes in which oils are preferred products, being the time frame much faster for this process. (Sinha *et al.*, 2000)

The main steps that occur during pyrolysis are presented below. (Sinha *et al.*, 2000)

- a) Heat transfer from a heat source, to increase the temperature of the material;
- b) The beginning of primary pyrolysis reactions promotes the releasing of volatiles and forms char;
- c) The presence of hot volatiles contacting with cooler solids results in heat transfer between hot volatiles and cooler unpyrolyzed material;
- d) Condensation of some of the volatiles in the cooler parts of the material, followed by secondary reactions, can produce tar;
- e) Autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition; and
- f) Further thermal decomposition, reforming, water gas shift reactions, radicals recombination, and dehydrations can also occur, which are a function of the process's residence time/ temperature/pressure profile.

Over the last twenty years, studies on pyrolysis have concluded that an efficient production of value-added products, including valuable chemicals, petrochemicals and fuels, could be obtained from carbonaceous raw materials. This way, the less valuable solid char

from conventional pyrolysis can be substituted by higher-value fuel gas, fuel oil, or chemicals from fast pyrolysis.(Bridgwater *et al.*, 1999) Characteristics of wood pyrolysis products depend on whether a hardwood or softwood species is pyrolyzed.

Pyrolysis processes can be mainly classified as conventional or fast pyrolysis, depending on the followed procedure and method.(Maschio *et al.*, 1992) Conventional pyrolysis has also been classified slow pyrolysis. Actually, despite the terms “slow” and “fast” being used, this terminology is not necessarily related with the times or heating rates involved in each. Many pyrolysis studies have been performed at rates that cannot be defined neither fast or slow but are conducted in a broad range between these extremes. A thermogravimetric study on beechwood flour showed that wood decomposition started at around 200 °C, reached a maximum rate of mass loss at 350 °C, and kept occurring until 500 °C, being capable of demonstrate the complex contributions of all the chemical constituents.(Jakab *et al.*, 2000)

### **Conventional Pyrolysis**

Conventional slow pyrolysis is an ancient technique and its main purpose has been producing charcoal. In slow wood pyrolysis, typically, biomass is heated until 500 °C. The vapor residence time varies.(Bridgwater *et al.*, 1999)(Bridgwater, 1994) The velocity of the release of vapors is not as high as it happens in fast pyrolysis. This way, components that are in the vapor phase continue to promote reactions between each other, as the solid char and some liquid are being formed. In slow pyrolysis, the heating rates practiced are less intense than in fast pyrolysis. A feedstock can be kept at constant temperature or slowly heated. The constant removal of formed vapors can occur. Vacuum pyrolysis is another type of pyrolysis.(Bridgwater, 1990)

### **Fast Pyrolysis**

Fast pyrolysis is a process where biomass is rapidly heated in an atmosphere without oxygen.(Boucher *et al.*, 2000)(Bridgwater, 1994) The decomposition of biomass during the process promotes the generation of vapors, aerosols and some charcoal. The formation of a liquid with a dark brown color occurs when vapors and aerosols cool down and condense, this liquid has a heating value that is about half that of conventional fuel oil.(Naik *et al.*, 2010) These processes produce different quantities of products being this related with the feedstock used. There is no generation of waste, because these products can each be used as a fuel and the gas can be reintroduced into the process. The heating rates in fast pyrolysis are much higher than conventional pyrolysis. Right now, the most technological advanced processes result in high liquid yields. There are essentially four features of a fast pyrolysis process.(Bridgwater, 2003) First, using very high heating and heat transfer rates, which usually requires a finely ground biomass feed. Second, a very rigorous pyrolysis reaction

temperature used, often between 425 and 500 °C. Third, vapor residence times having a very short duration (typically less than 2 s). Fourth and final, pyrolysis vapors and aerosols are rapidly cooled to origin bio-oil. Studies have been done using very high heating rates, at temperatures below 650 °C.(Bridgwater, 2003) A fast heating and rapid cooling are capable of producing the pyrolysis liquid products, which condense before occurring the breakdown of certain species promoting the formation of gaseous products. High reaction rates minimize char formation. It has been claimed that, under certain conditions, no char is formed.(Demirbas, 2005) At higher fast pyrolysis temperatures, the major product starts to be gas. Many researchers are studying these complex degradation mechanisms by conducting pyrolysis in unusual environments.(Thangalazhy-Gopakumar *et al.*, 2011)

### 3. Physiochemical Changes in Wood due to Pretreatments

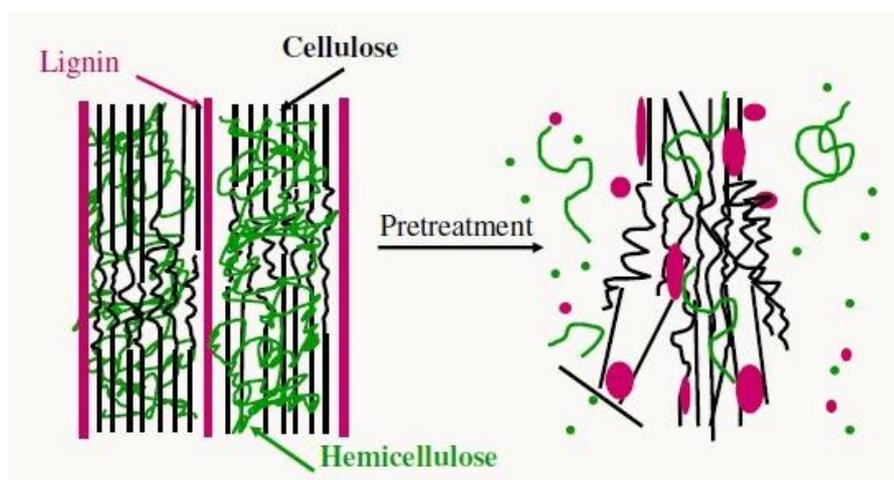
Performing a heat treatment on wood can cause the occurrence of a great variety of processes, which are related with the type of heating treatment employed. It is already clear that the extension of degradation in hemicelluloses is greater than in other macromolecular components, but the relative stability of the cellulose and lignin has been harder to determine.(Shafizadeh and Chin, 1977) Generally, above 180 °C, loss of polysaccharide material starts to increase, being this dependent on the treatment conditions. Identifying with precision the relative rates of degradation of the different components has been a difficult task because each experimental method employed provides different conclusions, and, as a consequence of this, the literature on this subject is sometimes contradictory and complex.

Biomass heat treatment results on a complex combination of products that have their origin on the treatment of cellulose, hemicellulose and remaining components, each of which with its own kinetic characteristics. Also, as previously discussed, the formation of secondary reaction products occurs from reactions between primary treatment products and between these components and the original constituents. Several chemicals produced from biomass were already presented.(Elliott 2004)(Elliott 2001) The heat treatment of each constituent is itself a complex process that depends on many factors. However, the major changes on the chemical components of plant biomass are discussed below.

Hemicellulose is the most thermosensitive compound being decomposed at temperatures between 200 °C and 260 °C, promoting the formation of more volatiles, less tars, and less chars than cellulose.(Weiland and Guyonnet, 2003) The majority of hemicelluloses do not yield significant amounts of levoglucosan. Much of the acetic acid released from wood during treatment is due to the deacetylation of the hemicellulose.

Typically, cellulose degradation starts between 240 °C and 350 °C to produce anhydrocellulose and levoglucosan. When the treatment of cellulose occurs at a heating rate of 12 °C/min under helium in differential thermal analysis (DTA) experiments, an endotherm reaction is observed at 335 °C (temperature of maximum weight loss). The reaction is complete at 360 °C. (Tang and Neill, 1964)

Analyzing now lignin, its characteristics differ, depending on the extraction or isolation process used to isolate them. Because lignin is irreversibly modified and partially degraded during isolation, thermal decomposition studies on separated lignin rarely match the pyrolysis behavior of this component when it is present in the original biomass. Lignin starts decomposing when heated between 280 °C and 500 °C. (Brebü and Vasile, 2010) Lignin pyrolysis results on the production of phenolic compounds due to the degradation of ether and carbon-carbon linkages. Lignin is a component harder to degrade than cellulose or hemicelluloses. Its pyrolysis leads to the production of higher quantities of char than does the pyrolysis of cellulose. The decomposition of this polymer in wood was proposed to start at 280 °C and continues to temperatures between 450 °C and 500 °C, with a maximum rate being observed at 350-450 °C. (Brebü and Vasile, 2010)



**Figure 3-** Simplified Impact of Pretreatment on Biomass. Adapted from Mosier et al. 2005.

Standard gravimetric methods have been vastly used to determine the relative proportions of the macromolecular components, and despite such studies being valuable, caution is required, since material loss is not the only factor indicating that degradation has occurred. Many studies have tried to determine the chemistry of thermolysis of wood by regarding the thermal behavior of isolated wood components, and much of the early work in this respect has been reviewed. (Beall and Eickner, 1969)

When using thermal analysis techniques, the results obtained can be quite different and heavily related with the method of preparation of the materials as well as the experimental parameters, particularly heating rate and atmosphere. Also relevant is the fact that the

chemistry of the thermal degradation of the isolated wood components is different from the one taking place within the cell wall, where, as seen before, several reactions can occur synergistically within the wood material. Due to processes competition occurring during heating, simultaneous endothermic and exothermic events happen, making it difficult to determine the precise temperature for the different processes.

The progressive heating of wood to higher temperatures produces condensable fractions, with loss of water and volatile extractives at temperatures below about 140 °C. Passing this temperature, cellular breakdown products start to appear deriving from the more sensitive species attached to the cell wall polymers, resulting in the production of acetic acid from the hemicelluloses; but also formic acid and methanol, as well the production of non-condensable gases (mainly CO<sub>2</sub>) as the temperature is increased. Furthermore, dehydration reactions also start to occur above 140 °C, as so-called “water of constitution” is lost, what leads to a decrease in OH content, gaining this importance as the temperature raises.(Bourgois and Guyonnet, 1988)

When the temperature increases even more, CO and CO<sub>2</sub> can be detected in great quantities in the gases produced. At around 270 °C, a significant change in the reaction kinetics occurs due to the onset of an exothermic reaction.(Stamm and Kline, 1946)

Despite the complexity of the chemistry of thermal modification being far from fully understood, it is possible to observe that there are obvious changes in the nature of the reactions taking place as the temperature increases. The exact points when the different reactions become dominant is the main question to be answered. As discussed, the atmospheric conditions have a significant influence. Under oxidizing conditions, the treatment leads to the formation of carbonyl-containing groups, while in a reducing or inert atmosphere the treatment promotes a loss of oxygen-containing species, although a reduction of OH groups can lead to a small increase in carbonyl functionality.(Hill, 2006)

According to some studies, the presence of oxygen promotes an initial decrease followed by an increase in carbonyl content (as determined from the IR spectrum) at extended heating times.(Chow, 1971) The decrease can be due to loss of ester-bonded and carboxylic-containing groups, with the following increase resulting from the oxidative carboxylation. When heating using nitrogen, a decrease in carbonyl content was detected, despite occurring a slight increase for longer treatment times. The influence of the temperature of treatment and the presence of wood extractives was clear on the results obtained.

The reaction chemistry is also affected by the presence of water, depending on the amount of water present and if the treatment can remove it or not. In the presence of water or steam the heat treatment contributes to the formation of organic acids (primarily acetic acid) that acts as a catalyst of the hydrolysis of hemicelluloses, and to a lesser extent the

amorphous cellulose.(Mitchell, 1988) The production of these acids can be improved in the presence of air (wet oxidation).

Hydrothermal processing results in the hydrolysis of polysaccharide due to the action of hydronium ions generated by auto-ionization of the water, although the production of hydronium ions from acetic acid is more important.(Garrote *et al.*, 1999) Temperature ranges from 150 °C to 230 °C are commonly used, because at lower temperatures the mechanisms of hydrolysis are very slow, whereas cellulose degradation starts between 210 °C and 220 °C. Cellulose degradation becomes predominant at 270 °C.

### **3.1. Effects on the Surface Characteristics of Wood**

#### **3.1.1. Torrefaction**

Particle size distribution curves, sphericity, and surface area are essential parameters for understanding the material's behavior during the process. Studies showed that torrefied biomass produces a narrower range of particle sizes compared to untreated biomass due to its characteristics being similar to coal.(Phanphanich and Mani, 2011)

Research on torrefied lignocellulosic materials found that, when comparing with untreated biomass, particles with smaller dimensions are produced. It was also observed that the particle distribution curve had an increase on the region of this particle size with increased torrefaction temperatures.(Phanphanich and Mani, 2011)

Torrefaction significantly affects the sphericity and particle surface area. The results of this study showed that sphericity and particle surface area increase as the temperature was increased to 300 °C. It was found, for ground, torrefied chips, that the sphericity increased from 0,48 to 0,62%, concluding that an increase in the surface area or decrease in particle size of torrefied biomass can be extremely important for efficient cofiring, combustion applications or even bioconversion.(Phanphanich and Mani, 2011) Also, the structure and particles of torrefied biomass become denser as the treatment diminishes the inter and intra particle empty spaces created after milling.(Esteban and Carrasco, 2006) Studies have indicated that torrefied material promotes the formation of powder with a favorable size distribution and sphericity, allowing it to respect the necessary regime for entrained-flow processes (gasifier and pulverized coal).(Ku *et al.*, 2016)

#### **3.1.2. Pyrolysis**

Studying the structural effects of the treatment and the influence of the particle size are important parameters for understanding material's behavior during the process of combustion. The fluid residence times for particles with bigger dimensions are long enough to allow secondary reactions of the volatiles produced by primary reactions (Bamford *et al.*,

1946)(Chan *et al.*, 1985). Large particle size also leads to large thermal gradient. If particles of the material have moisture, it escapes violently promoting cracking of the surface. Condensation of compounds and moisture can also take place. This aspect of pyrolysis requires further investigation. Despite reaction models being able to predict the general tar formation, the tar that results from condensation occurring locally is not considered.

Cracking of the wood surface during pyrolysis has been reported by many researchers (Pyle and Zaror, 1984)(Kansa *et al.*, 1977). Research has shown that serious structural failures, such as longitudinal channeling and surface cracking, occur.

The surface cracking alters the heating characteristics. Despite the total heat transfer remaining the same, heat is transferred faster due to the presence of cracks on the surface. Internal failures result in changed local porosity and permeability, promoting the development of pores with smaller dimensions and leading to major changes on the surface area of material.(Tinney, 1965)

## 3.2. The Wood-Water Relationship

Wood has a cell wall constituted by polymers containing hydroxyl groups what makes it a hygroscopic material. In an environment containing moisture, dry wood will absorb moisture until it is in equilibrium with the surrounding atmosphere. In the same way, saturated wood, in an atmosphere of lower relative humidity (RH), will lose moisture until equilibrium is reached. When the RH of the environment is stable, the wood will attain a constant moisture content (MC), known as the equilibrium moisture content (EMC). At this stage, the quantity of water molecules entering into the cell wall is exactly balanced by the quantity leaving into the atmosphere.(Glass and Zelinka, 2010)

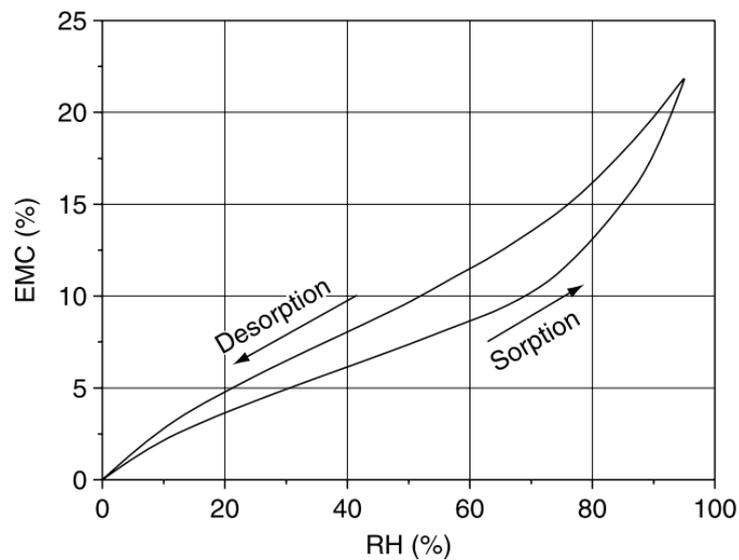
Wood adapts to the environment; in particular, it changes dimension in response to changes in atmospheric RH. As water vapor enters the wood cell wall, it promotes the swelling of the cell wall, causing the dimensions of the cell wall to increase, and as a consequence the wood increases in dimension, especially in the tangential direction, then the radial and least in the longitudinal direction.(Hiziroglu, 2007)

### 3.2.1. Moisture Sorption and Desorption

The sorption and desorption behavior of wood is studied by determining the relationship between EMC and RH at constant temperature (an isotherm). This plot produces the classic sigmoidal relationship shown in figure 4. It is not possible to study the relationship to 100% RH and, generally, experiments of this kind are terminated at around 95-98% RH. For high RH, the EMC of the wood is increasing rapidly. The relationship between EMC and RH in the sorption and desorption acts in a different way, giving rise to the phenomenon of hysteresis.(Hill, 2006)

Many studies and models have been developed that consider the sorption properties of wood in the presence of moisture: these have been discussed in a number of works. (Skaar, 1988)(Siau, 1984) The deconvolution of the curves of sorption or desorption isotherm can occur in two components. These are often taken to represent a single water layer (associated with the primary sorption sites, OH groups), and a component with several layers where the cell wall bound with water molecules is less intimately associated with the fixed cell wall OH groups. (Hill, 2006)

Studies of the water sorption properties of activated carbons, which are obtained by the pyrolysis of different carbonaceous materials in the presence of carbon dioxide, oxygen or water can be found in the literature. (Każmierczak *et al.*, 2013)(Popescu *et al.*, 2015)



**Figure 4** - A sorption and desorption isotherm, showing hysteresis. Adapted from Hill, 2006.

### III. Materials and Methods

#### Feedstock preparation

Poplar (genus *populus*) was used in the form of powder. For powder preparation was used an IKA M 20 Universal grinding mill (IKA), the powder was then sieved through a mesh with 0,63 mm of diameter to obtain particles with less than that size. The specifications of this device are in chapter I of the annex 1.

#### Surface structure characterization

The specific surface area and pore size distribution of untreated and treated poplar samples at temperatures of 250 °C, 300 °C, 350 °C, 400 °C, 450 °C and 500 °C were determined by nitrogen adsorption. Nitrogen isotherms were performed on a Micromeritics 3FLEX accelerated surface area and porosimetry system (Micromeritics Instrument, Norcross, GA). Nitrogen adsorption was performed at -196,15 °C with 5 s equilibration intervals using manufacturers settings. Data were collected from a relative pressure ( $P/P_0$ ) of 0,0001 to 0,995. For all samples, the degassing step was done overnight at 80 °C, in order to guarantee an efficient cleaning of the surface of the samples. The specifications of this device and the developed protocol are in chapter II of annex 1.

**BET Model:** Total specific surface area was calculated using the Brunauer, Emmett and Teller (BET) adsorption isotherm model (Sing, 2001) for the nitrogen isotherm data. Specific surface area was calculated from the slope and y-intercept of the linear region of the BET transformation versus relative pressure plot.

**Density functional theory:** Density functional theory (DFT) model predictions of pore size distributions were calculated using the DFT Plus Models Library. The model assumed a slit pore geometry. (Balbuena and Gubbins, 1993) Model DFT nitrogen isotherms were fit to the experimental isotherms using a deconvolution technique by a non-negative least squares method, as described in previous studies, (Olivier *et al.*, 1994) to calculate the pore size distribution. The DFT model isotherms ranged from 10 to 2000 Å in a 70-step geometric progression.

#### Thermogravimetric analysis

All samples prepared were subjected to a heat treatment in a thermogravimetric device Netzsch STA 449 F3 Jupiter (NETZSCH group), making use of 9 mg alumina crucibles as sample support for the weighting. Nitrogen was used as gas flow at flow rate of 50 mL/min under 0,5 bar of pressure. The specifications of the device are in chapter III of the annex 1.

Six temperatures (250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C) were tested at isothermal conditions during 2 hours, with a previous treatment of drying at 100 °C for 30 min and with a heating rate of 20 °C/min for all heating phases.

## Elemental Analysis

The elemental analysis was used to assess poplar samples' composition after being subject to different temperatures in the thermogravimetric device: treated at 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C.

Before elemental analysis, all samples were dried at 80 °C overnight and then conserved in a desiccator. This experiment was done in an organic elemental analyzer (Thermo Scientific) and was performed in two different analyses: determination of carbon, hydrogen, nitrogen and sulfur (CHNS), and determination of oxygen. For CHNS determination were used standard samples (BBOT, methionine and benzoic acid), in order to make the calibration curve for each element. Additionally, vanadium oxide  $V_2O_5$  was added to the samples, due to the high content of carbon expected, especially for samples treated at higher temperature, ensuring a good resolution of the peaks. For oxygen determination, the used standards were BBOT and benzoic acid to obtain the calibration curve. In this case,  $V_2O_5$  was not used since carbon wasn't measured in this experiment. The specifications of the elemental analyzer, as well as the calibration curves are presented in chapter IV of the annex 1.

