RES | THE SCHOOL *for* RENEWABLE ENERGY SCIENCE

Fungi tar degradation

Possible application for micro-scale slow pyrolysis rotary kiln

Petra Božič

UNIVERSITY OF ICELAND

University of Akureyri

FUNGI TAR DEGRADATION

Possible application for micro-scale slow pyrolysis rotary kiln

Petra Božič

A 30 credit units Master's thesis

Supervisors:
Francesco Fantozzi, prof. dr

A Master's thesis done at
RES │ the School for Renewable Energy Science
in affiliation with
University of Iceland &
the University of Akureyri

Akureyri, February 2009

Fungi tar degradation

Possible application for micro-scale slow pyrolysis rotary kiln

A 30 credit units Master's thesis

RES │ the School for Renewable Energy Science
Solborg at Nordurslod
IS600 Akureyri, Iceland
telephone: + 354 464 0100
www.res.is

Printed in 14/05/2009
at Stell Printing in Akureyri, Iceland

ABSTRACT

When gas is cleaned in the process of slow pyrolysis in small-scale applications, water scrubbing is the most commonly used technology. After gas cleaning the tar and water vapors are trapped in the water, which is used for scrubbing. This waste water consists of condensed water vapors and two fractions of tar (water soluble and heavy tar). The product of this slow pyrolysis process is considered waste. None of the tar fractions are adequate for direct use in co-firing technologies. First it (water soluble tar fraction) contains too much water and later in the heavy tar there is not a sufficient quantity. The percentage of tar yielded from the slow pyrolysis process is not sufficient to be distilled in order to chemically clean components for further industry use, but that is the case in fast pyrolysis. That is why it is treated as chemical waste and needs to be disposed properly, which is a costly process. In order to reduce this cost a bioremediation method of fungi tar degradation has been examined. Fungi have a more potent enzyme system and are therefore far more appropriate for tar degradation than bacteria.

PREFACE

Recently a lot of emphasis has been put on our environment and its preservation. The fossil fuel resources debate presents a few different outcome predictions. Those who defend the Hubbert´s peak theory say that fossil fuel reserves are already running low, while those who are more optimistic say that the world´s oil usage peek will be around 2030 (National Petroleum Council, 2007). Also, CO_2 emissions are a very important factor in the field of renewable energy and environmental protection. One renewable energy source that is available for fighting climate change, dropping CO_2 levels and prolonging fossil fuel reserves is biomass. Different technologies for the energy conversion of biomass are known.

The technology addressed in this work is biomass pyrolysis. Pyrolysis products are pyrogas (syngas), char and tar, the percentage of which differs as conditions of the process are changed (temperature, residence time, mass flow). As with any other industrial process, pyrolysis has its advantages and disadvantages. Apart from the fact that the technology is constantly developing and commercializing slowly, there is an issue with the disposal of waste tar from slow pyrolysis. Tar contains a large amount of phenols that are environmentally harmful. The goal of the thesis is to improve the existing disposal technology by exploring fungi tar degradation (known facts and what could be done in Perugia), which will contribute to the renewable and environmental aspects of the pyrolysis process.

First the pyrolysis is covered in general, with an explanation of the differences between fast and slow pyrolysis processes. Then woody biomass composition is covered, as it is important to understand the chemical composition of wood in order to understand the formation of pyrolysis products. Next bio-oil, e.g. tar, is discussed. And at the end fungi tar degradation theory follows, explaining the chemistry of phenols and other components found in tar (literature data). In the last section, troubleshooting and possible solutions are described.

The goals of the project were to analyze the tar produced during our tests while changing and improving different parameters and to design a vessel for fungi tar degradation. All the work was conducted on a micro-scale slow pyrolysis rotary kiln pyrolyser at the University of Perugia, Faculty of Engineering, Department for mechanical engineering, Pyrolysis laboratory in Perugia, Italy. The work was conducted under supervision of prof. dr Francesco Fantozzi and with assistance of Michele D´Amico, Pietro Bartoci, Paolo Laranci, Marco Mattogno and others.