## Water Sorption Study

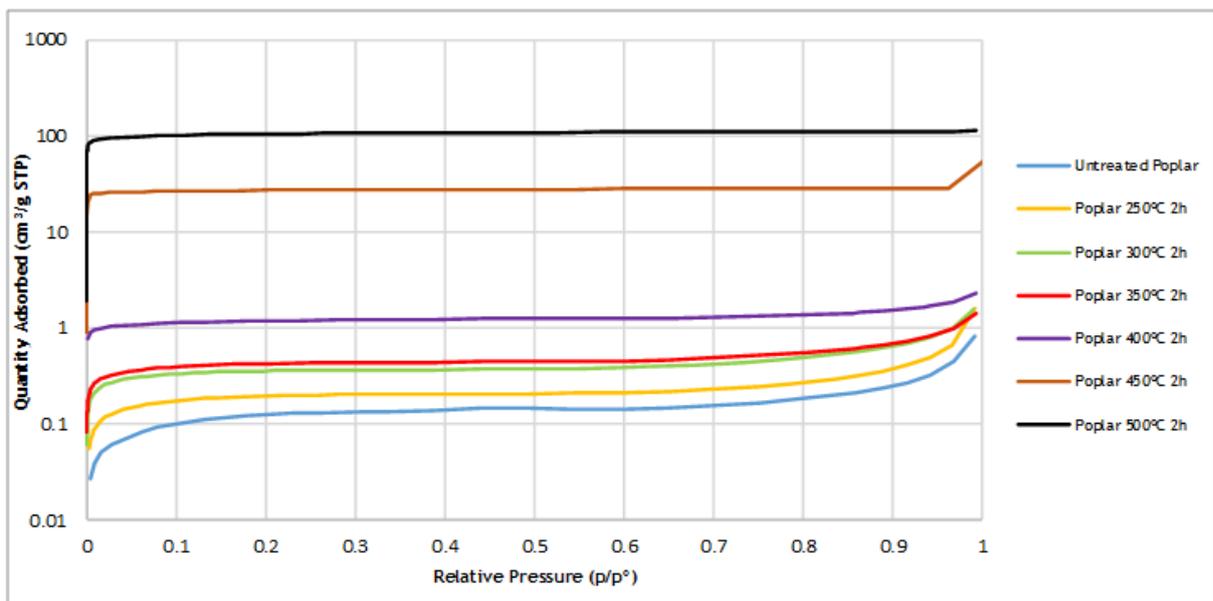
The water sorption isotherms of untreated and treated poplar samples at 500 °C were determined. These isotherms were performed on a Micromeritics 3FLEX accelerated surface area and porosimetry system (Micromeritics Instrument, Norcross, GA). The water sorption was performed at 30 °C with 5 s equilibration intervals using manufacturers settings. Data were collected from a relative pressure ( $P/P_0$ ) of 0,01 to 0,99. The samples were degassed overnight at 80 °C, in order to guarantee an efficient cleaning and drying of the samples. The specifications of this device and the developed protocol are in chapter V of annex 1.

## IV. Results and Discussion

### 1. Adsorption Study: Surface Area and Porosity Distribution Analysis

The nitrogen adsorption isotherms for the untreated and heat treated poplar samples obtained at different temperatures were determined. Figure 5 shows the adsorption isotherms of all samples. As can be seen from the figure, with the increasing of the temperature treatment the characteristics of the isotherms change. Until reaching the 400 °C, these isotherms show, at low relative pressures, a lower and less pronounced increase in the quantity of nitrogen adsorbed, which is followed by a plateau at higher relative pressures and would end with a huge increase at relative pressures close to 1 due to the condensation of the adsorptive, indicating a type II isotherm according to the IUPAC classification.(Rouquerol *et al.*, 1999) The type II isotherm represents a material with low porosity having its pores a bigger diameter, being in the range of meso and macropores.

However, above this temperature treatment, the isotherms start gradually to change their shape, becoming the initial increase bigger with the increasing of temperature treatment. When the temperature of treatment is 450 °C, it is already possible to see a different type of isotherm. As can be seen from figure 5, the major uptake of nitrogen occurs at very low relative pressures (lower than 0,001), for this kind of adsorption isotherm, which is followed by a plateau at higher relative pressures, indicating a type I isotherm according to the IUPAC classification.(Rouquerol *et al.*, 1999) The type I isotherm represents a material with meso and microporous structure. The major uptake occurs at low relative pressures indicating a highly porous material with narrow pore size distribution.



**Figure 5** -  $N_2$  adsorption isotherms at  $-196,15\text{ }^\circ\text{C}$  of Untreated and Heat Treated Poplar samples.

Looking at these two different types of isotherm, it can be concluded that the increasing of the temperature for the same time of treatment led to a change on the meso and microporous structure of the material what promoted a great increase on the surface area, as seen in table 1.

Micropores have molecular dimensions, the effective radii being less than 20 Å. The adsorption in these pores occurs through volume filling, and there is no capillary condensation taking place. The adsorption energy in these pores is much larger compared to larger mesopores or to the nonporous surface because of the overlapping of adsorption forces from the opposite walls of the micropores. In other hand, the mesopores, also called transitional pores, have effective dimensions in the 20 to 500 Å range and these pores are characterized by capillary condensation of the adsorbent with the formation of a meniscus of the liquefied adsorbate. Besides contributing significantly to the adsorption of the adsorbate, these pores act as conduits leading the adsorbate molecules to the micropore cavity.

From the results obtained, it was possible to explore and determine the pore size distribution of each sample.

Firstly, the choice fell on the classical macroscopic, thermodynamic concepts which are based on the assumption of a certain pore filling mechanism. Methods resulting on the application of Kelvin equation linked to the pore condensation phenomena.(Barrett *et al.*, 1951) Further studies led to conclude that these methods are only viable for mesopore size analysis, failing to correctly describe the pore filling of micropores and even narrow mesopores.

Other classical theories, like for example the Dubinin-Radushkevich approach (Dubinin and Stoeckli, 1980), and semiempirical treatments such those of Horváth and Kawazoe (Horváth and Kawazoe, 1983), and Saito and Foley (Saito and Foley, 1991) are focused on describing micropore filling but cannot be applied for mesopore size analysis. Hence, in case a material contains both, micro and mesopores, at least two different methods had to be used to obtain the pore size distribution from such an adsorption isotherm.

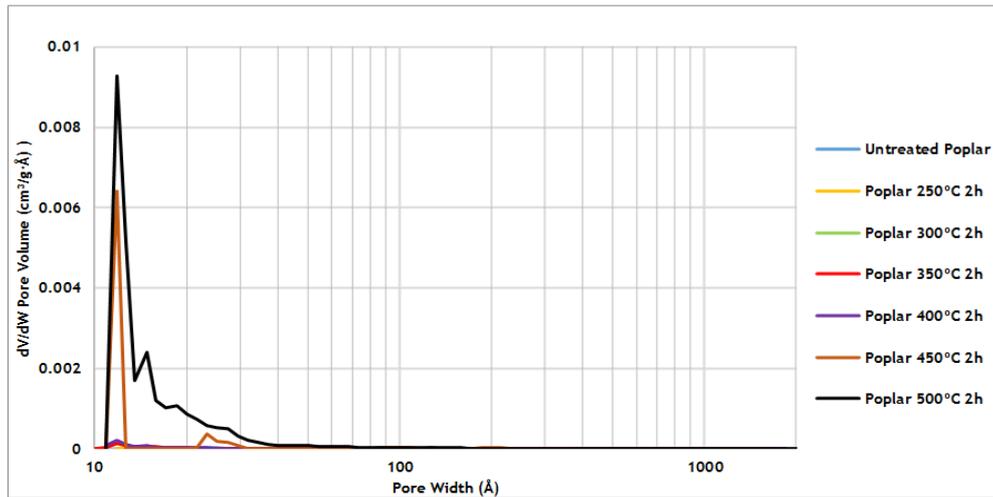
Furthermore, the accuracy of such thermodynamic, macroscopic methods is limited, because of the assumption that the pore fluid has similar thermophysical properties as the bulk fluid. (Madani *et al.*, 2015)

Contrasting with these macroscopic approaches, methods like the Density Functional Theory (DFT) or methods of molecular simulation (Monte Carlo simulation methods (MC), Molecular Dynamics methods (MD)) are capable of providing not only a microscopic model of adsorption but also a more realistic description of the thermodynamic properties of the pore fluid.

These theories, which are based on statistical mechanics, establish a connection between macroscopic properties and the molecular behavior. Therefore, to achieve a more realistic

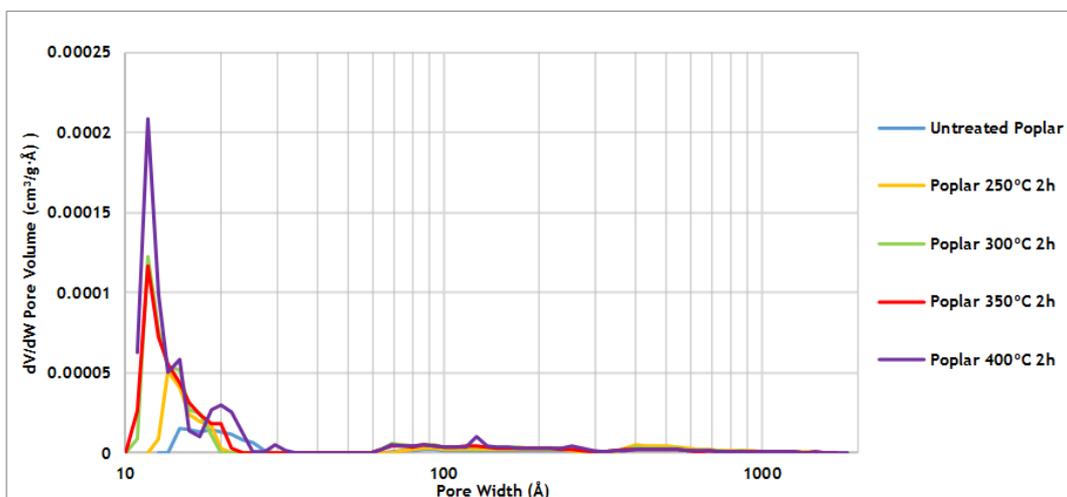
description of adsorption phenomena and an accurate and comprehensive pore size analysis, methods such as the DFT of inhomogeneous fluids and Monte Carlo simulations, which bridge the gap between the molecular level and macroscopic approaches, are taking a major role. (Landers *et al.*, 2013)

Ultimately, and taking in account the characteristics of samples, the method used to determine the pore size distribution was the Density Functional Theory (DFT). This way, figures 6 presents the DFT pore size distributions of the samples



**Figure 6** - DFT (Density Functional Theory) pore size distribution for Untreated and Heat Treated Poplar Samples

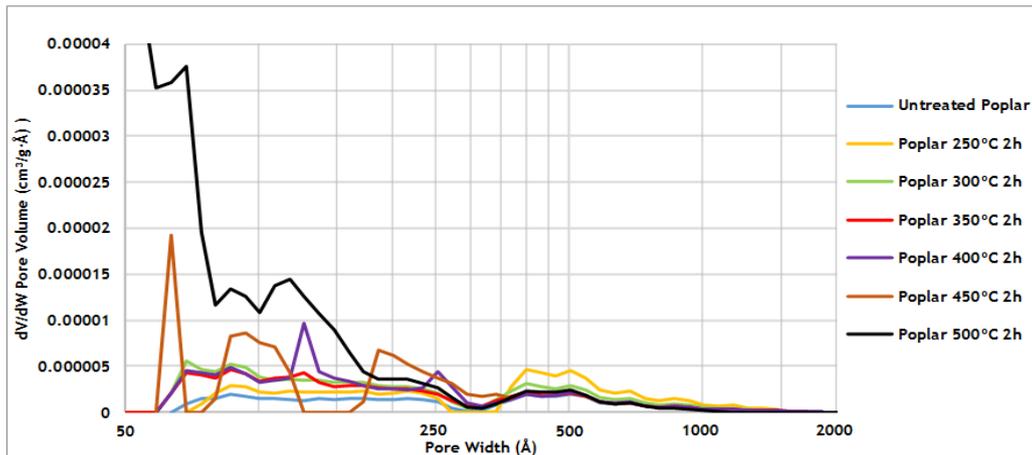
Due to the great differences between volume of pores on the micropores region, particularly between 450 °C and 500 °C and the rest of the samples, in figure 7, the 450 °C and 500 °C samples were not plotted, in order to allow the better evaluation of lower temperatures pore size distributions.



**Figure 7** - DFT (Density Functional Theory) pore size distribution for Untreated and Heat Treated Poplar Samples until 400 °C.

One interesting thing to regard in figure 7 is the differences between volume of pores on the micropores region and on the meso and macropores regions. This way, in figure 8, all the

samples are plotted but zooming only the meso and macropores regions, in order to better assess the pore size distributions only on this range.



**Figure 8** - DFT (Density Functional Theory) pore size distribution for Untreated and Heat Treated Poplar Samples  
(Zoom of the Meso and Macropores Region)

As can be seen comparing the results presented, the volume of pores on the micropores region for samples treated at higher temperatures is much greater compared with the volume of pores for samples below 400 °C. There are three mechanisms that occur during high-temperature treatment: thermal degradation, hornification and microscopic cell wall damage, that affect the physical and mechanical properties of wood. These three mechanisms are also capable of affecting its porosity. In the first case, thermal degradation of wood components after exposure to elevated temperatures (Esteves and Pereira, 2009) can lead to the formation of cavities within the cell wall. It has been reported that the removal of hemicelluloses and lignin during pulping created new pores within the fibre cell wall (Maloney and Paulapuro, 1999). In the second case, as water exits the pores during drying, the pore walls start to collapse, eventually leading to bigger pores closure and formation of smaller ones by irreversible hydrogen bonding called the process of hornification. (Diniz *et al.*, 2004) In the third and final case, anisotropic drying shrinkage of cell wall layers promotes internal drying stresses, which can lead to damage in the wood cell walls. (Thuvander *et al.*, 2001) Drying damage is manifested as microcracks irregularly distributed within the cell wall. (Wallström and Lindberg, 1999)

Looking at the figures, it is possible to see that during the process of heat treatment occurs a development of porosity which increases with the intensity of the treatment, this development of pores in the structure of poplar can be mainly due to the thermal degradation of the main components of the material, which promotes the appearance of micropores, as explained before.

Furthermore, this thermal degradation leads to a reduction on the oxygen and hydrogen molecules on the sample, which leads to the formation of a great quantity of micropores inside the carbon structures.

In the meso and macropores regions, it is possible to see that for pores with bigger dimensions, between 400 and 500 Å, the volume of pores increases for the lowest temperature treatment and then starts to decrease, this can occur because for lower temperatures the treatment will only lead to the formation of bigger cavities due to the process of drying and volatilization. Higher temperatures, in contrast, will lead to the formation of smaller pores, occurring a conversion of bigger pores in smaller ones due to the process of drying and structure degradation inside the material that promote the collapse of these macrostructures (hornification), being this increase visible for pores under 250 Å.

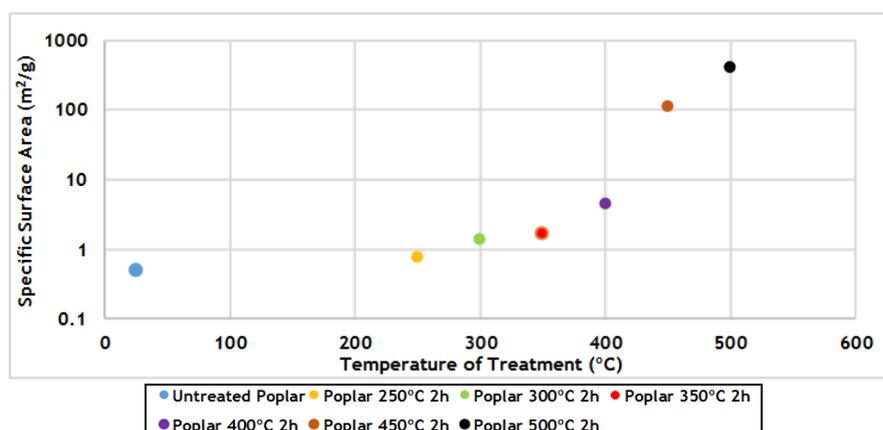
*Table 1 - Specific Surface areas of Untreated and Heat Treated Poplar Samples.*

Sample	Untreated Poplar	Poplar 250 °C 2h	Poplar 300 °C 2h	Poplar 350 °C 2h	Poplar 400 °C 2h	Poplar 450 °C 2h	Poplar 500 °C 2h
$S_{BET}$ (m <sup>2</sup> /g)	0,50	0,75	1,38	1,64	4,42	111,36	413,06

The effect of heat treatments on the BET specific surface area of samples are shown in table 1. BET specific surface areas were generally low for samples produced at temperatures until 400 °C, but after this temperature there was a great increase while increasing pyrolysis temperature up to 500 °C (413,06 m<sup>2</sup>/g).

Although the specific surface area tends to increase with pyrolysis temperature, as seen in table 1, being this increase most often associated with both physical and chemical changes in the material, namely the appearance of microporous structures; it is possible that, despite the degradation of the material, at temperatures between 300 °C and 400 °C the existing tars block the formed microporous structures; thus, yielding a lower surface area biochar compared to higher temperature samples where these same tars are volatilized leading to an abrupt increase in surface area.

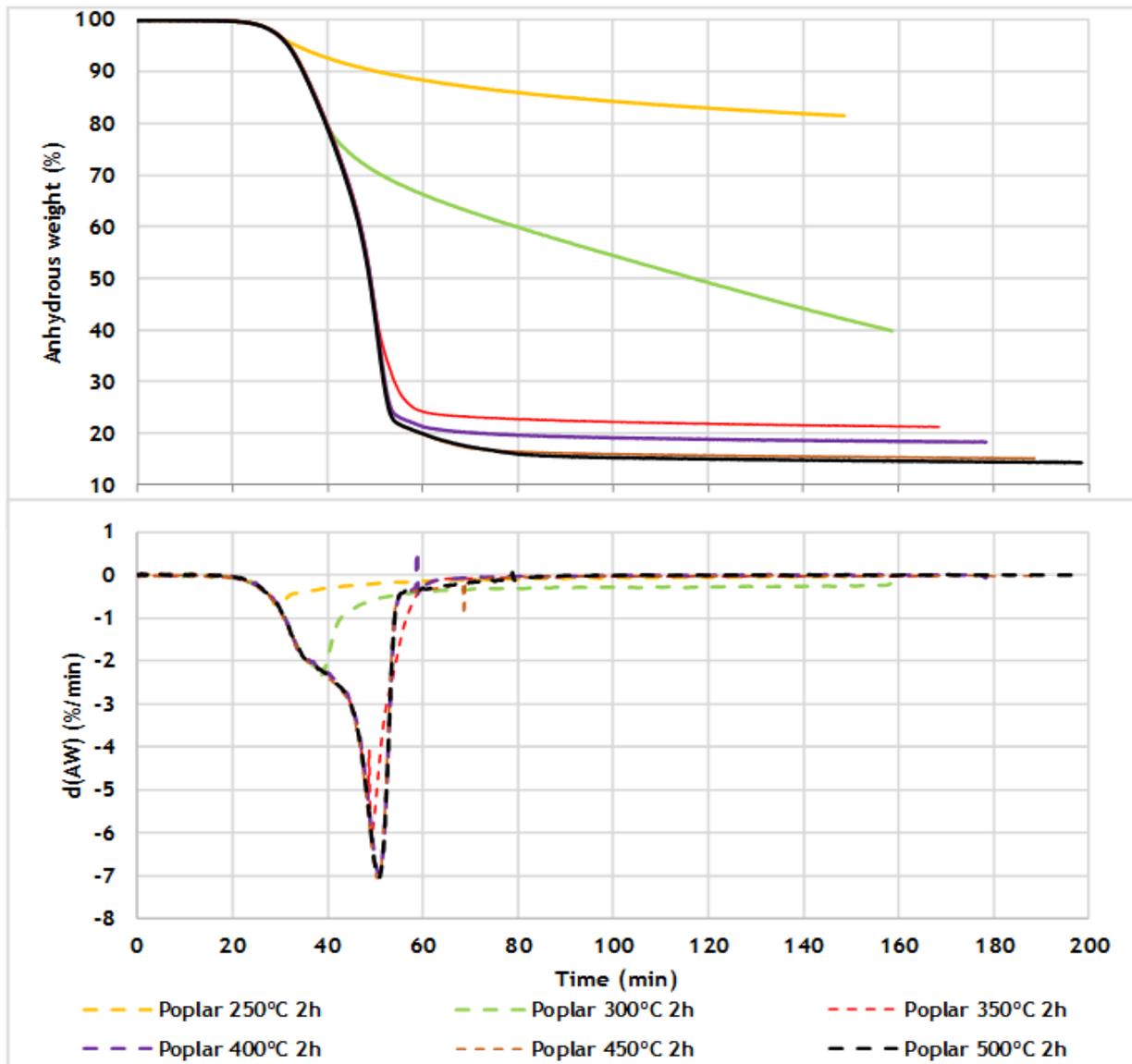
The relation between temperature and specific surface area is presented in figure 9 in order to understand its behavior. It was not detected any obvious relation, which reproduced a good correlation coefficient, despite that it is possible to see that the experimental points show an exponential behavior.