Special thanks go to professors dr. Francesco Fantozzi and dr. Umberto Desideri for giving me the opportunity to learn a lot and gain this very useful practical experience. Hereby the work of assistants and technical personnel is acknowledged.

Personal thanks go to my family and friends for all the moral support given.

TABLE OF CONTENTS

1 INTRODUCTION – PYROLYSIS PROCESS 1
1.1 What is pyrolysis? 1
1.2 Pyrolysis by stages 1
1.3 Driving forces of pyrolysis 2
1.4 Types of pyrolysis 4
1.4.1 Fast pyrolysis 4
1.4.2 Slow pyrolysis 5
1.5 Products of pyrolysis process 5
1.6 Gas cleaning 6
1.6.1 Wet scrubbing 7
1.7 Micro-scale slow pyrolysis rotary kiln pyrolyser for syngas and char production in Perugia, Italy – laboratory demonstration plant 8
2 WOODY BIOMASS COMPOSITION 12
2.1 Cellulose – hemicelluloses – lignin 12
2.1.1 Cellulose 12
2.1.2 Hemicelluloses 13
2.1.3 Lignin 14
2.2 Characteristics of thermo-chemical decomposition of three main components 16
3 BIO-OIL DERIVED FROM WOODY BIOMASS 18
3.1 Chemical composition of tar 18
3.2 Chemical characterization methods 21
4 TAR DEGRADATION BY FUNGI 25
4.1 Pathway of phenols degradation by fungi 28
5 POSSIBLE APPLICATION FOR MICRO-SCALE SLOW PYROLYSIS ROTARY KILN 32
5.1 Differences in research work and real life situation 32
5.2 Biomass preparation 32
5.3 Sealing system of the plant 35
5.4 Retention time 37
5.5 Scrubber cleaning 38
5.6 Pre-design of a tank for fungi tar degradation 39
6 CONCLUSIONS 41
REFERENCES 42
Appendix A 1

LIST OF FIGURES

Figure 1: Pyrolysis reactions. *2*

Figure 2: Wood chips (feedstock); gas, both fractions of tar, and char as products of slow pyrolysis *6*

Figure 3: Water scrubber for syngas cleaning – Micro-scale slow pyrolysis rotary kiln in Perugia, Italy. *8*

Figure 4: Micro-scale slow pyrolysis rotary kiln laboratory demonstration plant *9*

Figure 5: Reactor with four laminar fins *9*

Figure 6: Micro-scale slow pyrolysis rotary kiln laboratory demonstration plant layout. *11*

Figure 7: Chemical structure of cellulose *12*

Figure 8: Intrachain and interchain hydrogen-bonded bridging. *12*

Figure 9: Stucture of cellulose. (a) Cellulose fibers from a ponderosa pine. (b) Macrofibrils compose each fiber. (c) Each macrofibril is composed of bundles of microfibrils. (d) Microfibrils, in turn, are composed of bundles of cellulose chains. . *13*

Figure 10: Saccharides that form hemicellulose *13*

Figure 11: p-coumaryl, coniferyl and synapyl structures *14*

Figure 12: Small section of hardwood (Fagus sylvatica – European beech) lignin polymer with some typical lignin chemical linkages *15*

Figure 13: Pyrolysis curves of hemicelluloses, cellulose and lignin in TGA *16*

Figure 14: Releasing profile of gas product from lignin pyrolysis in packed bed. Order of graphs from top to bottom: hemicelluloses, cellulose and lignin. *17*

Figure 15: Tar – water soluble fraction and heavy tar fraction. *18*

Figure 16: Relationship between products and temperature to which vapors are exposed before quenching *19*

Figure 17: Some of the main components of tar *20*

Figure 18: Utilization of phenols by micromycetes Trichoderma and Penicillium at different WSF concentration in the medium *25*

Figure 19: Changes in qualitative composition of WSF phenols after microbial degradation: chromatogram of control sample (a); chromatograms of samples after 48 h growth of Penicillium tardum H-2 (b) and Trichoderma sp. H-1 (c). *26*

Figure 20: Utilization of phenols transferred to the aquatic phase from the tar (WSF-T). *28*

Figure 21: Ortho- cleavage pathway for catabolism of catechol *30*

Figure 22: Meta- cleavage pathway for catechol catabolism *30*

Figure 23: Proposed pathway for the degradation of p-cresol by S. apiospermum *31*

Figure 24: Catabolism of phenol via two possible routes in S. apiospermum *31*

Figure 25: Black locust (Accacia pseudorobinia) *32*

Figure 26: Ground biomass *33*

Figure 27: Clogged reactor because of inappropriate preparation of biomass 33

Figure 28: Grinding machine, the hammers that crush biomass and the sieve that determines the particle size. 34

Figure 29: Picea abia woodchips..... 35

Figure 30: Graphite stuffing between reactor and screw conveyer 35

Figure 31: Fiberglass sealing used at the back of the reactor and at the de-ashing device. 36

Figure 32: "BARLAN" inorganic fibers cardboard sealing that replaced fiberglass sealing..... 36

Figure 33: "BARLAN" sealing after two pyrolysis tests 37

Figure 34: Fiberglass sealing at the back of the reactor after one test and soot residue... 37

Figure 35: Inside of the reactor 38

Figure 36: Scrubber cleaning – washing with water. 39

Figure 37: Interior of the scrubber – bottom part clogged with heavy tar and soot. 39

LIST OF TABLES

Table 1: Fast reactor type and location *5*

Table 2: Pyrolysis methods and their variants *6*

Table 3: List of components of micro-scale slow pyrolysis rotary kiln laboratory demonstration plant *10*

Table 4: Application of some valuable phenols *21*

Table 5: Analytical methods for wood-based pyrolysis liquids *22*

Table 6: Typical properties and characteristics of wood derived crude bio-oil *23*

Table 7: Growth of microfungi on phenols with different structure *27*

Table 8: Growth of fungal isolates on soil media spiked with phenols *29*

Table 9: TGA analysis of Norway spruce woodchips *40*

1 INTRODUCTION – PYROLYSIS PROCESS

1.1 What is pyrolysis?

Pyrolysis of wood is a process that has been known for centuries. Its products, char and tar, were used for embalming, filling wood joints and other such uses. Large quantities of methanol, acetic acid and acetone, which were important chemical products of wood pyrolysis at the beginning of the 20th century, were produced until around 1970. After that economic pressure, caused by competition with petroleum derived products, became too great. In the 1980s a so called "flash" pyrolysis technology and its products became interesting for the market. But these products are specialty chemicals and not yet produced on a commodity scale (Elliott 2004).

To explain what pyrolysis is, the following definition can be used: Pyrolysis is the thermal decomposition of materials in the absence of oxygen or, when significantly less oxygen is present than required for complete combustion (Mohan et al. 2006). The terms gasification and pyrolysis do not describe the same process. Gasification of biomass means its decomposition to syngas by carefully controlling the amount of oxygen present in the reaction. But when it comes to pyrolysis, its exact definition is no longer so simple, especially when applied to biomass. Older literature equates pyrolysis to carbonization, in which solid char is the principal product. Today, the term pyrolysis often describes a process in which oils are preferred products (Mohan et al. 2006).

1.2 Pyrolysis by stages

The main steps of the pyrolysis process are heating, drying and thermo chemical decomposition of the fuel used. In the heating step, the temperature is increased from approximately 15 °C (ambient temperature) to 105 °C. The biomass is then dried at that temperature. The moisture evaporates from the pores (first from the macro and than from the micro pores) and causes particles to shrink. As temperature is increased, primary pyrolysis reactions begin and volatiles exit through the empty pores. The outer part of the particle that has already reacted turns to ash and fixed carbon (char). Under that is the pyrolysis front on which thermo chemical reactions take place. Below that is still the non-reacted zone. As described by Mohan et al. (2006) the flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolyzed fuel. Because of the condensation of some of the volatiles in the cooler parts of the fuel, a secondary reaction follows and tar can be produced. Autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition. 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 and pressure profile.

From solid fuel, which can be biomass or waste, primary reactions result in gas, tar and char. From tar acquired in primary reactions, gas and char are yielded with secondary (exothermic) reactions.