*Figure 9 - Comparison between specific surface area and temperature of treatment.*

## 2. Thermogravimetric Analysis

The anhydrous weight (AW, defined as the ratio of instantaneous mass as a function of time and the initial mass after drying) of poplar at six different isothermal temperatures of 250 °C, 300 °C, 350 °C, 400 °C, 450 °C and 500 °C are plotted in figure 10. Making use of the same time axe, the correspondent derivation of AW (dAW) is represented as well, facilitating the comprehension of thermogravimetric curves. Since the degradation of biomass begins before stabilization of temperature, it was taken from the end of drying at 100 °C.



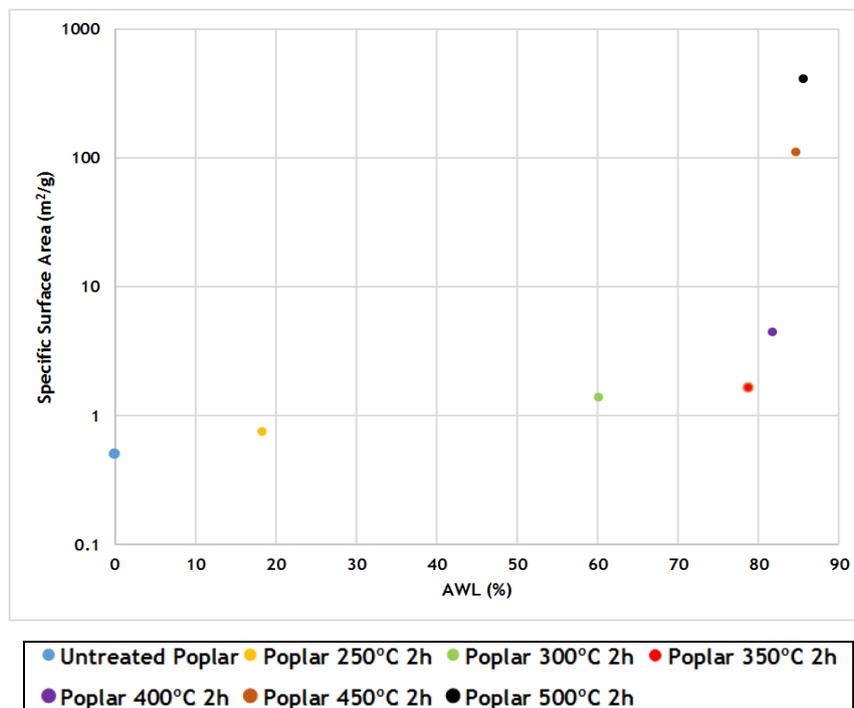
*Figure 10 - Measured anhydrous weight and its derivate for poplar samples in function of time*

The characteristics of thermal degradation of lignocellulosic materials are strongly influenced by the chemical composition of these materials (cellulose, hemicellulose and lignin) (Antal and Varhegyi, 1995) and the TG curves provide a semi-quantitative understanding of thermal degradation processes that occur during thermochemical conversion

(González *et al.*, 2009). Other works showed that pyrolysis of wood proceeds by successive degradation of its principal lignocellulosic constituents (hemicelluloses, cellulose and lignin) which vary in thermal behavior. (Balci *et al.*, 1993) According to studies, hemicelluloses decompose before the cellulose and lignin. (Gröndahl *et al.*, 2003) Several studies identified two areas of pyrolysis: the first, called the active zone, can be attributed to the volatile components generated during the decomposition of hemicelluloses and part of celluloses (mainly amorphous cellulose) and the second, passive area, is due to the conversion of the remaining cellulose (crystalline cellulose) and lignin. (García-Ibañez *et al.*, 2006)

The thermogravimetric analysis data of samples showed a small weight loss at a temperature close to 100 °C, which can be attributed to water loss (not presented on the figure). The thermal degradation of the heat treated samples occurs in mainly three steps. The first weight loss occurs around 250 °C mainly due to degradation of hemicelluloses. At 300 °C, besides the degradation of hemicelluloses, cellulose starts to be degraded as well and, after 2h of treatment, its full amount was almost totally degraded. The final poplar weight loss starts at about 350 °C due to the degradation of remaining celluloses and the start of degradation of lignin. The major mass loss of the samples occurs until 350 °C with a weight loss of about 80%.

The relation between the anhydrous weight loss and the specific surface area is presented in figure 11, in order to understand its behavior. It was not detected any obvious relation, which reproduced a good correlation coefficient, despite it is possible to detect that the experimental points show an exponential behavior.



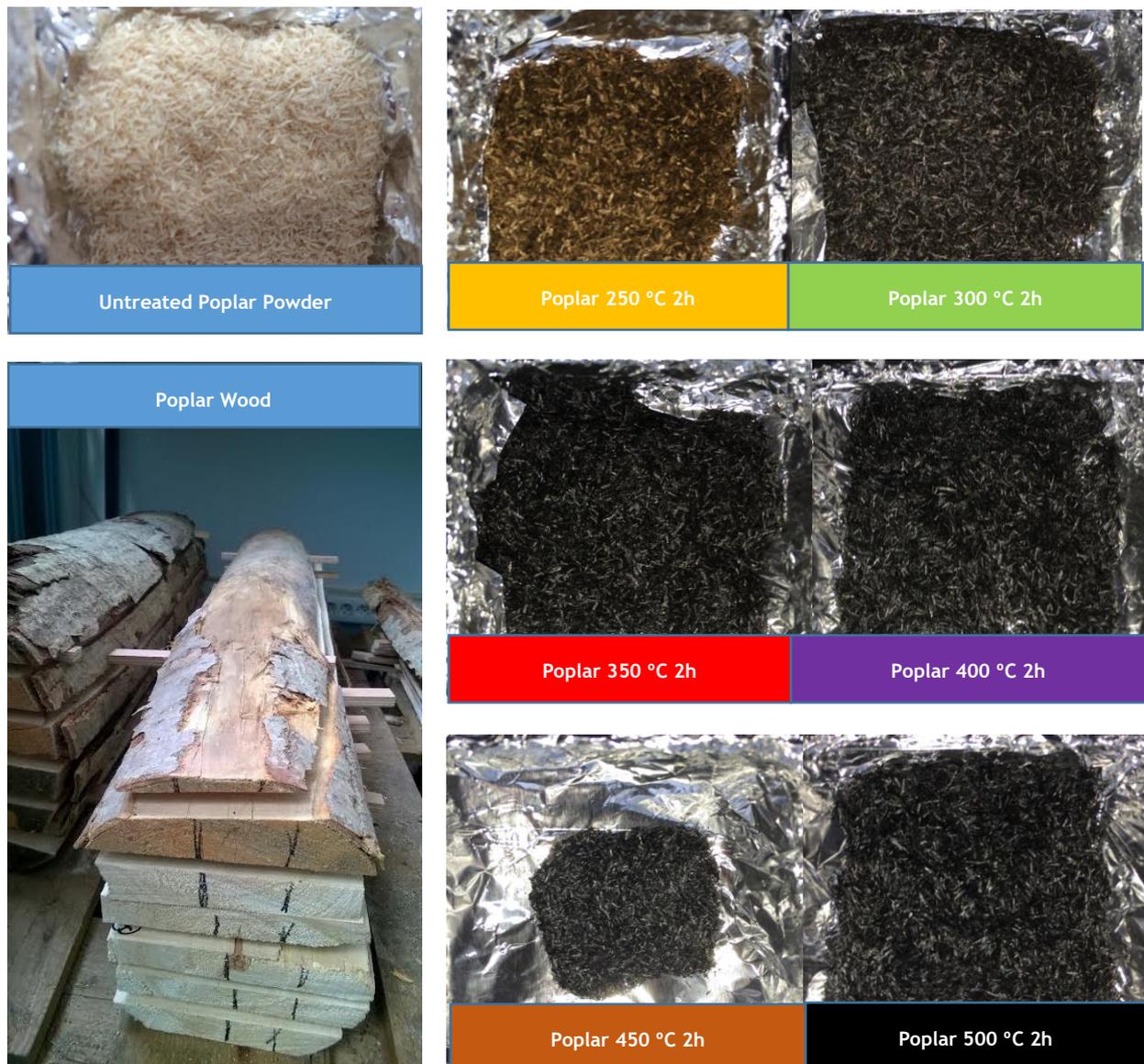
**Figure 11** - Comparison between specific surface area and anhydrous weight loss.

A visual analysis of the samples can also help the interpretation of the results. Figure 12 shows the untreated sample and the different heat treated samples.

It is possible to visualize that for 250 °C, the sample shows a brown color due to the less intense treatment, which leads to a minor degradation of the structure of the material.

For 300 °C, the color of the sample has already changed to a darker brown color, which means that the sample is already starting to change its characteristics due to the degradation of hemicellulose and cellulose.

From 350 °C to 500 °C, the samples already show a black color characteristic of the charcoals.



**Figure 12** - Photos of the original poplar wood; untreated poplar powder and heat treated poplar samples after 2h of heat treatment.

### 3. Elemental Analysis

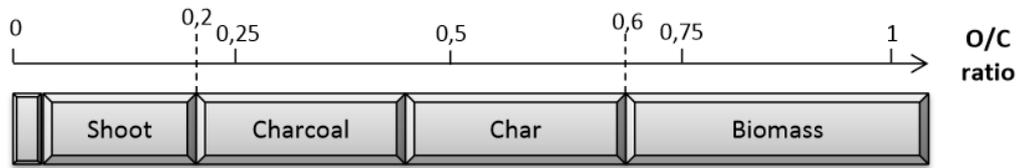
The elemental composition of biomass/biochar is presented in Table 2. Nitrogen and sulfur were not detected for any condition. These results were expected since lignocellulosic materials like poplar have a very low content of these two compounds. The calibration curves are presented on chapter IV of the annex 1.

**Table 2** - Elemental composition of poplar after different heat treatments and untreated. Also H/C and O/C ratios.

Sample	Carbon	Hydrogen	Oxygen	Total	H/C	O/C
	% by dry weight					
Untreated Poplar	48,3	5,98	46,1	100,4	0,124	0,954
Poplar 250°C 2h	50,2	5,74	44,9	100,8	0,114	0,893
Poplar 300°C 2h	61,9	4,72	32,4	99,0	0,076	0,523
Poplar 350°C 2h	71,5	3,66	21,3	96,5	0,051	0,298
Poplar 400°C 2h	74,7	3,22	18,3	96,3	0,043	0,245
Poplar 450°C 2h	78,4	3,13	13,4	95,0	0,040	0,171
Poplar 500°C 2h	82,1	2,83	9,44	94,4	0,034	0,115

The carbon, hydrogen, nitrogen and oxygen contents found in poplar by means of elemental analysis are presented and it is possible to observed that the carbon content increases and the levels of hydrogen and oxygen decrease. This is mostly because the process of heat treatment causes a release of volatile compounds, such as water and smaller hydrocarbons. This way, the heat treatment decreases the atomic ratio of oxygen to carbon (O/C ratio) and hydrogen to carbon ratio (H/C ratio), what is attributed to the loss of hydrogen and oxygen as explained. The atomic H/C ratio can be used to estimate the possibility of bond arrangement: low atomic H/C ratio in treated wood and high atomic H/C ratio in the raw biomass suggests that the aliphatic carbon containing compounds decrease and aromatic compounds increase during treatment.(Qian *et al.*, 2013) Also, the H/C ratio has been accepted as an indication of condensation reactions or flavoring reactions, common in the carbonization and activation processes.(Chattopadhyaya *et al.*, 2006) This decrease in the H/C values when comparing different temperature treatments indicates an increase of the degree of aromaticity after the process of pyrolysis. Thus, the atomic H/C ratio in biochar reflects higher content of aromatic compounds. On other hand, O/C ratio allows to predict the final state of the treated sample. Visualizing figure 13, which correspond to general biomass, with about less than 0,6 of O/C ratio, biochar begins to be formed.

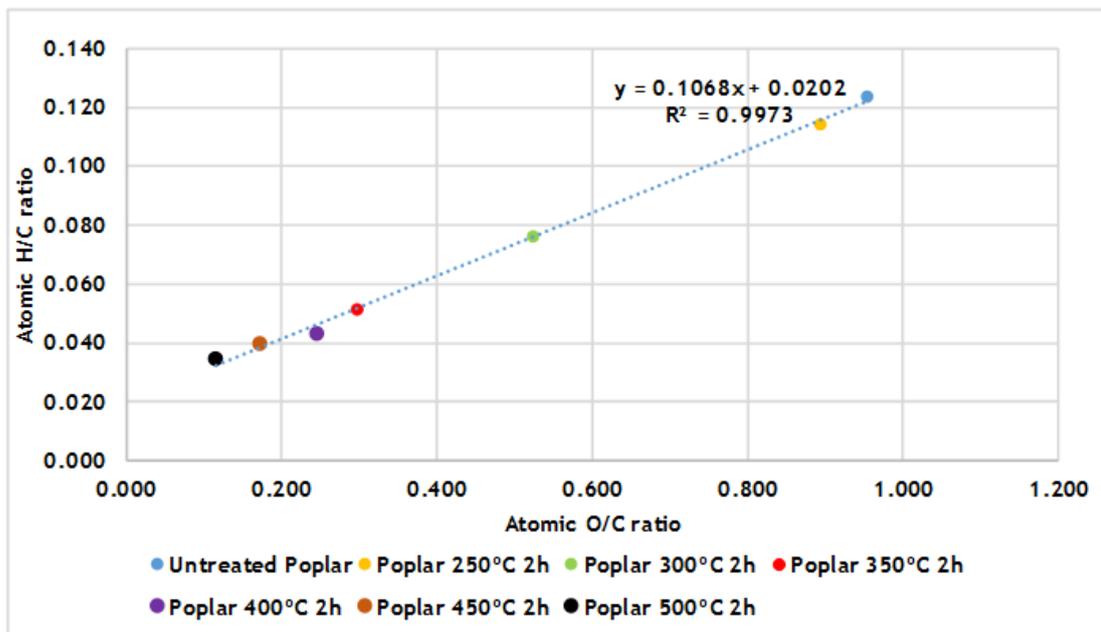
Elemental analysis also shows that drastic changes occurred in the material and indicates the efficiency of the process of heat treatment, since the material produced contains higher amount of fixed carbon and aromatic units.



**Figure 13** - The spectrum of the combustion product continuum as a result of the chemical-thermal conversion of biomass.

*Adapted from Spokas, 2010*

Others conclusions can be taken analyzing the Van Krevelen plot (Figure 14). This diagram is mostly used for determination of different types of kerogen. In this case, it is possible to verify three distinct groups, which means three distinct structures: the first one containing the untreated sample and the sample treated at 250 °C, after there is another group at 300 °C and the third group from 350 °C to 500 °C. These observations can be compared with what happen in figure 10, where at 250 °C only hemicellulose is degraded, at 300 °C celluloses are also degraded and, above this temperature lignin starts to be degraded.



**Figure 14** - Van krevelen plot for all experiments measured in elemental analyzer.

Therefore, there is a transition between 250 °C and higher temperatures where biomass is converted, firstly, to biochar and after to charcoal. In order to understand better these changes, a graph was made to facilitate this interpretation (Figure 15) representing the anhydrous weight (AW) after 2 hours and its variation through the different treatments. This percentage change was calculated using the following equation:

$$\% \text{ change} = \frac{AW_1 - AW_2}{AW_2} \times 100 \tag{1}$$

Where  $AW_2$  is the AW after 2 hours at one specific temperature treatment and  $AW_1$  the AW after 2 hours of the previously temperature treatment. It is possible to observe a great variation between 250 °C and 300 °C due to the degradation of cellulose and hemicellulose and between 300 °C and 350 °C, the moment when lignin starts to be degraded.

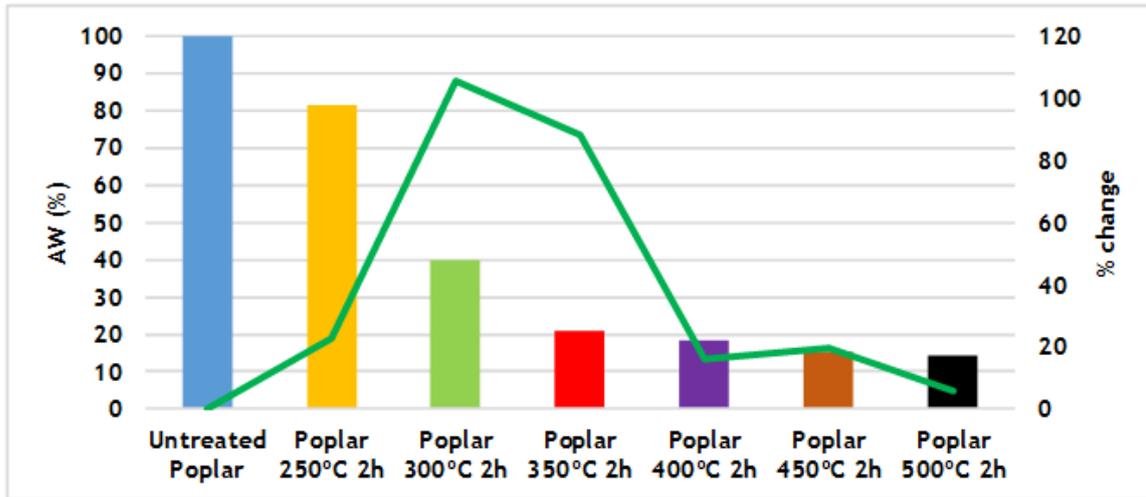


Figure 15 - Measured anhydrous weight for an untreated sample and at different temperatures of treatment after 2h and its change in percentage.

In figure 16, the anhydrous weight loss (AWL, defined as the percentage of mass loss after drying) was represented instead of AW. The same distinction among biomass, biochar and charcoal is verified like before, with three visible regions. However, there is not a linear relation between the AWL and the H/C and O/C ratios. This is due to the decreasing of weight loss that starts to occur between 350 °C and 400 °C, mostly because of the major degradation of the thermosensitive compounds on the sample that has already occurred.

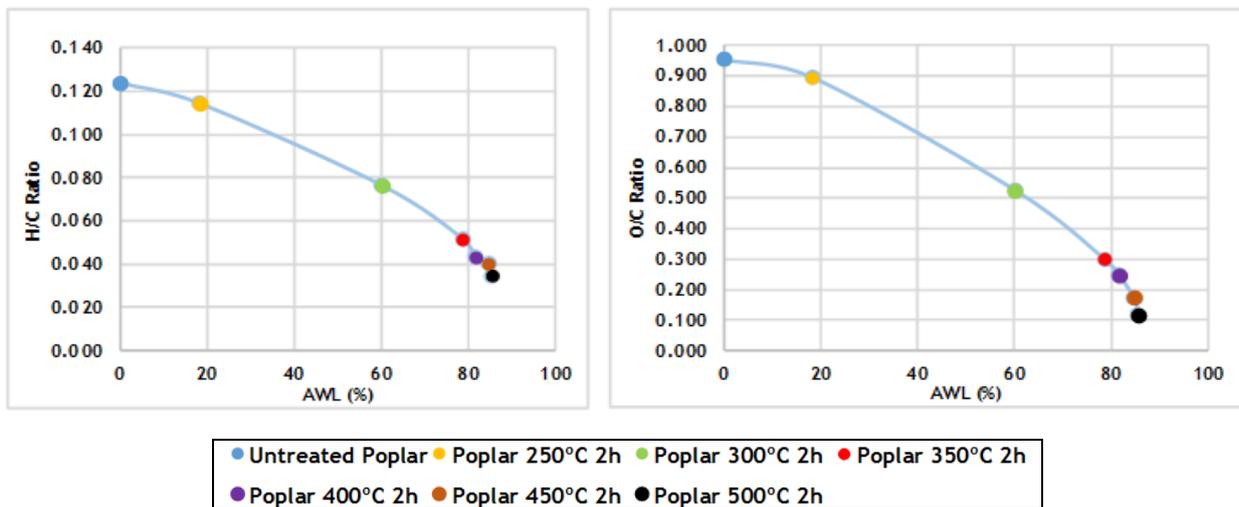


Figure 16 - Comparison between anhydrous weight loss and composition in terms of H/C and O/C ratio.

## 4. Perspectives and Future Work

As already stated before, wood is a complex material consisting mainly of three chemical polymers: cellulose, hemicellulose and lignin. In the multilayered wood cell walls, the cellulose molecules form long unbranched chains called microfibrils which are embedded in a matrix substance composed of short branched chains of hemicelluloses and of amorphous phenolic lignin. Due to the hygroscopic character of primarily the hemicellulosic constituents and secondly cellulose, physical and mechanical properties of wood are highly affected by the change in its moisture content (Fengel and Wegener, 1983)

In detail, the most important binding sites for water molecules are hydroxyl groups being readily available in hemicelluloses but only on the surface of microfibrils in the case of cellulose (Berthold *et al.*, 1994)(O'Sullivan, 1997). Unlike the two hydrophilic polysaccharides, lignin is considered as a three-dimensional hydrophobic adhesive substance in the cell wall with less hydroxyl groups. (Skaar, 1988)

As the conditions of the environment (temperature, relative humidity) change continuously, constant moisture adsorption and desorption take place leading to swelling and shrinkage. Wood exhibits a sigmoidal sorption isotherm, characteristic of the gas-solid solution sorption of deformable solids, commonly found in cellulosic and lignocellulosic materials. It seldom reaches equilibrium with the environment, but under the same temperature and RH conditions, equilibrium moisture content (EMC) of wood is found to be higher during desorption compared to adsorption. Many studies have been focused attention a phenomenon known as sorption hysteresis, and several explanations have been given from chemical and physical viewpoints. (Neimark *et al.*, 2000)(Lu and Pignatello, 2002)

Wood treatment is an established technology to decrease the hygroscopicity of wood and, consequently, to diminish the moisture-induced deformation processes and abiotic and biotic damages such as weathering and fungal decay.(Rowell, 2006)

When absorbing water, the wood cell walls increase their volume to accommodate water molecules located in the transient microcapillary network. Swelling of the cell wall due to the ingress of water involves expansion of the lignin-hemicelluloses matrix in which the cellulose microfibrils are embedded. In most resin-based wood modifications, the cell wall properties are permanently changed as for example the reduction in flexibility due to the rigid, three-dimensional corset of resins in the wood structure. (Kielmann *et al.*, 2013)

The main objective of this exploratory study is to start establishing the effect of heat treatment on poplar wood vapor sorption properties. The innovative component of this study is related with the method used for the determination of the sorption isotherms. These first sorption isotherms in figure 17 were obtained using a Micromeritics 3Flex, a volumetric device mainly used for the determination of adsorption isotherms. Its configuration was changed in

order to allow the use of water vapor and the sorption isotherms were determined at 30 °C following a protocol similar to the determination of adsorption isotherms, the specific components of the developed protocol for water sorption are described on chapter V of the annex 1.

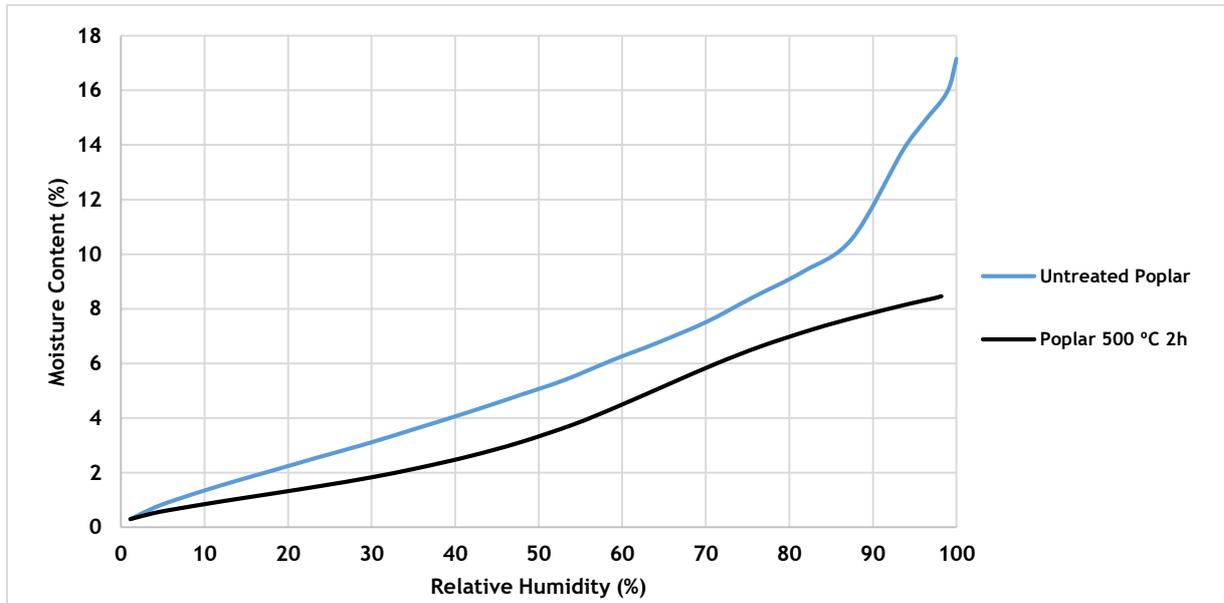


Figure 17 - Vapor sorption isotherms at 30 °C of Untreated and Heat Treated Poplar sample at 500 °C.

Looking at this first results obtained from this innovative method, it is possible to see that the results show the predictable trend. Since the primary objective of the modification is to lower the sorption isotherms to prevent attacks from fungi, examining the sorption isotherms, it is clear that, after a 500 °C treatment for 2 hours, the moisture content of poplar wood decreased approximately 50%. This way, the hygroscopicity of heat-treated wood decreased with the increase mass loss. This was a direct consequence of mass loss being due to the degradation of the hygroscopic components of wood like hemicelluloses. However, reduced hygroscopicity of wood is not only explained by the mass loss, but other mechanism explained before called the process of hornification. This induced irreversible hydrogen bonding (hornification) within the wood structure promotes the reduction of the amount of bonding sites available for water sorption.

This preliminary results were very encouraging since they are in accordance with the results presented in literature.(Engelund *et al.*, 2010) Despite requiring further work and improvements, this innovative method arises as a valuable alternative to the classical methodologies for determination of vapor sorption isotherms, like the dynamic vapor sorption.

## V. Conclusions

In this study, heat treatments on poplar (*Populus*) wood specimens were conducted under different temperature conditions. The structural characteristics of the heat treated wood were then studied. Four properties associated with the structure of heat treated wood were evaluated.

Firstly, it was developed a study of the effects of different heat treatments on the adsorption isotherms of poplar wood using nitrogen as the adsorptive gas and applying the Density Functional Theory for determination of the pore size distribution of each sample. The results showed that the volume of pores on the micropores region for samples treated at higher temperatures is much greater compared with the volume of pores for samples below 400 °C. Three mechanisms occurring during high-temperature treatments were studied in order to explain this phenomenon. Thermal degradation, hornification and microscopic cell wall damage can both three affect the physical and mechanical properties of wood. In the meso and macropores regions, especially for pores with bigger dimensions, between 400 and 500 Å, the volume of pores increases for the lowest temperature treatment and then starts to decrease, resulting this from the formation of bigger cavities due to the process of drying and volatilization. In opposition, higher temperatures promote the formation of smaller pores, occurring a conversion of bigger pores in smaller ones due to processes of drying and structure degradation inside the material that promote the collapse of these macrostructures (hornification), being this increase visible for pores under 250 Å.

Furthermore, with the results from adsorption isotherms of heat treated poplar wood using nitrogen as the adsorptive gas and applying the BET theory, it was possible to determine the specific surface area of each sample. The results obtained were in accordance with the results of the pore size distribution showing that, until 400 °C, there isn't a major increasing on the surface area of the samples, however, after that temperature, the specific surface area starts to increase exponentially.

Secondly, a thermogravimetric analysis was done on the heat treated poplar wood samples regarding the mass loss during each treatment and its consequences on the structure. The results showed that the degradation of poplar wood occurs in mainly three steps. The first weight loss occurred around 250 °C mainly due to degradation of hemicelluloses. At 300 °C, besides the degradation of hemicelluloses, cellulose is also degraded during the 2h treatment. The final poplar weight loss starts at about 350 °C due to the degradation of remaining celluloses and the start of degradation of lignin.

The third study performed was an elemental analysis of the samples and the results allowed to confirm the results obtained on the other studies. It was possible to observed that,

with the increasing of temperature, the carbon content increases and the levels of hydrogen and oxygen decrease, mostly because the process of heat treatment causes a release of volatile compounds, such as water and smaller hydrocarbons. This way, the heat treatment decreases the atomic ratio of oxygen to carbon (O/C ratio) and hydrogen to carbon ratio (H/C ratio), what suggests that the aliphatic carbon containing compounds decrease and aromatic compounds increase during treatment. Furthermore, the O/C ratio allows to predict the final state of the treated sample.

Finally, an exploratory study on the water vapor sorption properties of poplar was performed using an innovative method that comprises the utilization of a volumetric device, in order to evaluate the hygroscopicity of samples. These first results were very encouraging showing that, as expected, the hygroscopicity of poplar wood decreased after heat treatment.

As a conclusion, the improved characteristics of heat treated poplar wood that were verified during this project can be very important for the creation of new products and opportunities on the timber product industry, being capable of offering new features and possibilities to new products and improving the efficiency of bioconversion. This way, lignocellulosic materials can play even a larger part in the future of the industry and, consequently, in the future of the Earth.

## VI. References

- Antal, Michael Jerry Jr., and Gabor Varhegyi. 1995. "Cellulose Pyrolysis Kinetics: The Current State of Knowledge." *Industrial & Engineering Chemistry Research* 34(3): 703-17. <http://pubs.acs.org/doi/abs/10.1021/ie00042a001> (June 20, 2016).
- Balbuena, Perla B., and Keith E. Gubbins. 1993. "Theoretical Interpretation of Adsorption Behavior of Simple Fluids in Slit Pores." *Langmuir* 9(7): 1801-14. <http://pubs.acs.org/doi/abs/10.1021/la00031a031> (June 21, 2016).
- Balci, Suna, Timur Dogu, and Hayrettin Yucel. 1993. "Pyrolysis Kinetics of Lignocellulosic Materials." *Industrial & Engineering Chemistry Research* 32(11): 2573-79. <http://pubs.acs.org/doi/abs/10.1021/ie00023a021> (June 20, 2016).
- Bamford, C. H., J. Crank, D. H. Malan, and A. H. Wilson. 1946. "The Combustion of Wood. Part I." *Mathematical Proceedings of the Cambridge Philosophical Society* 42(02): 166. [http://www.journals.cambridge.org/abstract\\_S030500410002288X](http://www.journals.cambridge.org/abstract_S030500410002288X) (June 24, 2016).
- Barrett, Elliott P., Leslie G. Joyner, and Paul P. Halenda. 1951. "The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms." *Journal of the American Chemical Society* 73(1): 373-80. <http://pubs.acs.org/doi/abs/10.1021/ja01145a126> (June 20, 2016).
- Beall, F. C., and H. W. Eickner. 1969. "Thermal Degradation of Wood Components: A Review of the Literature." [http://www.researchgate.net/publication/236367987\\_Thermal\\_Degradation\\_of\\_Wood\\_Components\\_A\\_Review\\_of\\_the\\_Literature](http://www.researchgate.net/publication/236367987_Thermal_Degradation_of_Wood_Components_A_Review_of_the_Literature) (November 8, 2015).
- Benjamin, M., S. Woods, and J. Ferguson. 1984. "Anaerobic Toxicity and Biodegradability of Pulp Mill Waste Constituents." *Water Research* 18(5): 601-7. <http://www.sciencedirect.com/science/article/pii/0043135484902100> (November 6, 2015).
- Berthold, J., J. Desbrières, M. Rinaudo, and L. Salmén. 1994. "Types of Adsorbed Water in Relation to the Ionic Groups and Their Counter-Ions for Some Cellulose Derivatives." *Polymer* 35(26): 5729-36. <http://linkinghub.elsevier.com/retrieve/pii/S0032386105800485> (June 24, 2016).
- Birkinshaw, C. 1998. "Chemically Modified Wood - a Review with Consideration of the Opportunities for Application to Irish Timber." *Irish Forestry*.
- Bobleter, O., and R. Concin. 1979. "Degradation of Poplar Lignin by Hydrothermal Treatment." *Cellulose chemistry and technology*. <http://agris.fao.org/agris-search/search.do?recordID=US201302808092> (November 8, 2015).

- Bobleter, Ortwin. 1994. "Hydrothermal Degradation of Polymers Derived from Plants." *Progress in Polymer Science* 19(5): 797-841. [http://www.researchgate.net/publication/244307327\\_Hydrothermal\\_degradation\\_of\\_polymers\\_derived\\_from\\_plants.\\_Prog\\_Polym\\_Sci](http://www.researchgate.net/publication/244307327_Hydrothermal_degradation_of_polymers_derived_from_plants._Prog_Polym_Sci) (February 23, 2015).
- Boucher, M. E., A. Chaala, H. Pakdel, and C. Roy. 2000. "Bio-Oils Obtained by Vacuum Pyrolysis of Softwood Bark as a Liquid Fuel for Gas Turbines. Part II: Stability and Ageing of Bio-Oil and Its Blends with Methanol and a Pyrolytic Aqueous Phase." *Biomass and Bioenergy* 19(5): 351-61.
- Bourgois, J., and R. Guyonnet. 1988. "Characterization and Analysis of Torrefied Wood." *Wood Science and Technology* 22(2): 143-55. <http://link.springer.com/10.1007/BF00355850> (November 8, 2015).
- Brebu, Mihai, and Cornelia Vasile. 2010. "Thermal Degradation of Lignin - A Review." *Cellulose Chemistry and Technology* 44(9): 353-63. [https://www.researchgate.net/publication/237090542\\_Thermal\\_degradation\\_of\\_lignin\\_-\\_A\\_Review](https://www.researchgate.net/publication/237090542_Thermal_degradation_of_lignin_-_A_Review) (June 2, 2016).
- Bridgwater, A. V. 1990. "A Survey of Thermochemical Biomass Processing Activities." *Biomass* 22(1): 279-92.
- Bridgwater, A. V. 1994. "Catalysis in Thermal Biomass Conversion." *Applied Catalysis A: General* 116(1): 5-47.
- Bridgwater, A. V., D Meier, and D Radlein. 1999. "An Overview of Fast Pyrolysis of Biomass." *Organic Geochemistry* 30(12): 1479-93.
- Bridgwater, A. V. 2003. "Renewable Fuels and Chemicals by Thermal Processing of Biomass." *Chemical Engineering Journal* 91(2-3): 87-102. <http://www.sciencedirect.com/science/article/pii/S1385894702001420> (May 15, 2016).
- Brownell, H. H., E. K. Yu, and J. N. Saddler. 1986. "Steam-Explosion Pretreatment of Wood: Effect of Chip Size, Acid, Moisture Content and Pressure Drop." *Biotechnology and bioengineering* 28(6): 792-801.
- Chan, Wai-Chun R., Marcia Kelbon, and Barbara B. Krieger. 1985. "Modelling and Experimental Verification of Physical and Chemical Processes during Pyrolysis of a Large Biomass Particle." *Fuel* 64(11): 1505-13. <http://linkinghub.elsevier.com/retrieve/pii/0016236185903643> (June 24, 2016).
- Chattopadhyaya, Goutam et al. 2006. "Preparation and Characterization of Chars and Activated Carbons from Saskatchewan Lignite." *Fuel Processing Technology* 87(11): 997-1006.
- Chen, Wei-Hsin, Jianghong Peng, and Xiaotao T. Bi. 2015. "A State-of-the-Art Review of Biomass Torrefaction, Densification and Applications." *Renewable and Sustainable Energy Reviews* 44: 847-66.

- <http://www.sciencedirect.com/science/article/pii/S1364032114010910>.
- Cherubini, Francesco. 2010. "The Biorefinery Concept: Using Biomass instead of Oil for Producing Energy and Chemicals." *Energy Conversion and Management* 51(7): 1412-21. <http://linkinghub.elsevier.com/retrieve/pii/S0196890410000373>.
- Cherubini, Francesco. 2012. "Toward a Common Classification Approach for Biorefinery Systems." *Biofuels, Bioproducts and Biorefining* 6(3): 246-56.
- Chow, S. Z. 1971. "Infrared Spectral Characteristics and Surface Inactivation of Wood at High Temperatures." *Wood Science and Technology* 5(1): 27-39. <http://link.springer.com/10.1007/BF00363118> (November 8, 2015).
- Cole, Barbara. 2013. "Extractive Components of Wood."
- Demirbas, Ayhan. 2005. "Pyrolysis of Ground Beech Wood in Irregular Heating Rate Conditions." *Journal of Analytical and Applied Pyrolysis* 73(1): 39-43. <http://www.sciencedirect.com/science/article/pii/S0165237004000889> (May 31, 2016).
- Demirbas, M. Fatih. 2009. "Biorefineries for Biofuel Upgrading : A Critical Review." *Applied Energy* 86: S151-61. <http://dx.doi.org/10.1016/j.apenergy.2009.04.043>.
- Dubin, M. M., and H. F. Stoeckli. 1980. "Homogeneous and Heterogeneous Micropore Structures in Carbonaceous Adsorbents."
- Elliott, Douglas C. 2001. "Issues in Value-Added Products from Biomass." *Progress in Thermochemical Biomass Conversion*: 1186-96.
- Elliott, Douglas C. 2004. Encyclopedia of Energy *Encyclopedia of Energy*. Elsevier. <http://www.sciencedirect.com/science/article/pii/B012176480X003582> (June 2, 2016).
- Engelund, Emil Tang, Morten Klamer, and Thomas Mark Venås. 2010. "Acquisition of Sorption Isotherms for Modified Woods by the Use of Dynamic Vapour Sorption Instrumentation. Principles and Practice." *International Research Group on Wood Protection IRG/WP 10-*.
- Esteban, Luis S., and Juan E. Carrasco. 2006. "Evaluation of Different Strategies for Pulverization of Forest Biomasses." *Powder Technology* 166(3): 139-51. <http://www.sciencedirect.com/science/article/pii/S0032591006001719> (November 8, 2015).
- Esteves, Bruno M., and Helena M. Pereira. 2009. "Wood Modification by Heat Treatment: A Review." *BioResources* 4(1): 370-404.
- Fengel, Dietrich, and Gerd Wegener. 1983. *Wood: Chemistry, Ultrastructure, Reactions*. <https://books.google.com/books?hl=pt-PT&lr=&id=x1B4uITKnt0C&pgis=1> (November 6, 2015).
- Fernandes Diniz, J. M. B., M. H. Gil, and J. A. A. M. Castro. 2004. "Hornification - Its Origin and Interpretation in Wood Pulps." *Wood Science and Technology* 37(6): 489-94. <http://link.springer.com/10.1007/s00226-003-0216-2> (June 20, 2016).
- Fox, M. H., T. Noike, and T. Ohki. 2003. "Alkaline Subcritical-Water Treatment and Alkaline

- Heat Treatment for the Increase in Biodegradability of Newsprint Waste.” *Water science and technology: a journal of the International Association on Water Pollution Research* 48(4): 77-84. [http://www.researchgate.net/publication/9062153\\_Alkaline\\_subcritical-water\\_treatment\\_and\\_alkaline\\_heat\\_treatment\\_for\\_the\\_increase\\_in\\_biodegradability\\_of\\_newsprint\\_waste.\\_Water\\_Sci\\_Technol](http://www.researchgate.net/publication/9062153_Alkaline_subcritical-water_treatment_and_alkaline_heat_treatment_for_the_increase_in_biodegradability_of_newsprint_waste._Water_Sci_Technol) (November 6, 2015).
- García-Ibañez, P., M. Sánchez, and A. Cabanillas. 2006. “Thermogravimetric Analysis of Olive-Oil Residue in Air Atmosphere.” *Fuel Processing Technology* 87(2): 103-7.
- Garrote, G., H. Dominguez, and J. C. Parajó; 1999. “Hydrothermal Processing of Lignocellulosic Materials.” *Holz als Roh- und Werkstoff* 57(3): 191-202.
- Glass, Samuel V., and Samuel L. Zelinka. 2010. “Moisture Relations and Physical Properties of Wood.”
- González, J. F., S. Román, J. M. Encinar, and G. Martínez. 2009. “Pyrolysis of Various Biomass Residues and Char Utilization for the Production of Activated Carbons.” *Journal of Analytical and Applied Pyrolysis* 85(1): 134-41.
- Gossett, J. M., D. C. Stuckey, W. F. Owen, and P. L. McCarty. 1982. “Heat Treatment and Anaerobic Digestion of Refuse.” 108. [http://www.researchgate.net/publication/255116302\\_Heat\\_treatment\\_and\\_anaerobic\\_digestion\\_of\\_refuse](http://www.researchgate.net/publication/255116302_Heat_treatment_and_anaerobic_digestion_of_refuse) (November 8, 2015).
- Grabber, John H. 2005. “How Do Lignin Composition, Structure, and Cross-Linking Affect Degradability? A Review of Cell Wall Model Studies.” *Crop Science* 45(3): 820. <https://dl.sciencesocieties.org/publications/cs/abstracts/45/3/0820> (September 27, 2015).
- Gray, Matthew C., Alvin O. Converse, and Charles E. Wyman. 2003. “Sugar Monomer and Oligomer Solubility: Data and Predictions for Application to Biomass Hydrolysis.” *Applied biochemistry and biotechnology* 105 -108: 179-93. <http://www.ncbi.nlm.nih.gov/pubmed/12721484> (November 6, 2015).
- Green, David W., Jerrold E. Winandy, and David E. Kretschmann. 1999. “Mechanical Properties of Wood.”
- Gregg, David, and John N. Saddler. 1996. “A Techno-Economic Assessment of the Pretreatment and Fractionation Steps of a Biomass-to-Ethanol Process.” *Applied Biochemistry and Biotechnology* 57-58(1): 711-27. <http://link.springer.com/10.1007/BF02941753> (November 8, 2015).
- Gröndahl, Maria, Anita Teleman, and Paul Gatenholm. 2003. “Effect of Acetylation on the Material Properties of Glucuronoxylan from Aspen Wood.” *Carbohydrate Polymers* 52(4): 359-66.
- Hendriks, A. T. W. M., and G. Zeeman. 2009. “Pretreatments to Enhance the Digestibility of Lignocellulosic Biomass.” *Bioresource Technology* 100(1): 10-18.