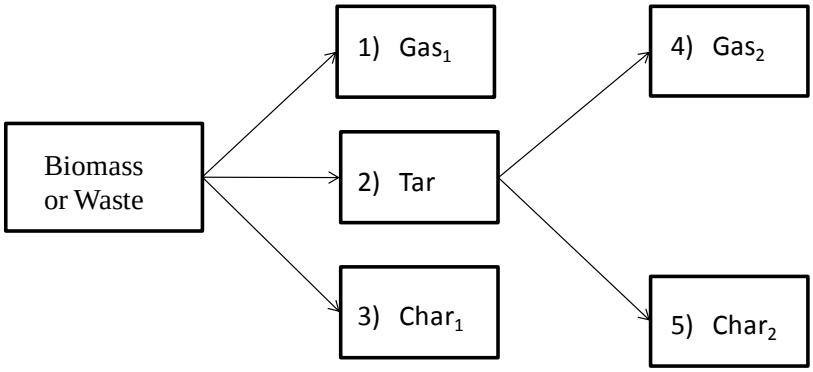


Figure 1: Pyrolysis reactions.[1]

The whole process is partially endothermic and driven by heat and mass transfer. Products from the solid fuel ($C_xH_yO_z$) and added heat are: carbon, CO_2, CO, H_2O, H_2, CH_4, C_2H_6, CHOH and tar.

1.3 Driving forces of pyrolysis

The role of internal and external heat transfer and pyrolysis kinetics (coupled effects of particle size and external heating conditions) may be addressed through characteristic adimensional numbers:

Internal pyrolysis number (P_i): The ratio of the reaction time to the conduction time, is a measure of the relative importance of intra-particle processes

$P_i = \frac{k}{\rho c \tau^2 r}$	k = Thermal conductivity	[W/(m*K)]
	ρ = Density	[kg/m^3]
	c = Heat capacity	[kJ/(kg*K)]
	τ = Particle half-thickness	[m]
	r = Reaction rate	[s^{-1}]

Thus, for *P*i >>1, the process is under kinetic control and for *P*i << 1 it is under heat transfer control.

[1] Shafizadeh & Chin 1977

Biot number (B) measures the relative importance of internal and external heat transfer.

Constant flux heating	Convective heating
$B = \frac{q\tau}{k\Delta T}$	$B = \frac{h_c\tau}{k}$
k = Thermal conductivity	[W/(m*K)]
τ = Particle half-thickness	[m]
q = Heat flux	[W/m^2]
h_c = Convective heat transfer coefficient	[W/(m^2*K)]

For B >>1, the internal heat transfer is relatively slow compared to external heat transfer, and large spatial temperature gradients are observed. This regime has also been identified as “thermally thick”;

For B << 1 the internal heat flux is fast and intraparticle temperature is uniform, though this may continue to change depending on external conditions. This regime has also been identified as “thermally thin”.

External pyrolysis number (P_e) defines the different regimes of solid pyrolysis given the relative importance of external heat transfer with respect to chemical kinetics.

$$P_e = P_i B$$

For $B \geq 1$ (internal heat transfer control), the Internal Pyrolysis Number P_i should also be used to evaluate the relative importance between kinetics and internal heat transfer;

For $B \leq 1$ (external heat transfer control), the External Pyrolysis Number P_e should also be considered in order to measure the importance of chemical kinetics with respect to external heat transfer.

Driving forces of pyrolysis process can be described and divided according to different parameters.

Composition related parameters:

- humidity content
- cellulose-hemicellulose-lignin proportion
- volatiles
- fixed carbon
- ash content

Feedstock related parameters:

- dimension
- density
- porosity

Reactor related parameters:

- heating rate
- residence time
- temperature

1.4 Types of pyrolysis

There are three different types of pyrolysis: fast or flash pyrolysis, carbonization or slow pyrolysis and gasification. The latter was explained above. These can also be divided and defined based on yields acquired. Fast pyrolysis is conducted at moderate temperature and short residence time, resulting in approximately 75 % liquid, 12 % char and 13 % gas. Slow pyrolysis is, on the other hand, conducted at low temperature and long residence time and results in approximately 30 % liquid, 35 % char and 35 % gas. And gasification is carried on at high temperatures and long residence time and its result is approximately 5 % liquid, 10 % char and 85 % gas (Fantozzi 2008).