- <http://linkinghub.elsevier.com/retrieve/pii/S0960852408004574> (June 23, 2016).
- Hill, Callum. 2006. *Wood Modification Chemical , Thermal and Other Processes*.
- Hiziroglu, Salim. 2007. "Dimensional Changes in Wood."
- Hon, David N. S., and Nobuo Shiraishi. 2000. *Wood and Cellulosic Chemistry, Second Edition, Revised, and Expanded*. <https://books.google.com/books?hl=pt-PT&lr=&id=pKiTzbEDy1QC&pgis=1> (November 8, 2015).
- Horváth, Géza, and Kunitaro Kawazoe. 1983. "Method for the Calculation of Effective Pore Size Distribution in Molecular Sieve Carbon." *Journal of Chemical Engineering of Japan* 16(6): 470-75. <http://joi.jlc.jst.go.jp/JST.Journalarchive/jcej1968/16.470?from=CrossRef> (June 20, 2016).
- Jakab, E., G. Varhegyi, and O. Faix. 2000. "Thermal Decomposition of Polypropylene in the Presence of Wood-Derived Materials." *Journal of Analytical and Applied Pyrolysis* 56(2): 273-85.
- Jansen., Roland A. 2013. "Second Generation Biofuels and Biomass: Essential Guide for Investors, Scientists and Decision Makers, First Edition." : 21-29.
- Jin, Wenjia, Kaushlendra Singh, and John Zondlo. 2013. "Pyrolysis Kinetics of Physical Components of Wood and Wood-Polymers Using Isoconversion Method." *Agriculture* 3(1): 12-32. <http://www.mdpi.com/2077-0472/3/1/12/htm>  
<http://www.mdpi.com/2077-0472/3/1/12/>.
- Kamm, Birgit, and Patrick R. Gruber. 2006. 1 Biorefineries - Industrial Processes and Products *Handbook of Fuels Beyond Oil and Gas : The Methanol Economy Bailey ' S Industrial Oil and Fat Products Oil Refineries in the 21st Century*.
- Kamm, Birgit. "Definition and Technical Status of Biorefineries." [http://www.biorefinery.nl/fileadmin/biorefinery/BioreFuture\\_2008/Definition\\_and\\_Technical\\_status\\_of\\_biorefineries1.pdf](http://www.biorefinery.nl/fileadmin/biorefinery/BioreFuture_2008/Definition_and_Technical_status_of_biorefineries1.pdf) (November 1, 2015).
- Kansa, Edward J., Henry E. Perlee, and Robert F. Chaiken. 1977. "Mathematical Model of Wood Pyrolysis Including Internal Forced Convection." *Combustion and Flame* 29(3): 311-24. <http://linkinghub.elsevier.com/retrieve/pii/0010218077901213> (June 24, 2016).
- Kaźmierczak, Justyna, Piotr Nowicki, and Robert Pietrzak. 2013. "Sorptions Properties of Activated Carbons Obtained from Corn Cobs by Chemical and Physical Activation." *Adsorption* 19(2-4): 273-81. <http://link.springer.com/10.1007/s10450-012-9450-y> (June 24, 2016).
- Kennedy, John F., Glyn O. Phillips, Peter A. Williams, and Lennart. Piculel. 1995. *Cellulose and Cellulose Derivatives : Physico-Chemical Aspects and Industrial Applications*.
- Kielmann, Bodo Caspar, Holger Miltz, Carsten Mai, and Stergios Adamopoulos. 2013. "Strength changes in ash, beech and maple wood modified with a n-methynol melamine

- compound and a metal-complex dye.” *Wood research* 58(3): 343-50.
- Koppejan, Jaap, Shahab Sokhansanj, Staffan Melin, and Sebnem Madrali. 2012. “Status Overview of Torrefaction Technologies.” (December): 1-54.
- Ku, Xiaoke, Jianzhong Lin, and Fangyang Yuan. 2016. “Influence of Torrefaction on Biomass Gasification Performance in a High-Temperature Entrained-Flow Reactor.”
- Kumar, Satish. 2007. “Chemical Modification of Wood.” *Wood and Fiber Science* 26(2): 270-80.
- Landers, John, Gennady Yu Gor, and Alexander V Neimark. 2013. “Density Functional Theory Methods for Characterization of Porous Materials.” *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 437: 3-32.
- Laser, Mark et al. 2002. “A Comparison of Liquid Hot Water and Steam Pretreatments of Sugar Cane Bagasse for Bioconversion to Ethanol.” *Bioresource Technology* 81(1): 33-44. <http://www.sciencedirect.com/science/article/pii/S0960852401001031> (November 6, 2015).
- Laureano-Perez, Lizbeth, Farzaneh Teymouri, Hasan Alizadeh, and Bruce E. Dale. 2005. “Understanding Factors That Limit Enzymatic Hydrolysis of Biomass: Characterization of Pretreated Corn Stover.” *Applied Biochemistry and Biotechnology* 124(1-3): 1081-1100. <http://link.springer.com/10.1385/ABAB:124:1-3:1081> (November 6, 2015).
- Lawther, J. Mark, Runcang Sun, and W. B. Banks. 1996. “Effects of Extraction Conditions and Alkali Type on Yield and Composition of Wheat Straw Hemicellulose.” *Journal of Applied Polymer Science* 60(11): 1827-37. <http://doi.wiley.com/10.1002/%28SICI%291097-4628%2819960613%2960%3A11%3C1827%3A%3AAID-APP6%3E3.0.CO%3B2-N> (November 6, 2015).
- LeVan, Susan L., Robert J. Ross, and Jerrold E. Winandy. 1990. “Effects of Fire Retardant Chemicals on the Bending Properties of Wood at Elevated Temperatures.” : 26.
- Liu, Chaogang, and Charles E. Wyman. 2003. “The Effect of Flow Rate of Compressed Hot Water on Xylan, Lignin, and Total Mass Removal from Corn Stover.” *Industrial & Engineering Chemistry Research* 42(21): 5409-16. <http://dx.doi.org/10.1021/ie030458k> (November 8, 2015).
- Lora, Jairo H., and Morris Wayman. 1978. “Delignification of Hardwoods by Autohydrolysis and Extraction. TAPPI J 61: 47-50.” 61(6). [https://www.researchgate.net/publication/245859704\\_Delignification\\_of\\_hardwoods\\_by\\_autohydrolysis\\_and\\_extraction\\_TAPPI\\_J\\_61\\_47-50](https://www.researchgate.net/publication/245859704_Delignification_of_hardwoods_by_autohydrolysis_and_extraction_TAPPI_J_61_47-50) (June 5, 2016).
- Lu, Yuefeng, and Joseph J. Pignatello. 2002. “Demonstration of the ‘Conditioning Effect’ in Soil Organic Matter in Support of a Pore Deformation Mechanism for Sorption Hysteresis.”
- Madani, S. Hadi, Alexander Badalyan, Mark J. Biggs, and Phillip Pendleton. 2015. “Uncertainty in Pore Size Distribution Derived from Adsorption Isotherms: I. Classical Methods.”

- Microporous and Mesoporous Materials* 214: 210-16.  
<http://linkinghub.elsevier.com/retrieve/pii/S1387181115002383> (June 20, 2016).
- Maloney, T. C., and H. Paulapuro. 1999. "The Formation of Pores in the Cell Wall." *Journal of Pulp and Paper Science* 25(12): 432.
- Maschio, G., C. Koufopoulos, and A. Lucchesi. 1992. "Pyrolysis, a Promising Route for Biomass Utilization." *Bioresource technology* 42(3): 219-31.
- Mitchell, P. H. 1988. "Irreversible Property Changes of Small Loblolly Pine Specimens Heated in Air, Nitrogen, or Oxygen." *Wood and fiber science : journal of the Society of Wood Science and Technology (USA)*. <http://agris.fao.org/agris-search/search.do?recordID=US8858222> (November 8, 2015).
- Mosier, Nathan et al. 2005. "Features of Promising Technologies for Pretreatment of Lignocellulosic Biomass." *Bioresource technology* 96(6): 673-86.  
<http://www.ncbi.nlm.nih.gov/pubmed/15588770> (July 11, 2014).
- Naik, S. N., Vaibhav V Goud, Prasant K Rout, and Ajay K Dalai. 2010. "Production of First and Second Generation Biofuels : A Comprehensive Review." 14: 578-97.
- Negro, M. J. et al. 2003. "Changes in Various Physical/chemical Parameters of Pinus Pinaster Wood after Steam Explosion Pretreatment." *Biomass and Bioenergy* 25(3): 301-8.  
<http://www.ingentaconnect.com/content/els/09619534/2003/00000025/00000003/art00017> (November 8, 2015).
- Neimark, Alexander V., Peter I. Ravikovitch, and Aleksey Vishnyakov. 2000. "Adsorption Hysteresis in Nanopores." *Physical Review E* 62(2): R1493-96.  
<http://link.aps.org/doi/10.1103/PhysRevE.62.R1493> (June 24, 2016).
- Norimoto, M., and Kyoto 611 (Japan) Gril, J. (Wood Research Institute, Kyoto University, Uji. 1993. "Structure and Properties of Chemically Treated Woods." <http://agris.fao.org/agris-search/search.do?recordID=GB9415258> (May 25, 2016).
- O'Sullivan, Antoinette C. 1997. "Cellulose: The Structure Slowly Unravels." *Cellulose* 4(3): 173-207. <http://link.springer.com/10.1023/A:1018431705579> (June 24, 2016).
- Olivier, J. P., W. B. Conklin, and M. V. Szombathely. 1994. "Determination of Pore Size Distribution from Density Functional Theory: A Comparison of Nitrogen and Argon Results." *Studies in Surface Science and Catalysis* 87: 81-89.
- Phanphanich, Manunya, and Sudhagar Mani. 2011. "Impact of Torrefaction on the Grindability and Fuel Characteristics of Forest Biomass." *Bioresource technology* 102(2): 1246-53.  
<http://www.ncbi.nlm.nih.gov/pubmed/20801023> (November 8, 2015).
- Popescu, Carmen-Mihaela et al. 2015. "Equilibrium and Dynamic Vapour Water Sorption Properties of Biochar Derived from Apple Wood." *Polymer Degradation and Stability* 111: 263-68.

- Pyle, D. L., and C. A. Zaror. 1984. "Heat Transfer and Kinetics in the Low Temperature Pyrolysis of Solids." *Chemical Engineering Science* 39(1): 147-58. <http://linkinghub.elsevier.com/retrieve/pii/0009250984801402> (June 24, 2016).
- Qian, Kezhen et al. 2013. "Effects of Biomass Feedstocks and Gasification Conditions on the Physiochemical Properties of Char." *Energies* 6(8): 3972-86. <http://www.mdpi.com/1996-1073/6/8/3972/> (June 20, 2016).
- Ramos, Luiz Pereira. 2003. "The Chemistry Involved in the Steam Treatment of Lignocellulosic Materials." *Química Nova* 26(6): 863-71. [http://www.scielo.br/scielo.php?script=sci\\_arttext&pid=S0100-40422003000600015&lng=en&nrm=iso&tlng=en](http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0100-40422003000600015&lng=en&nrm=iso&tlng=en) (November 8, 2015).
- Rouquerol, Françoise, Jean Rouquerol, and Kenneth Sing. 1999. Adsorption by Powders and Porous Solids *Adsorption by Powders and Porous Solids*. Elsevier. <http://www.sciencedirect.com/science/article/pii/B9780125989206500178> (January 29, 2016).
- Rowell, Roger M. 2006. "Chemical Modification of Wood: A Short Review." *Wood Material Science and Engineering* 1(1): 29-33.
- Saha, Badal C. 2003. "Hemicellulose Bioconversion." *Journal of industrial microbiology & biotechnology* 30(5): 279-91. <http://www.ncbi.nlm.nih.gov/pubmed/12698321> (August 4, 2014).
- Saito, A., and H. C. Foley. 1991. "Curvature and Parametric Sensitivity in Models for Adsorption in Micropores." *AIChE Journal* 37(3): 429-36. <http://doi.wiley.com/10.1002/aic.690370312> (June 20, 2016).
- Shafizadeh, Fred, and Peter P. S. Chin. 1977. 43 *Wood Technology: Chemical Aspects*. ed. Irving S. Goldstein. Washington, D. C.: American Chemical Society. <http://dx.doi.org/10.1021/bk-1977-0043.ch005> (June 2, 2016).
- Siau, John Finn. 1984. *Transport Processes in Wood*. Berlin, Heidelberg: Springer Berlin Heidelberg. <http://link.springer.com/10.1007/978-3-642-69213-0> (June 24, 2016).
- Sing, Kenneth. 2001. "The Use of Nitrogen Adsorption for the Characterisation of Porous Materials." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 187-188: 3-9. <http://www.sciencedirect.com/science/article/pii/S0927775701006124> (November 24, 2015).
- Sinha, S., A. Jhalani, M. R. Ravi, and Anjan Ray. 2000. "Modelling of Pyrolysis in Wood: A Review." *SESI Journal* 10(1): 41-62.
- Skaar, Christen. 1988. *Wood-Water Relations*. Berlin, Heidelberg: Springer Berlin Heidelberg. <http://link.springer.com/10.1007/978-3-642-73683-4> (June 24, 2016).
- Spokas, Kurt A. 2010. "Review of the Stability of Biochar in Soils: Predictability of O:C Molar Ratios." *Carbon Management* 1(2): 289-303.

- Sriram, N., and M. Shahidehpour. 2005. "Renewable Biomass Energy." *IEEE Power Engineering Society General Meeting, 2005*: 1-6.
- Stamm, A. J., Burr, H. K., and A. L. Kline. 1946. "Heat Stabilized Wood (Staybwood)." 1621: 8. <http://www.bcin.ca/Interface/openbcin.cgi?submit=submit&Chinkey=67074> (November 8, 2015).
- Sweet, M. S., and J .E. Winandy. 1999. "Influence of Degree of Polymerization of Cellulose and Hemicellulose on Strength Loss in Fire-Retardant-Treated Southern Pine." *Holzforschung* 53(3): 311-17. [http://www.researchgate.net/publication/249924923\\_Influence\\_of\\_Degree\\_of\\_Polymerization\\_of\\_Cellulose\\_and\\_Hemicellulose\\_on\\_Strength\\_Loss\\_in\\_Fire-Retardant-Treated\\_Southern\\_Pine](http://www.researchgate.net/publication/249924923_Influence_of_Degree_of_Polymerization_of_Cellulose_and_Hemicellulose_on_Strength_Loss_in_Fire-Retardant-Treated_Southern_Pine) (November 6, 2015).
- Tang, Walter K., and Wayne K. Neill. 1964. "Effect of Flame Retardants on Pyrolysis and Combustion of  $\alpha$ -Cellulose." *Journal of Polymer Science Part C: Polymer Symposia* 6(1): 65-81. <http://doi.wiley.com/10.1002/polc.5070060109> (June 2, 2016).
- Thangalazhy-Gopakumar, Suchithra et al. 2011. "Production of Hydrocarbon Fuels from Biomass Using Catalytic Pyrolysis under Helium and Hydrogen Environments." *Bioresource Technology* 102(12): 6742-49.
- Thuvander, F., L. Wallström, L. A. Berglund, and K. A. H. Lindberg. 2001. "Effects of an Impregnation Procedure for Prevention of Wood Cell Wall Damage due to Drying." *Wood Science and Technology* 34(6): 473-80. <http://link.springer.com/10.1007/s002260000065> (June 20, 2016).
- Tinney, E. Roy. 1965. "The Combustion of Wooden Dowels in Heated Air." *Symposium (International) on Combustion* 10(1): 925-30. <http://linkinghub.elsevier.com/retrieve/pii/S0082078465802351> (June 24, 2016).
- Tomme, P., R. A. Warren, and N. R. Gilkes. 1995. "Cellulose Hydrolysis by Bacteria and Fungi." *Advances in microbial physiology* 37: 1-81. <http://www.ncbi.nlm.nih.gov/pubmed/8540419> (February 2, 2016).
- Uemura, Yoshimitsu et al. 2015. "Torrefaction of Oil Palm Kernel Shell in the Presence of Oxygen and Carbon Dioxide." *Fuel* 144: 171-79. <http://www.sciencedirect.com/science/article/pii/S0016236114012599>.
- Vernois, Michel. 2001. "Heat Treatment of Wood in France -state of the Art."
- Wallström, L., and K. A. H. Lindberg. 1999. "Measurement of Cell Wall Penetration in Wood of Water-Based Chemicals Using SEM/EDS and STEM/EDS Technique." *Wood Science and Technology* 33(2): 111-22. <http://link.springer.com/10.1007/s002260050103> (June 20, 2016).
- Weiland, J. J., and R. Guyonnet. 2003. "Study of Chemical Modifications and Fungi Degradation of Thermally Modified Wood Using DRIFT Spectroscopy." *Holz als Roh- und*

- Werkstoff* 61(3): 216-20. <http://link.springer.com/article/10.1007/s00107-003-0364-y/fulltext.html> (June 2, 2016).
- Weimer, P. J., J. M. Hackney, and A. D. French. 1995. "Effects of Chemical Treatments and Heating on the Crystallinity of Celluloses and Their Implications for Evaluating the Effect of Crystallinity on Cellulose Biodegradation." *Biotechnology and bioengineering* 48(2): 169-78. <http://www.ncbi.nlm.nih.gov/pubmed/18623473> (September 29, 2015).
- Winandy, Jerrold E. 1995. "Effects of Fire Retardant Treatments After 18 Months of Exposure at 150 ° F ( 66 ° C )." *Scientist*.
- Zhu, Yongming, Y Y Lee, and Richard T Elander. 2004. "Dilute-Acid Pretreatment of Corn Stover Using a High-Solids Percolation Reactor." *Applied biochemistry and biotechnology* 117(2): 103-14. <http://www.ncbi.nlm.nih.gov/pubmed/15159554> (November 8, 2015).
- Zhu, Yongming, Y Y Lee, and Richard T Elander. 2005. "Optimization of Dilute-Acid Pretreatment of Corn Stover Using a High-Solids Percolation Reactor." *Applied biochemistry and biotechnology* 121-124: 1045-54. <http://www.ncbi.nlm.nih.gov/pubmed/15930580> (November 8, 2015).

# Annex 1

# I. Feedstock preparation

## IKA M 20 Universal Grinding Mill

### Specifications of the Device

**Table A. 1** - Specifications of the IKA M 20 Universal Grinding Mill.

<i>Process type</i>	batch
<i>Operating principle</i>	cutting/impact
<i>Motor rating input</i>	450 W
<i>Motor rating output</i>	225 W
<i>Speed max.</i>	20000 rpm
<i>Circumferential speed max.</i>	72 m/s
<i>Usable volume max.</i>	250 ml
<i>Feed hardness max.</i>	5 Mohs
<i>Feed grain size max.</i>	7 mm
<i>Material beater/cutter</i>	stainless steel 1.4034
<i>Material milling chamber</i>	stainless steel 1.4301
<i>Power-on time ON</i>	7 min
<i>Power-on time OFF</i>	10 min
<i>Milling chamber, can be cooled with water</i>	yes
<i>Mill feed can be cooled in milling chamber with dry ice</i>	yes
<i>Mill feed can be cooled in milling chamber with liquid nitrogen</i>	no
<i>Dimensions (W x H x D)</i>	170 x 350 x 170 mm
<i>Weight</i>	6,6 kg
<i>Permissible ambient temperature</i>	5 - 40 °C
<i>Permissible relative humidity</i>	80 %
<i>Protection class according to DIN EN 60529</i>	IP 21
<i>RS 232 interface</i>	no
<i>Analog output</i>	no
<i>Voltage</i>	230 / 115 V
<i>Frequency</i>	50/60 Hz
<i>Power input</i>	550 W



**Figure A. 1** -IKA M 20 Universal Grinding Mill.

#### Operating Program:

Number of cycles: 30

Working time per cycle: 20 s

Stopping time per cycle: 10 s

## II. Surface structure characterization

### Micromeritics 3FLEX Surface Characterization Analyzer

#### Specifications of the Device

Table A. 2 - Specifications of the Micromeritics 3FLEX Surface Characterization Analyzer.

Specification	Instrument Specification	Performance Specifications	Discussion
<b>Sample Analysis Ports</b>	3 ports	1, 2, or 3 micropore - capable ports	Mesopore to micropore and chemisorption capability - ability to upgrade mesopore ports to micropore in the future
<b>Vacuum System</b>	Turbo molecular drag pump in series with hybrid - turbo diaphragm pump		Two pumps ensure a superior high-vacuum system - one to pull pressure down to a level where the turbo molecular drag pump provides additional performance
<b>Pumping Speed</b>	53 L/s (hydrogen) 61 L/s (nitrogen)	53 L/s (hydrogen) 61 L/s (nitrogen)	High pumping speed is essential to permit fast and clean evacuation
<b>Ultimate Vacuum</b>	$3,75 \times 10^{-10}$ mmHg	$8,0 \times 10^{-6}$ mm Hg (at sample port)	Determines the quality and speed of analysis - critical specification is the vacuum produced at the sample port, not just the rating of the vacuum system
<b>Vacuum gauge</b>	Dual Cold Cathode/ microPirani gauge	Gauge placed in close proximity to sample port	For proper monitoring, the gauge must be placed close to the sample port. Measuring vacuum at the pump is not indicative of pressure at the sample. The 3Flex design permits automatic zeroing, ensuring greater accuracy and repeatability
<b>Minimum measurable surface area</b>	0,01 m <sup>2</sup> /g	0,0005 m <sup>2</sup> /g (krypton)	Standard krypton capability permits very low surface area material to be accurately analyzed
<b>Transducers</b>	$\pm 1000$ mmHg, 0,12% of reading $\pm 10$ mmHg, 0,12% of reading $\pm 0.1$ mmHg, 0,15% of reading	10 mmHg, $\pm 0,12\%$ of reading accuracy display resolution $10^{-4}$ mmHg 0,1 mmHg, $\pm 0,15\%$ of reading accuracy display resolution $10^{-6}$ mmHg	Percent of actual reading is more accurate than percent of full scale deflection Due to our proprietary temperature control, the actual analysis performance of the transducer has demonstrated better accuracy than the manufacturer specification
<b>Sample Tubes</b>	Metric, flat bottom, 9 and 12mm		Tubes are clearly marked for diameter and feature a convenient ID location
<b>Adsorptive Gas Inputs</b>	6	Expandable to 12	Expandable versatility extends adsorptive gas range investigation to extend the range of application
<b>Degas</b>	3 <i>In situ</i> , 6 additional with each optional Smart VacPrep	Ambient to 450 °C, programmable - 5 heating and 5 soak periods	Helium free space can be performed after analysis to prevent helium entrapment

**Dewar**

3,2 L capacity, >80hrs (single tube no isothermal jacket)

>70 hrs (3 sample tubes, isothermal jackets, P<sub>0</sub> tube)

Redesigned dewar can provide analysis time greater than listed specification with a unique design that permits refilling without interrupting the analysis

**Control of Cryogen Level on Sample Tube**

Isothermal jacket

Assures a constant thermal profile along the length of both the sample and P<sub>0</sub>tubes throughout the extended analysis. Maintains constant free space for the best analysis



Figure A. 2 - Micromeritics 3FLEX Surface Characterization Analyzer

## Protocol for the Measurement of Specific Surface Area (BET method)

Gonçalo de Bastos Monteiro; gdbmonteiro@gmail.com

### 1. Method

The specific surface area of a powder is estimated from the amount of nitrogen adsorbed in relationship with its pressure, at the boiling temperature of liquid nitrogen under normal atmospheric pressure. The observations are interpreted following the model of Brunauer, Emmett and Teller (BET Method).

### 2. Protocol

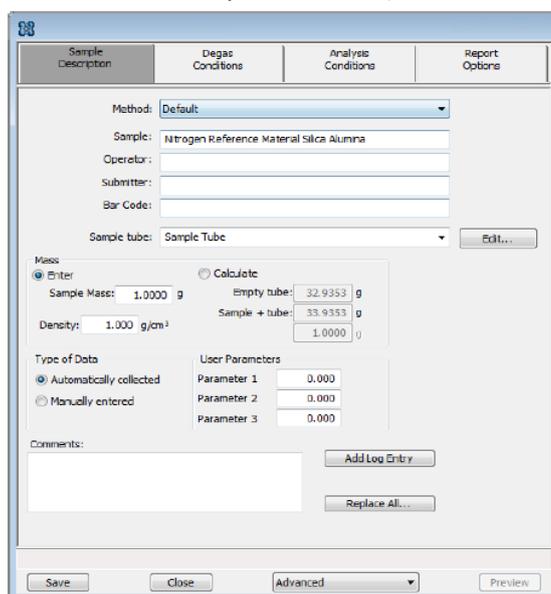
#### 2.1. Create a Sample File

Sample files include the information required by the analyzer to perform analyses and collect data. It identifies the sample, guides the analysis, and specifies report options and may be created in either *Advanced*, *Basic*, or *Restricted* presentation format.

- Create a Sample File using Advanced Presentation Option

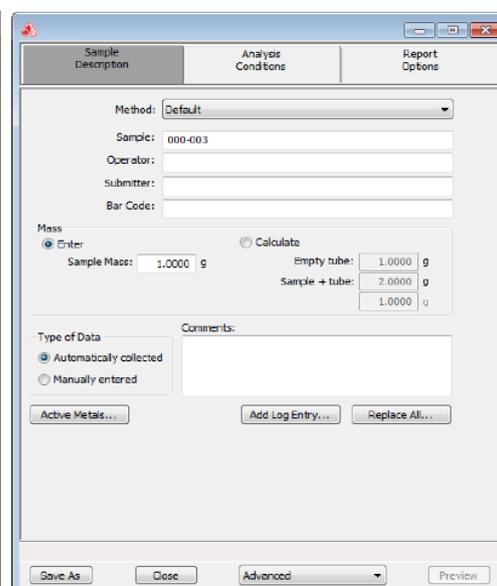
#### I. Sample Description

1. Go to **Options > Option Presentation > Advanced** and ensure *Advanced* has a checkmark.
2. Go to **File > New Sample**.
3. Select either **Physical Adsorption** or **Chemical Adsorption**.
4. Select a method from the *Method* drop-down list. (Leave the Default if there isn't any specific method for the analyzed material)



The screenshot shows the 'Sample Description' tab of the software interface for Physisorption. The 'Method' is set to 'Default'. The 'Sample' field contains 'Nitrogen Reference Material Silica Alumina'. The 'Operator', 'Submitter', and 'Bar Code' fields are empty. The 'Sample tube' is set to 'Sample Tube'. Under the 'Mass' section, 'Enter' is selected, with 'Sample Mass' at 1.0000 g, 'Density' at 1.000 g/cm<sup>3</sup>, 'Empty tube' at 32.9353 g, 'Sample + tube' at 33.9353 g, and a calculated 'Sample' mass of 1.0000 g. There are also 'User Parameters' for Parameter 1, 2, and 3, all set to 0.000. A 'Comments' field is at the bottom with an 'Add Log Entry' button.

Physisorption



The screenshot shows the 'Sample Description' tab of the software interface for Chemisorption. The 'Method' is set to 'Default'. The 'Sample' field contains '000-003'. The 'Operator', 'Submitter', and 'Bar Code' fields are empty. Under the 'Mass' section, 'Calculate' is selected, with 'Sample Mass' at 1.0000 g, 'Empty tube' at 1.0000 g, 'Sample + tube' at 2.0000 g, and a calculated 'Sample' mass of 1.0000 g. There are also 'User Parameters' for Parameter 1, 2, and 3, all set to 0.000. A 'Comments' field is at the bottom with buttons for 'Active Metals...', 'Add Log Entry...', and 'Replace All...'. The 'Type of Data' section has 'Automatically collected' selected.

Chemisorption

5. Enter a sample description in the *Sample* text box.
6. Enter *Operator*, *Submitter*, and *Bar Code* identification information in the respective text boxes. This information will display on the *Sample Description* tab of new sample information files. This

option may not display (or may have a different field label) if modified in the method from which the sample file was created, either through **Options > Default Method** or **File > Open > Method. (Optional)**.

7. **For Physisorption:** In the *Sample Tube* drop-down list, select a sample tube. If the sample tube you are using does not appear in this list, click **Edit** and enter the description and other parameters for this tube. Then go to **File > Save As > Sample Tube** to save these values for the next time this sample tube is used (**More information on page 82 of the Operator Manual**).
8. In the *Mass* group box, indicate if mass is to be manually entered by the operator (*Enter*) or calculated by the system (*Calculate*).

If mass = 1, the reported surface area equals the total surface area but it is always shown as m<sup>2</sup>/g. If the actual mass is entered, the surface area is reported as m<sup>2</sup>/g. Choose whether to enter mass manually or have the system automatically calculate mass. Enter a value for sample mass. Mass can be changed any time before, during, or after analysis.

- **Enter.** Enables the *Sample Mass* field. Enter a value for the sample mass.
- **Calculate.** Enables the *Empty tube* and *Sample + tube* fields. Enter the values necessary to calculate the sample mass. Equation used to calculate sample mass:

$$MASS_{sample} = MASS_{sample+tube} - MASS_{tube}$$

- **Density. For Physisorption:** Value is used for the calculated free space method only. Use 0.000 for a blank analysis.
9. In the *Type of Data* group box, indicate if the data is to be automatically collected by the system or manually entered by the operator.
    - **Automatically collected.** Select for all sample runs where the data are collected.
    - **Manually entered.** Select when another sample has been run on a different analyzer or different model analyzer so that data can be analyzed or used for comparison.

Choose **automatically collected**.

10. **For Physisorption** The optional user-defined fields in the *User Parameters* group box may be used to enter and track information from another analyzer or source, along with other statistical process control (SPC) data.

## 2.2. Preparation of Sample

- Sample tubes and filler rods must be clean and dry before samples are added and weighed. Use rubber gloves to ensure no oils or residue are transferred to the clean tubes and filler rods. Clean the interior of the sample tubes with the brush supplied with the analyzer. Rinse the sample tubes and filler rods thoroughly with alcohol. After rinsing, dry them.
- Weigh one empty test tube using the analytical balance. Carefully write down the result  $W_T$  [g];
- With the spatula add a sufficient amount of powder to the test tube (the total surface available should range from 5 and 10 [m<sup>2</sup>]);
- Weigh the test tube containing the powder. Carefully write down the result  $W_B$  [g].
- The mass of powder to insert to the measuring system is calculated from:  $W_P = W_B - W_T$  [g].

**Or** the analytical balance can be tared after weighting the empty test tube and the mass of powder can be directly weighed.

**Recommendations:**

- When analyzing different materials try to use as minimal sample mass and weigh:
  - More than 0,5 g for weakly adsorbing materials (start with 1,0 g) **Ex: Untreated Wood;**
  - Around 0.2–0.3 g for moderately adsorbing materials **Ex: Heat Treated Wood;**
  - Less than 0.1 g for strongly adsorbing materials **Ex: Activated Carbon.**
- Use filler rods to decrease the free space volume.

## II. Degas Conditions – Skip this Step because it's only valid for Degassing operations in specialized equipment designed for the procedure (Ex: Smart VacPrep)

## III. Analysis Conditions

1. The *Analysis Conditions* and *Adsorptive* gaps are already set, **no need for changing it.**



2. Click **Insert Range** to enter starting and ending relative pressure points.
3. Enable *Absolute pressure dosing* to specify pressure targets in mmHg, mbar, or kPa instead of relative pressure. This option is typically selected when using adsorptives at analysis conditions above the critical point of the gas; for example, H<sub>2</sub> adsorption on carbon at liquid nitrogen temperature.
4. Use the following buttons to specify:

Button	Use to Specify...
Dosing	Options for dosing tolerance, low pressure dosing, and dosing near saturation pressure.
Free Space	How the free space is to be measured.
P <sup>0</sup> and T	How the saturation pressure (P <sub>0</sub> ) is to be measured or calculated and the analysis bath temperature.
<i>For Physisorption</i>	
Preparation	Evacuation rate/time/level, leak test and time values, elevator prompts, and in situ degassing or activation.

5. **Preparation:** Use to enter analysis preparation details. Here, the Degas *in situ* will be **activated** and the conditions will be specified.
  - **Backfill and match transducer.** Use to backfill the sample tube to 760 mmHg at the beginning of the analysis and to recalibrate the sample port pressure transducer scale to match the manifold pressure transducer. Select the backfill gas to be used.
  - **Evacuation rate.** The rate for restricted evacuation.
  - **Unrestricted evac. from.** The pressure at which unrestricted evacuation is to begin.
  - **Vacuum level.** The pressure for unrestricted evacuation.
  - **Evacuation time.** Length of time for evacuation before proceeding with the temperature schedule. The timer starts when the vacuum level is reached.
  - **Degas in situ.** Select to degas the sample on the analysis port prior to analysis.
  - **Evacuation Temperature.** Temperature of the sample during evacuation.
  - **Ramp Rate.** Rate at which the temperature is to change when advancing to the target temperature.
  - **Hold pressure.** Pressure at which heating will stop and hold the sample temperature approximately constant until the pressure falls below the *Hold pressure*. This feature prevents

damage to the sample structure due to 'steaming,' as well as sample elutriation due to excessive escaping gas velocity.

- **Leak test.** Select if a leak test is to be performed.
- **Leak test duration.** Enter the duration of the leak test.
- **Elevator.** Select the appropriate elevator control option.
  - **Automatic.** The elevator is raised and lowered automatically.
  - **Wait for operator.** The operator will be prompted to set the elevator or analysis bath to the preferred height. When the prompt is acknowledged, the analysis will continue. This option should be used if the analysis bath must be placed manually in the preferred position, or the elevator must be raised to a height other than the standard analysis height.
  - **Do not move.** Use to have the analysis proceed without pausing or moving the elevator. This option should be used when the analysis bath is already in position and should not be moved during analysis.

**The following image shows the correct parameters to select:**

	Temperature (°C)	Temperature Ramp Rate (°C/min)	Time (min)
1	100	10.0	1440

#### **Additional Information:**

For a Standard Test, the only parameters that should be changed are:

1. Evacuation Temperature
2. Degassing Temperature
3. Degassing Time
4. Confirm a Leak Test
5. Elevator must wait for operator

The values for the parameters chosen for the majority of the tests done were:

**Evacuation Temperature: 70°C**

**Degassing Temperature: 80°C**

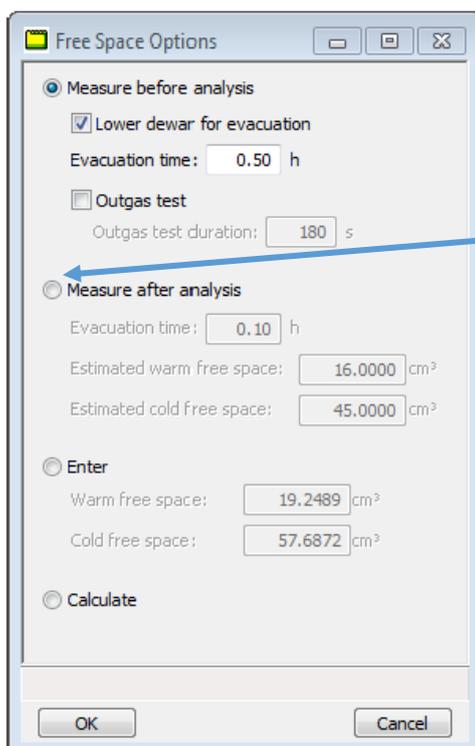
**Degassing Time: Overnight**

**The Evacuation and Degas Temperatures, as well as the time of Degassing should be chosen by the operator (this is only an example). However, for sensitive materials, the operator must take it in account and choose lower temperatures for longer times.**

6. **Free Space:** Use to enter the free space measurement type and if it should be measured before or after analysis.
  - **Measure before analysis. For Physisorption** Select if the free space is to be measured before the analysis begins. **Lower dewar for evacuation.** If the dewar is to be lowered for evacuation, select this options and enter the length of time for evacuation after the free-space measurement in the *Evacuation time* field. **Outgas test.** If an outgas test is to be performed after the free space evacuation, select this option and enter the duration of the outgas test in the *Outgas test duration* field.
  - **Measure after analysis.** Select if free space is to be measured after analysis ends. Enter the evacuation time, the estimated warm free space measurement, and the estimated cold free space measurement.

- **Enter.** Select to enter warm and cold free space manually, then enter the amounts in the text boxes.
- **Calculate. For Physisorption** Use to have the free space measurement calculated using the sample and tube parameters.
- For a first experiment, choose the **Measure before analysis** with **Lower dewar for evacuation** and **Outgas test to have an idea of the Cold and Warm free space values.**
- However, for next experiments, choose the **Measure after analysis** with an **evacuation time: 0,20h** and **the estimated warm and cold free space measurements obtained before.**

**Reason:** The free space measurement is made with Helium and some materials have the capacity to retain the helium even after the evacuation, before analysis. The remaining helium on the sample will affect the analysis of the nitrogen adsorption.



#### Additional Information:

For a Standard Test, the Free Space should be: **Measured after analysis!**

The Evacuation time chosen depends on the characteristics of the sample (Higher Surface Areas lead to Higher Evacuation times), however, in order to save liquid nitrogen, this evacuation time shouldn't be very long!

The value for the Evacuation Time chosen for the majority of the tests done

## Physisorption

7. **p° and Temperature:** Use to select options for obtaining the saturation pressure (p°) and analysis bath temperature.

**p° and Temperature Options**

**p° Options**

- Measure p° in the p° tube for each isotherm point.
- Measure p° over the sample. Enter an initial estimate for p°.  
p°: 760.000 mmHg
- Measure p° in the p° tube for each isotherm point. Measure p° over the sample and adjust the p° tube measurements.
- Determine p° from pressure measured over the dosing source. Note that the Adsorptive Properties must specify dosing from Psat tube, Sample port 3, or Vapor source.
- Measure Psat of the gas specified below for each isotherm point. Calculate p° of the adsorptive from the measured Psat.  
Psat gas: Nitrogen Edit...
- Calculate p° from the analysis temperature.
- Enter p°.  
p°: 760.000 mmHg

**Analysis Temperature Options**

- Enter the analysis temperature.  
Analysis temperature: -195.850 °C
- Calculate the analysis temperature from p° or Psat.

OK Cancel

**Additional Information:**

For a Standard Test choose:

**p° Option:** Measure p° in the p° tube for each isotherm point. Measure p° over the sample and adjust the p° tube measurements

**Analysis Temperature Option:** Calculate the

- **p° Options:** Select one option indicating how p° is to be measured or calculated.
  - **Psat Gas:** If choosing to measure the Psat for each isotherm point using a gas other than the adsorptive, select the Psat gas from the drop-down list, then click **Edit** to modify the Psat adsorptive properties. Refer to the *Adsorptive* drop-down list earlier in this table for details on editing this window.
  - **Analysis Temperature Options:** Select an option to enter analysis temperature manually, or choose to have it automatically calculated from p° or Psat.
- **Choose the p° Option: Measure p° in the p° tube for each isotherm point. Measure p° over the sample and adjust the p° tube measurements and the Analysis Temperature Option: Calculate the analysis temperature from p° or Psat.**
8. **Dosing:** This parameter is already set for the type of materials used in this lab, **no need for changing it.** (However, if the sample requires specific dosing parameters -> See more details on page 91 of the Operator Manual)

#### IV. Report Options

Use to specify report options for data collected from an analysis or manually entered data. Report Options files also help in customizing report details such as axis scale, axis range, column headings, and components of thickness curve equations. These files may contain tabular reports, plots, or both, as well as user-defined report tables. (More information on page 107 of the Operator Manual). **[Additional Information: For a Standard Test, choose "Summary", "Isotherm", "BET", "Langmuir", "t-plot", "DFT pore size" to see these parameters being measured and calculated live]**

## 2.3. Preparation of the Analysis

### I. Degas in situ for Physisorption

Most solid materials absorb moisture and other contaminants when exposed to the atmosphere. The sample must be clean when an analysis is performed. The degas process heats the sample and places it under vacuum to remove the moisture and contaminants.

1. Install the sample tubes and dewar lid on the analysis port. **(Don't forget to install the filler rod inside each tube – It is very important!)**
2. Go to **Unit 1 > Sample Analysis**, then click **Browse** to locate an existing sample file or click **New** to create a new one. The sample file *Analysis Conditions Preparation* section must specify *In Situ Degas*.
3. Click **Start**. The *Sample Analysis* window will display a prompt to raise the dewar lid and install the degas heating mantle.
4. Lift the dewar lid up against the sample port nuts. If isothermal jackets are installed, slide the jackets up to touch the dewar lid.
5. **Do not put the pressure sensor in the Analysis position before Degassing! (The high temperatures can seriously damage the sensor!)**
6. Install the heating mantle.
7. **Do not let the sample tubes touch the bottom of the heating mantle! (The contact with the resistance can seriously damage the tubes!)**
8. Acknowledge the prompt on the *Sample Analysis* window; the degas will proceed.
9. Observe the temperatures on the analyzer schematic.
10. When the degas is completed and the mantle has cooled, the *Sample Analysis* window will display a prompt to remove the degas heating mantle, properly position the isothermal jackets and dewar lid, then install the dewar.
11. Remove the heating mantle (it is not necessary to unplug the mantle), support the bottom of the tubes, then remove the mantle cover.



**To prevent potential burns, do not touch the sample tube or the heating mantle until they have cooled below 45 °C!**

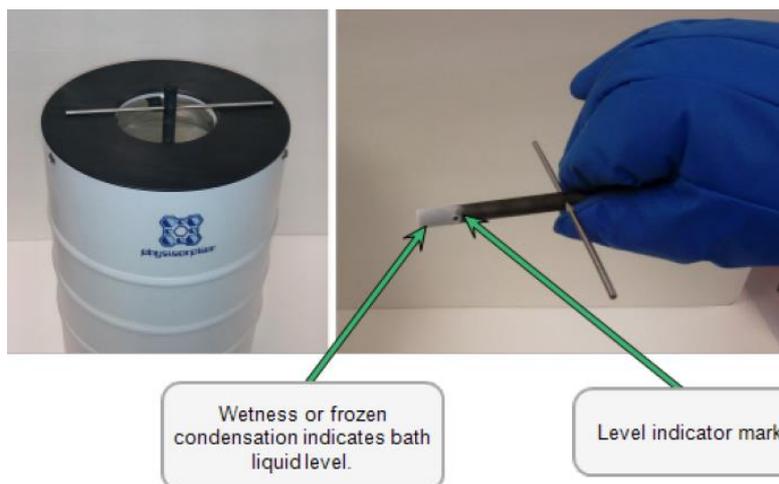
### II. Filling and Installation of the Dewar

Prepare the analysis dewar after degassing of the sample tubes.

**Always handle the dewar with care. Any product incorporating a vacuum is a potential safety hazard and should be treated with caution. Always observe the precautions listed in the Operator Manual (page 132).**

1. Fill the dewar with the analysis bath liquid (liquid nitrogen) to no higher than 2 1/4 in (5.7 cm) from the top. **Filling the dewar higher than this will cause an error in the free space measurement. Incorrect fluid levels can lead to measurement errors. Check the level of the bath liquid before each analysis.**

2. Insert the dipstick into the dewar and check the level of the analysis bath liquid. Condensation should not exceed the level indicator mark.



3. For best results, if the dewar has not been used for a while, allow approximately 30 minutes for the temperature of the dewar to stabilize with the bath liquid, then recheck the level of the bath liquid. Add additional liquid if necessary.
4. If using isothermal jackets, slide the jackets down the sample tube until the jackets touch the sample tube bulbs.
5. Slide the dewar lid to approximately 3/4 in (19 mm) from the sample port nuts to ensure a proper seal on the top of the dewar.
6. Attach the safety shield to the brackets on the front of the analyzer.



**Before Analysis starts, the installation must be similar to the image.**

### III. During Analysis

Follow the instructions the equipment gives and be constantly checking the level of liquid nitrogen inside the dewar. **Great variations in the level of liquid nitrogen could lead to errors in the free space measurement and, consequently, errors during all the analysis. – This is very important!**

**Additional Information:***How to move the elevator*

- *Go to Unit 1*
- *Select “Enable Manual Control”*
- *Move the Mouse to the Elevator*



- *Click in the Right Button of the Mouse*
- *Press “Raise” or “Lower” depending on the position of the elevator*
- *Press Again “Enable Manual Control” to put the Equipment again in Automatic Control*

***Safety Measure: Always put the Shield on during Analysis!***

When the analysis is complete, remove the sample tube and store (or dispose of) the sample material as applicable.

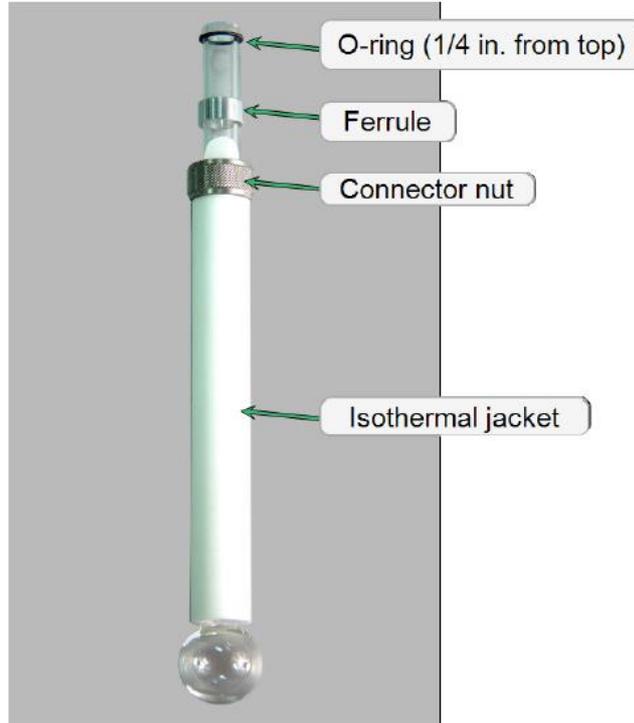


***For Physisorption*** Use caution when removing the sample tube if using a hanging filler rod. The sample tube O-ring or dewar lid may snag the filler rod retaining ring. Loosen the snag gently; excessive force may break the tip of the filler rod.

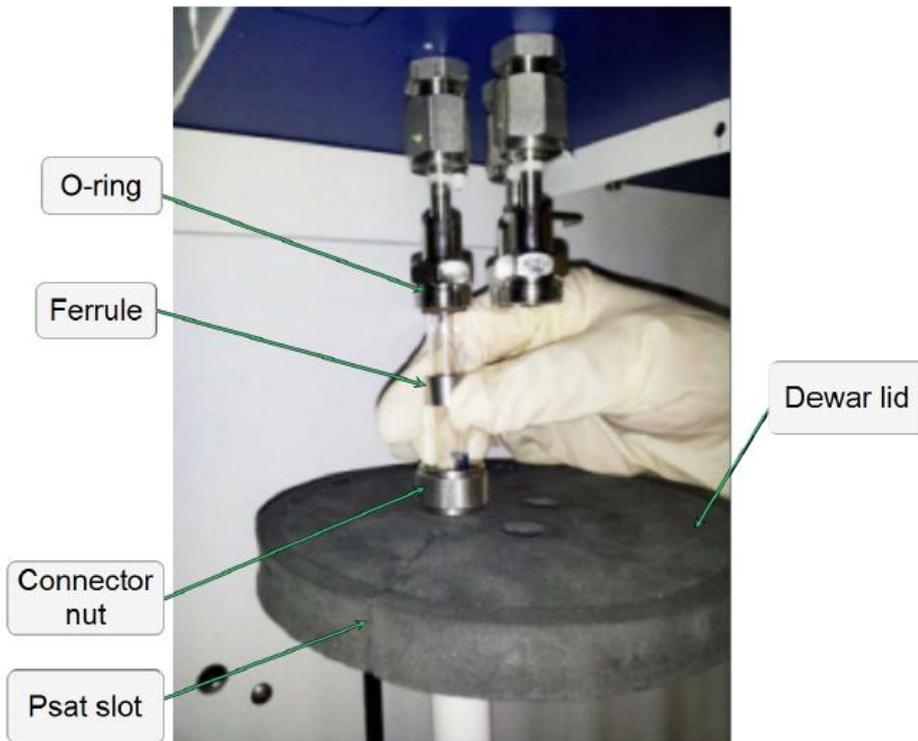
**Appendix:**

**Equipment's Information**

**Components of the Sample Tube**



**Installation of the sample tubes before Degassing**



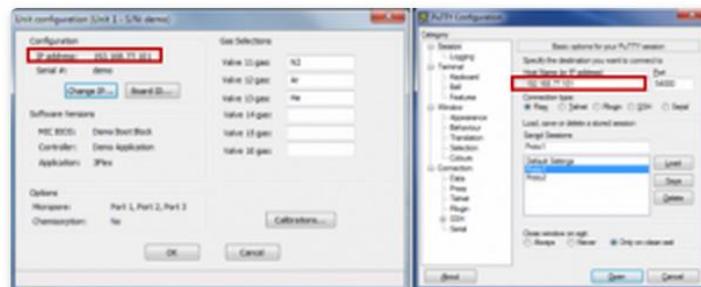
### Installation of the P<sub>sat</sub> tube after Degassing

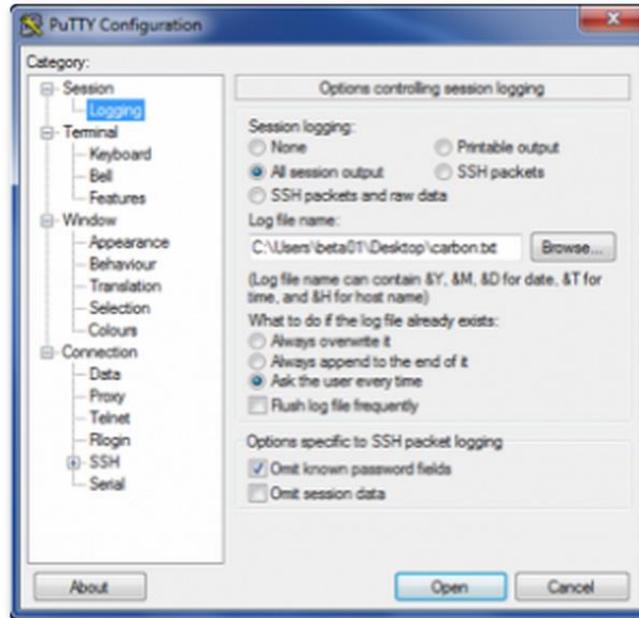


### COLLECTING ALL THE OUTPUTS OF THE EQUIPMENT DURING ANALYSIS

In order to connect to the instrument, the following items have to be configured:

1. Input 3FLEX IP address, found in the Unit Configuration, into the PuTTY software
2. Input 54000 in the 'Port' field
3. Select 'Raw' connection type
4. Save session settings (optional)
5. To save the data, go to the 'Logging' settings (see Figure).
  - a) Select 'All session output'
  - b) Select destination (using 'Browse...') to save file and create a .txt file (helpful to name this file the same as your sample file to be analyzed)
  - c) Click 'Open' to start collecting the data (note: this program can be started before the 3FLEX starts collecting data—it will be 'waiting' for when data output from the 3FLEX begins).





The text file containing the transient data can be accessed using any means that accepts tab separated values. Possibilities include Notepad, Microsoft Excel (or other spreadsheet software), or programming languages that read .txt or .xls files. Within programming languages, MATLAB®, Octave, and Python may be a few that come to mind. MATLAB® has the xlsread() function and Octave has the textread() function which are easy to use.

#### DESCRIPTION OF ALL COLUMNS IN COLLECTED DATA FILE

The data file generated during this collection process has 58 columns of tab-delimited, or separated, values. When viewed in Microsoft Excel or other spreadsheet program, the data occupy columns 'A' through 'BF'. The identity of each of these columns of data is given below:

```

a = 'manifold pressure (torr)';
b = 'manifold volume (cc)';
c = 'manifold temperature (K)';
d = 'time (ms)';

e = 'port 1 pressure (torr)';
f = 'port 1 volume (cc)';
g = 'port 1 temperature (K)';
h = 'port 1 ambient temperature (K)';
i = 'port 1 analysis temperature (K)';
j = 'port 1 warm freespace (cc STP)';
k = 'port 1 cold freespace (cc STP)';
l = 'port 1 quantity dosed (cc STP)';
m = 'port 1 quantity adsorbed (cc STP)';
n = 'port 1 has manifold?';
o = 'port 1 valve open?';
p = 'port 1 data points taken';
q = 'port 1 current pressure table index';
r = 'port 1 last data point elapsed time (ms)';
s = 'port 1 last data point pressure (torr)';
t = 'port 1 last data point quantity dosed (cc STP)';
u = 'port 1 last data point quantity adsorbed (cc STP)';
v = 'port 1 last data point Po (torr)';

w = 'port 2 pressure (torr)';
x = 'port 2 volume (cc)';
y = 'port 2 temperature (K)';
z = 'port 2 ambient temperature (K)';
aa = 'port 2 analysis temperature (K)';
ab = 'port 2 warm freespace (cc STP)';
ac = 'port 2 cold freespace (cc STP)';
ad = 'port 2 quantity dosed (cc STP)';
ae = 'port 2 quantity adsorbed (cc STP)';

af = 'port 2 has manifold?';
ag = 'port 2 valve open?';
ah = 'port 2 data points taken';
ai = 'port 2 current pressure table index';
aj = 'port 2 last data point elapsed time (ms)';
ak = 'port 2 last data point pressure (torr)';
al = 'port 2 last data point quantity dosed (cc STP)';
am = 'port 2 last data point quantity adsorbed (cc STP)';
an = 'port 2 last data point Po (torr)';

ao = 'port 3 pressure (torr)';
ap = 'port 3 volume (cc)';
aq = 'port 3 temperature (K)';
ar = 'port 3 ambient temperature (K)';
as = 'port 3 analysis temperature (K)';
at = 'port 3 warm freespace (cc STP)';
au = 'port 3 cold freespace (cc STP)';
av = 'port 3 quantity dosed (cc STP)';
aw = 'port 3 quantity adsorbed (cc STP)';
ax = 'port 3 has manifold?';
ay = 'port 3 valve open?';
az = 'port 3 data points taken';
ba = 'port 3 current pressure table index';
bb = 'port 3 last data point elapsed time (ms)';
bc = 'port 3 last data point pressure (torr)';
bd = 'port 3 last data point quantity dosed (cc STP)';
be = 'port 3 last data point quantity adsorbed (cc STP)';
bf = 'port 3 last data point Po (torr)';

```

### **Additional Information, Advices and Warnings**

- Always use rubber gloves when contacting with the tubes;
- All the weight measurements should be very rigorous, in order to prevent errors on the specific surface area values;
- If the room temperature is too high, this can lead to a problem on the equipment, especially during the evacuation and degassing step, and consequent stoppage of the degassing. This is due to the high temperatures on the vacuum pump that lead to a shutdown of the analysis. – In this case, the operator should wait until the room temperature decreases.
- The pressure on the gas tubes connected to the equipment shouldn't be too high (lower than 0,8 bar), in order to prevent overpressure problems during analysis.

### III. Thermogravimetric analysis

Netzsch STA 449 F3 Jupiter

#### Specifications of the Device

Table A. 3 - Specifications of the Netzsch STA 449 F3 Jupiter

Temperature Range	-150 °C to 2400 °C
Resolution TGA	0,1 µg, DSC: < 1 µW
Cooling Time Rate	0,001 to 50 K/min
Measuring Range	Up to 35000 mg
Heating Rate	0,001 to 50 K/min
Balance Type	Inquire
Weight Range	1 µg to 35 g
Weight Resolution	Up to 0,00001 %
Method	TGA-DSC

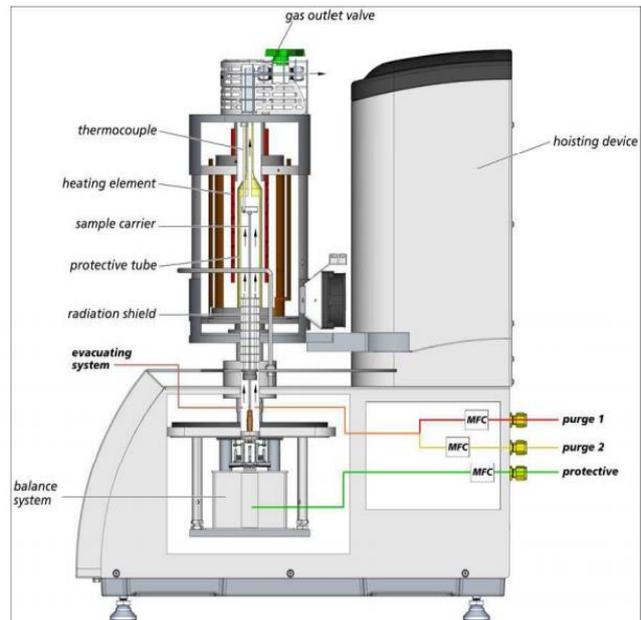


Figure A. 3 - Structure of the Netzsch STA 449 F3 Jupiter



Figure A. 4 - Netzsch STA 449 F3 Jupiter

## IV. Elemental analysis

Table A. 4 - Specifications of the FLASH 2000 Series (elemental analyzer)

<i>Depth (Metric) Exterior</i>	580 mm
<i>Height (Metric) Exterior</i>	500 mm
<i>Hertz</i>	50/60 Hz
<i>Voltage</i>	230 V
<i>Weight (Metric)</i>	67 kg
<i>Width (Metric) Exterior</i>	590 mm
<i>Measurement Ranges:</i>	0,01 (100 ppm) to 100% for nitrogen and carbon
<i>Sample Type(s):</i>	Soils, sediments or particulate materials obtained by filtration of sea, river, lake, or tap water
<i>Sample Size:</i>	10 mg to 1 g according to sample nature
<i>Gas Requirements:</i>	Base Unit Requirement: Helium (GC Grade), Oxygen (99,9995% purity) Optional FPD Requirement: Helium (GC Grade), Air (99,995%), Hydrogen (99,995%)
<i>Control:</i>	Eager Xperience*



Figure A. 5 - FLASH 2000 Series (elemental analyzer)

## Calibration Curves for Determination of Carbon, Hydrogen and Oxygen

### Calibration Curve for Determination of Carbon

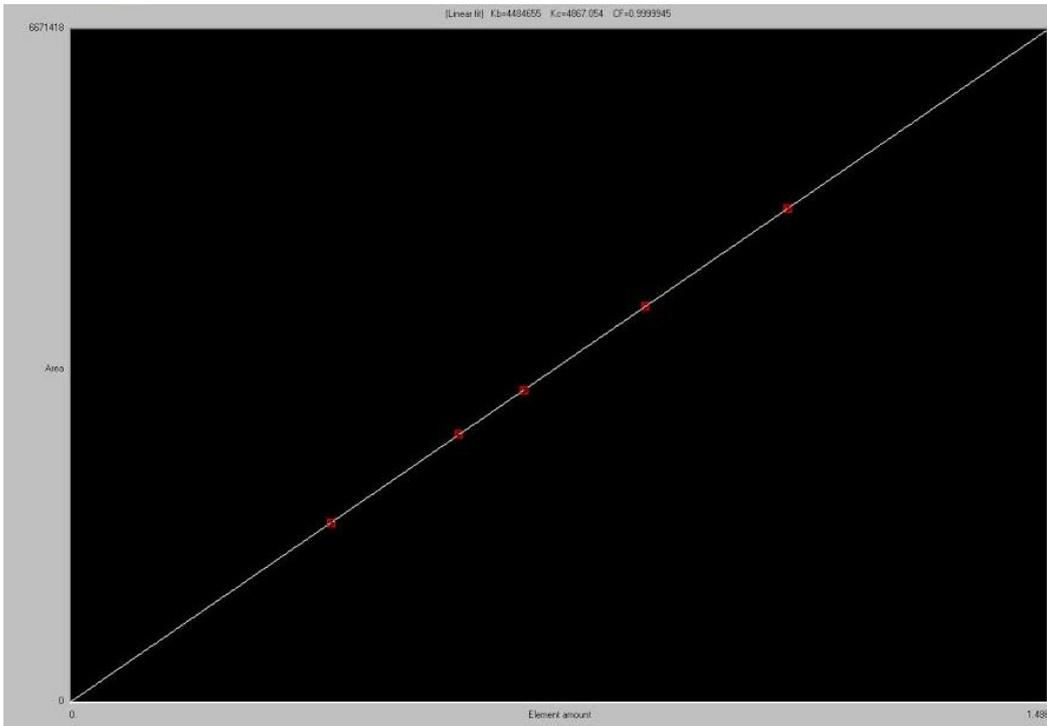


Figure A. 6 - Calibration Curve for Determination of Carbon

### Calibration Curve for Determination of Hydrogen

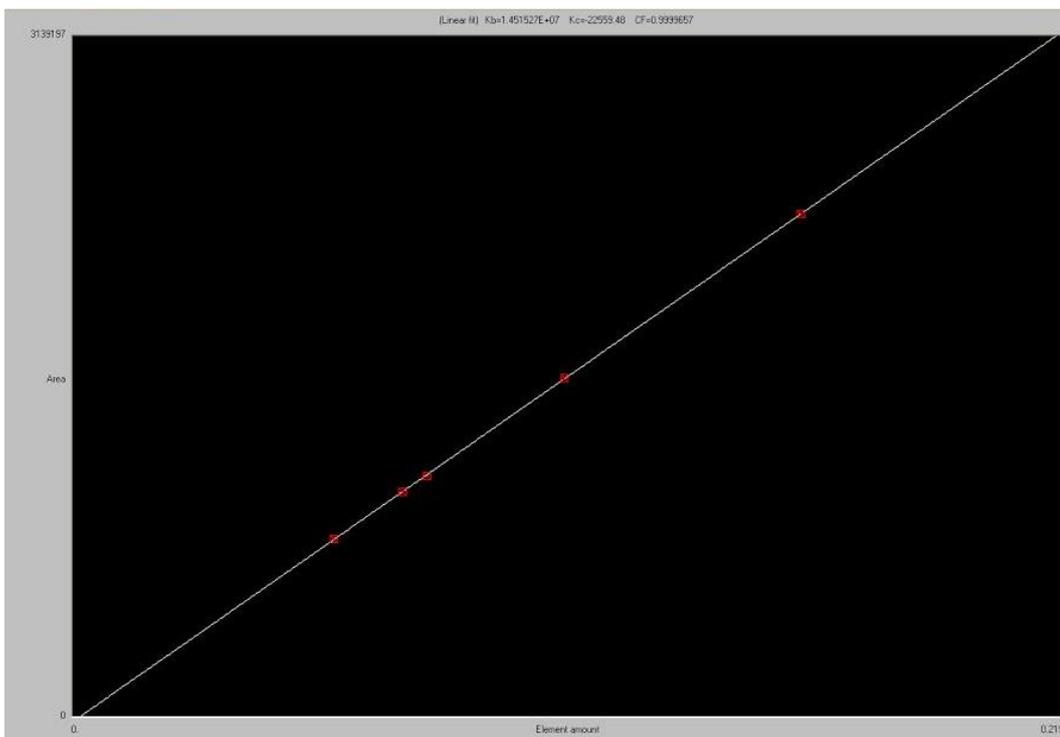
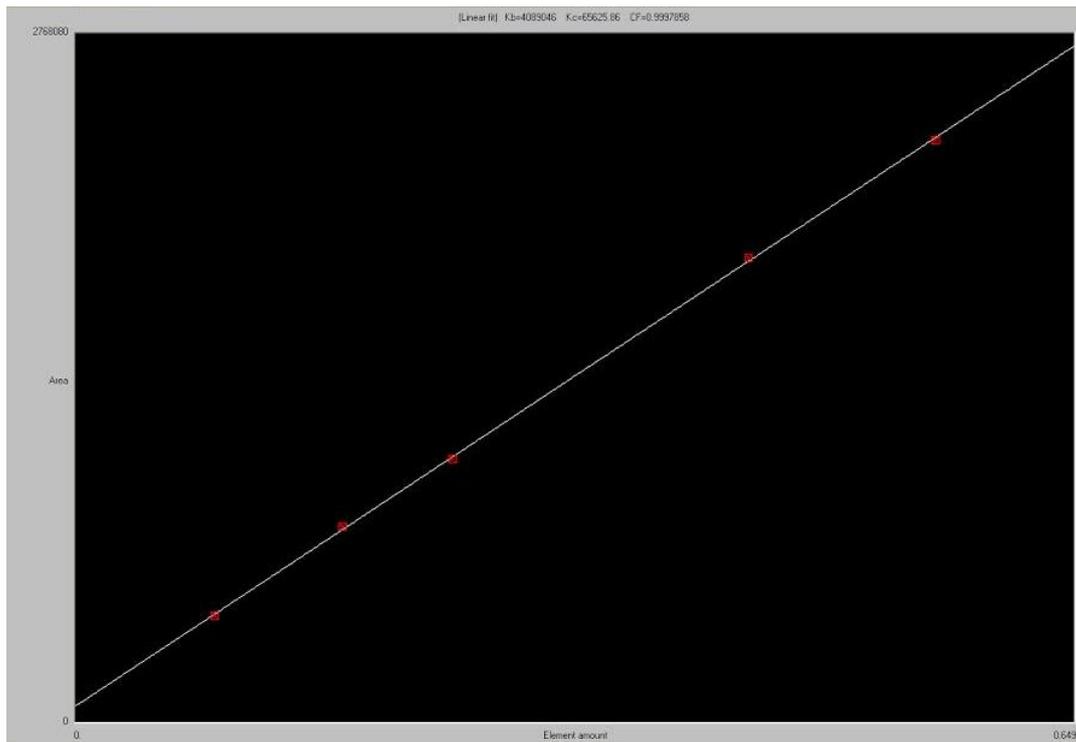


Figure A. 7 - Calibration Curve for Determination of Hydrogen

### Calibration Curve for Determination of Oxygen



**Figure A. 8** - Calibration Curve for Determination of Oxygen

## V. Water Sorption Study

### Micromeritics 3FLEX Surface Characterization Analyzer

#### Specifications of the Device

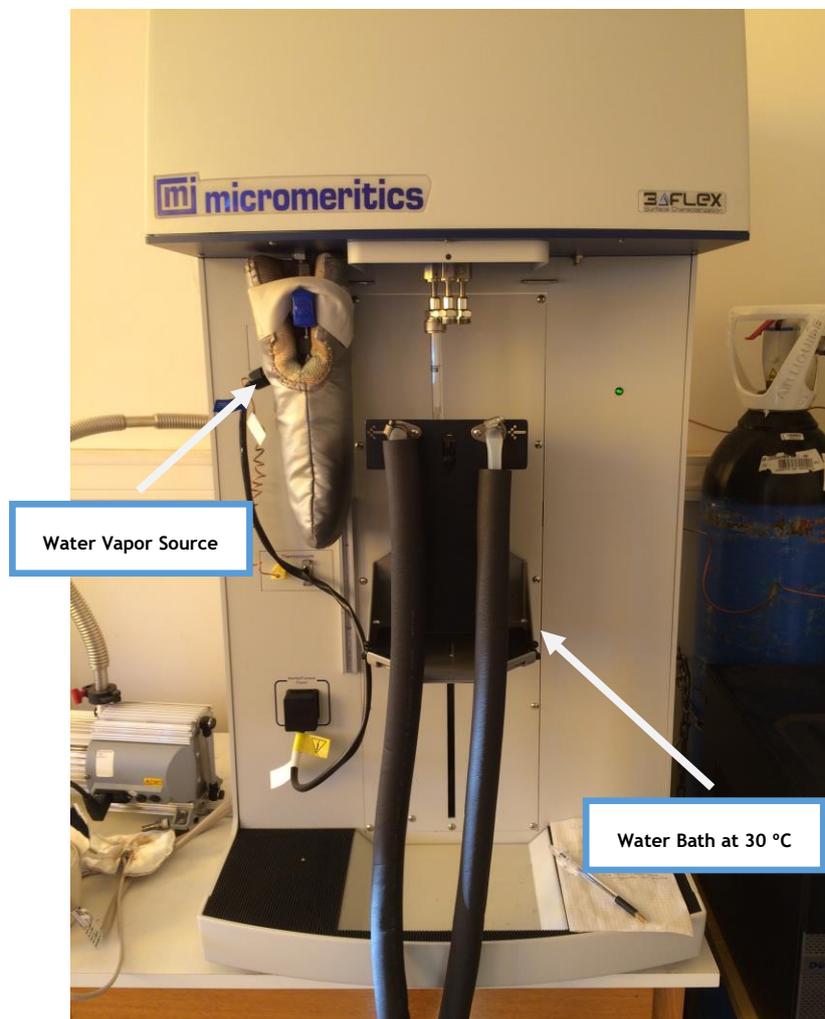
The specifications of the device were already presented in chapter II of the annex 1.

#### Protocol for Water Sorption Studies

The protocol for these studies is similar to the one presented in chapter II of the annex, however with two major changes, the adsorptive gas is water vapor and the temperature of analysis is 30 °C.

This way, two additional protocols were developed:

- Protocol for the Installation of the Vapor Source
- Protocol for Vapor Purification

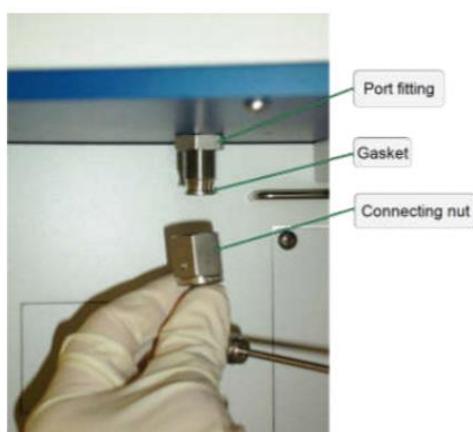


*Figure A. 9 - Installation of the Micromeritics 3FLEX Surface Characterization Analyzer for the Water Vapor Sorption Measurements*

## ***Protocol for the Installation of the Vapor Source***

*Gonçalo de Bastos Monteiro; gdbmonteiro@gmail.com*

1. Use an appropriate wrench to loosen the connecting nut from the port fitting by turning the connecting nut counterclockwise while using a second wrench to hold the port fitting stationary.

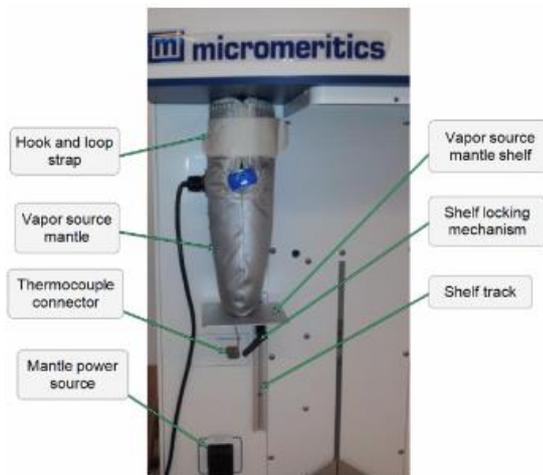


2. Remove the connecting nut and the attached assembly. After removal, the existing seal or a tightfitting plastic cap can be used to protect the sealing surface assembly from scratches. Prior to reassembly, remove the existing seal or cap, then insert a new seal.
3. Install the vapor source container with a new seal by attaching the connecting nut to the port fitting. Hand tighten the connecting nut by turning clockwise. Use an appropriate size wrench to tighten the assembly an additional 1/8 to 1/4 turn beyond finger tight, while using a second wrench to hold the port fitting stationary on the analyzer.



Turn the vapor source isolation valve to adjust the vapor flow

4. Use the manual controls on the analyzer schematic, evacuate the space above the vapor source by opening valves 4 and 6 with all other valves closed. Then close valve 4 before turning the vapor source isolation valve to the vertical (open) position. The  $P_0$ /vapor port pressure reading on the instrument schematic will show the vapor pressure.



5. Slide the vapor source mantle over the vapor source container. Extend the blue knob through the circular hole. Secure the hook and loop strap.
6. Insert the thermocouple plug into the connector labeled Thermocouple. Insert the power plug into the outlet labeled Mantle/Furnace Power.
7. Insert the thermocouple plug into the connector labeled Thermocouple. Insert the power plug into the outlet labeled Mantle/Furnace Power.
8. If using a support shelf, slide the shelf locking mechanism of the vapor source mantle shelf into the shelf track on the front of the analyzer. Raise the shelf until the vapor mantle is pushed as close as possible to the underside of the upper cabinet. To tighten the shelf, turn the locking mechanism clockwise.

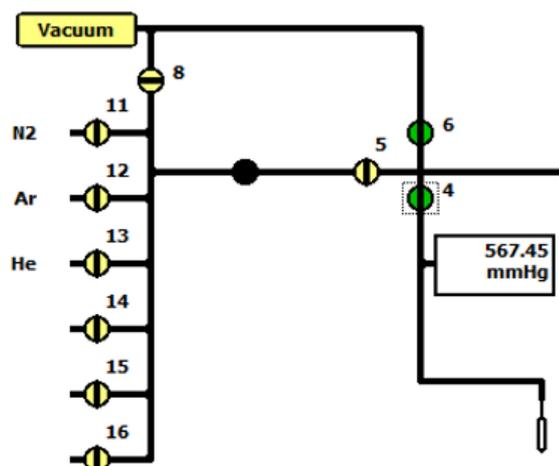
## ***Protocol for Vapor Purification on the Micromeritics 3FLEX***

### **Introduction**

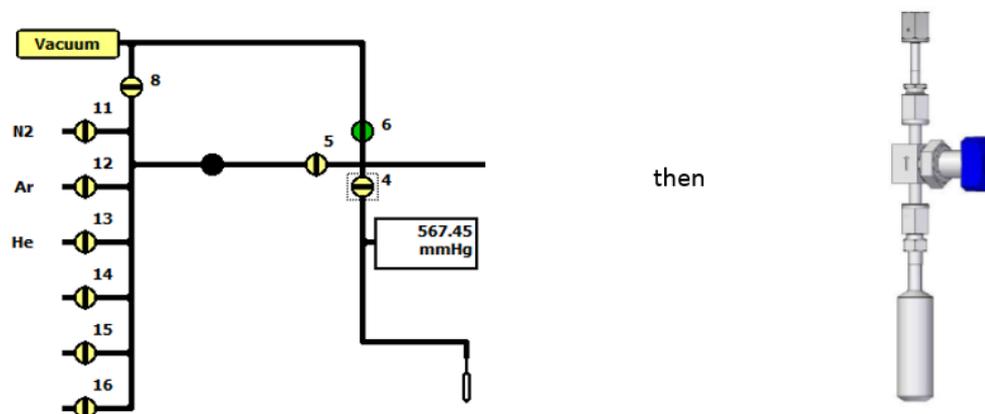
Physical adsorption of gases is generally used to calculate pore size and surface area of solid materials. Using vapor adsorptives allows the sorption capacity and isosteric heat of adsorption, the energy released as molecules adsorb on the sample surface, to be calculated by using isotherms collected at different temperatures with the same vapor and adsorbent. Heats of adsorption data are very useful in research applications. In the case of competitive adsorption, the vapor with the highest heat of adsorption will adsorb first and have the strongest interaction with the surface. However, if the heat of adsorption is too high, the molecule will be so strongly adsorbed that desorption or regeneration of the material may be difficult. In order to properly collect vapor isotherms, a purified vapor must be used. A liquid-filled reservoir is used as the source of the vapor. This procedure describes a freeze-thaw method to remove dissolved gases and air within the reservoir so the vapor purity is suitable for analysis on the Micromeritics 3FLEX. The general principles of this method could also apply to vapor purification on other gas adsorption instruments. The basic principle is to evacuate non-condensed species while the vapor reservoir is immersed in a cryogenic bath. At the pressures achieved during the purification process, nitrogen and oxygen are not condensed. The use of liquid nitrogen is limited to vapors that will not sublime at cryogenic temperatures.

### **Method**

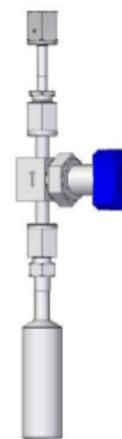
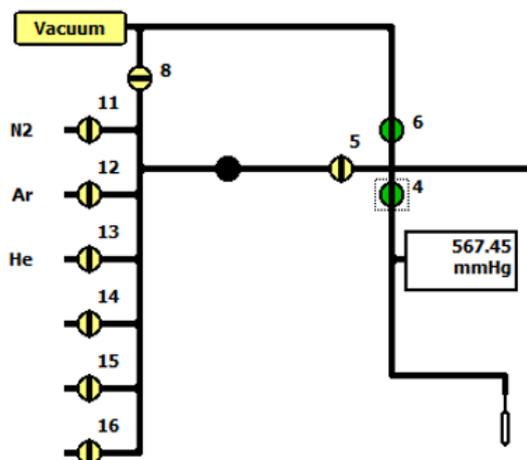
1. Fill a clean vapor reservoir with liquid. Fill halfway (10 ml) if using water. Fill with approximately 20 ml for other liquids.
2. Attach vapor reservoir to the 3FLEX as instructed on page 2-44 of the operator's manual.
3. Firmly close the vapor close-off valve above the liquid-filled reservoir (blue valve on the vapor container).
4. On the instrument schematic, open valve 4 to evacuate the space above the vapor close-off valve



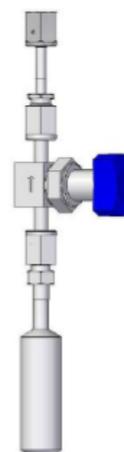
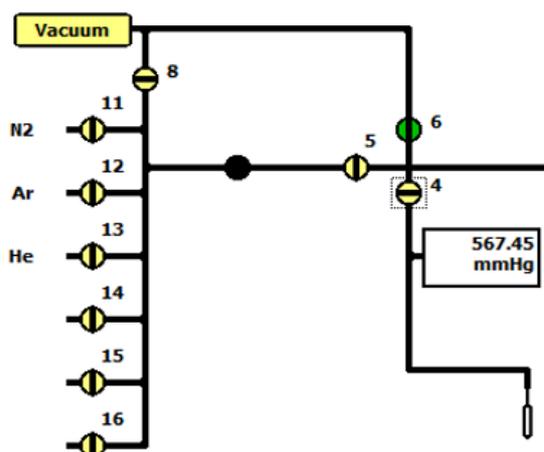
5. Close instrument valve 4 on the instrument schematic and open the vapor close-off valve on the reservoir (in that order). Allow the pressure to equilibrate in the vapor container.



6. Submerge the vapor reservoir in a cryogen bath. The use of liquid nitrogen as the cryogen should be limited to vapors with no sublimation pressure at cryogenic temperatures. Wait for the pressure in the vapor container to drop as low as possible. This may only be 150 torr for the first cycle but should be near zero after two or three cycles. A lab jack is useful in order to hold and adjust the dewar filled with liquid nitrogen.
7. Once the vapor has condensed and has frozen, open valve 4 on the instrument schematic with the cryogen bath still in place and evacuate the vapor container (the vapor close-off valve should still be opened). Pressures in the range between  $10^{-4}$  and  $10^{-5}$  torr should be achievable.



8. Close valve 4 on the instrument schematic and remove the cryogen bath. Let the vapor container thaw. The vapor close-off valve is still open during this step. To expedite the process, a warm water bath may be used temporarily to raise the temperature of the vapor container closer to the ambient temperature. However, a layer of ice formed on the reservoir could also create a barrier for heat transfer, so it is best to not introduce the water bath immediately. If pressure stabilizes near the calculated saturation pressure at room temperature, the vapor is free of impurities.



9. If the pressure does not stabilize around the calculated saturation pressure, **repeat steps 3-8** until the pressure at the last step stabilizes near the calculated saturation pressure of the vapor. When the vapor is pure, the pressure should stabilize around the same value after each thawing cycle. Typically, three total purification cycles (two repeats) is sufficient.

# Annex 2

# THERMOGRAVIMETRIC ANALYSIS, COMPOSITION AND PORE DEVELOPMENT DURING PYROLYSIS OF COCONUT CORE

S. Duarte<sup>a,b\*</sup>, P. Lu<sup>b</sup>, G. Monteiro<sup>b,c</sup>, J.C. Rolón<sup>d</sup>, P. Perré<sup>b</sup>

\* corresponding author : [sduarte@qui.una.py](mailto:sduarte@qui.una.py), [shirley.duarte-chavez@ecp.fr](mailto:shirley.duarte-chavez@ecp.fr)

<sup>a</sup> Faculty of Chemical Sciences, National University of Asunción, Mcal. Estigarribia km 11.5, San Lorenzo, Paraguay.

<sup>b</sup> Laboratoire de Génie des Procédés et Matériaux, CentraleSupélec, Université Paris-Saclay, Grande Voie des Vignes, 92295, Chatenay-Malabry, France.

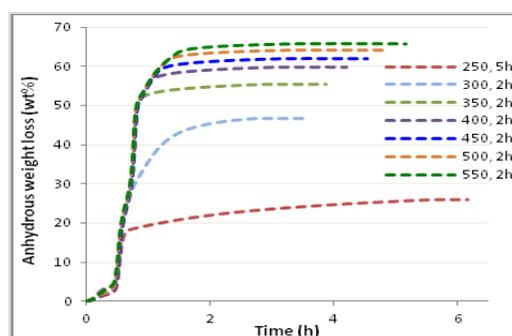
<sup>c</sup> Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

<sup>d</sup> Faculty of Engineering, National University of Asunción, Mcal. Estigarribia km 11.5, San Lorenzo, Paraguay.

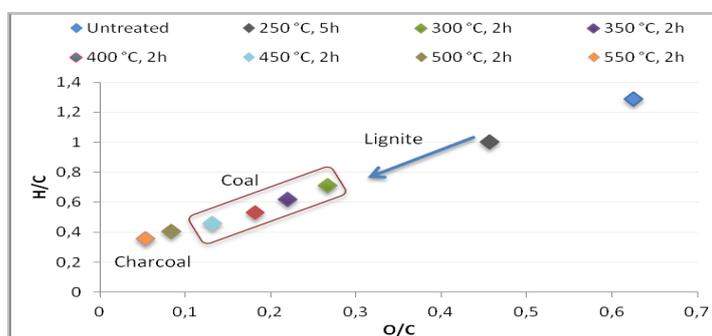
## I. ABSTRACT

Presently, the coconut core or coconut endocarp *Acrocomia aculeata* variety present in the central-eastern region of South America, is an agro-industrial waste. A major feature of this biomass, is the high calorific value (HHV) of approximately 19,3 MJ/kg [1], which enable enormous potential of industrialization of coconut fruit in biorefinery to obtaining fuels, materials and chemicals, which justify a thorough study.

In this work, clean and dry particles of coconut core between 0.2 and 0.63 mm of size, were thermally decomposed at different temperatures (250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C) in a nitrogen atmosphere. From the thermogravimetric curves, the most important weight loss was observed between 250 and 350 °C (Fig. 1). The change of the elemental composition after treatment, together with the untreated samples, was determined using an organic elemental analyzer (Thermo Scientific). From the evolution of the atomic ratio H/C as function of the atomic ratio O/C it can be seen that elementary composition changes to lignite [2, 3] under the treatment at 250 °C and towards a characteristic coal and charcoal at higher temperatures (Fig. 2).



**Fig. 1** Anhydrous weight loss (wt%) of coconut core.



**Fig. 2** Van Krevelen plot for the treated and untreated coconut.

The specific surface of all samples was evaluated by adsorption of nitrogen using BET method at 77 K in a surface characterization analyzer (Micromeritics). The specific surface, increases with the treatment intensity, with a particular increase above 500 °C (Table 1).

**Table 1.** Surface area BET results.

	Untreated	250 °C, 1h	300 °C, 2h	350 °C, 2h	400 °C, 2h	450 °C, 2h	500 °C, 2h	550 °C, 2h
<b>Average BET (m<sup>2</sup>/g)</b>	0.4	0.4	0.4	0.5	0.5	5.8	44.8	202.3

From the observation of coconut outer section with an environmental scanning electron microscope (ESEM), we registered for the first time the evolution of the pore structure with the treated temperature.

[1] S. J. Duarte, M. B. Sarubbi, J. Lin, P. J. Torres, In: 3rd Conference of Computational Interdisciplinary Sciences, Paraguay, 2014.

[2] J.J. Chew, V. Doshi, Recent advances in biomass pretreatment – Torrefaction fundamentals and technology. Renewable and Sustainable Energy Reviews 15 (2011) 4212–4222.

[3] Sofien Cavagnol. Approche multi échelle de l'emballement des réactions exothermiques de torréfaction de la biomasse lignocellulosique: de la cinétique chimique au lit de particules. PhD manuscript, Ecole Centrale Paris, 2013. French.