1.4.1 Fast pyrolysis

Fast pyrolysis is a high temperature process in which biomass is rapidly heated in the absence of oxygen. Biomass decomposes to generate vapors, aerosols, and some charcoal-like char. After cooling and condensation of the vapors and aerosols, a dark brown mobile liquid is formed that has a heating value that is about half that of conventional fuel oil. No waste is generated because the bio-oil and solid char produced can each be used as fuel and the gas can be recycled back into the process. Fast pyrolysis uses much faster heating rates than traditional pyrolysis. Advanced processes are carefully controlled to give high liquid yields. There are four essential features of a fast pyrolysis process. First, very fast heating and heat transfer rates are used, which usually requires a finely ground biomass feed. Second, a carefully controlled pyrolysis reaction temperature is used, often in the 425-500 °C range. Third, short vapor residence times are used (typically <2 s). Fourth, pyrolysis vapors and aerosols are rapidly cooled to give bio-oil (Mohan et al. 2006).

Reactors for fast pyrolysis

The reactor is the most important part of the pyrolyser and that is why there is a lot of emphasis on its development. Different companies and academic institutions have developed different reactor types (see *Table 1*). Each of them offers an improved approach to more efficient bio-oil production.

Table 1: Fast reactor type and location[2]

Reactor type	*Location(s)*
Ablative	Aston University, NREL, BBC, Castle capital
Auger	ROI and Mississippi State University
Circulating fluidized bed	CPERI, CRES, ENEL
Entrained flow	GTRI, Egemin
Fluidized bed	Aston University, Dynamotive, Hamberg University, Leeds University, NREL, Oldenberg University, VTT
Rotating cone	Twente University, BTG/Schelde/Kara
Transported bed	Ensyn (at ENEL, Red Arrow, VTT)
Vacuum moving bed	Laval University/Pyrovac

1.4.2 Slow pyrolysis

As was said in the introduction, conventional slow pyrolysis has been applied for thousands of years and has mainly been used for the production of charcoal. In slow wood pyrolysis, biomass is heated to ~ 500 °C. The vapor residence time varies from 5 min to 30 min. Vapors do not escape as rapidly as they do in fast pyrolysis. Thus components in vapor phase continue to react with each other, as the solid char and any liquid are being formed. The heating rate in conventional pyrolysis is typically much slower than that used in fast pyrolysis. A feedstock can be held at constant temperature or slowly heated. Vapors can be continuously removed as they are formed. Vacuum pyrolysis at slow heating rates is another variant. The definition of a "slow" heating rate versus a "fast" heating rate is arbitrary in many cases (Mohan et al. 2006).

1.5 Products of pyrolysis process

Products of the pyrolysis process are pyrogas (syngas), char (fixed carbon) and tar. Depending on which pyrolysis type is used and under what conditions the process is conducted, different proportions of these products are yielded. Table 2 shows different pyrolysis technologies and their product outcome.

An example of pyrogas composition, acquired at Integrated Pyrolysis Regenerated Plant (IPRP), in Italy, is: 29.5 % CO, 26.9 % CO_2, 21 % CH_4, 16 % H_2, 3.5 % C_2H_4, 1.7 % C_2H_6, 0.9 % N_2 and 0.1 % O_2 and C_2H_2.

The char produced in one of the tests conducted in microscale laboratory rotary kiln pyrolyser at University of Perugia, Engineering Faculty, Department for Mechanical engineering had 2,34 % humidity, 49,75 % volatiles d.b., 1,34 % ash d.b., and 48,91 % of fixed carbon.

[2] Mohan et al. 2006

Figure 2: Wood chips (feedstock); gas, both fractions of tar, and char as products of slow pyrolysis

In the next table different pyrolysis technologies and their products are assembled.

Table 2: Pyrolysis methods and their variants[3]

Pyrolysis technology	*Residence time*	*Heating rate*	*Temperature (°C)*	*Products*
Carbonization	Days	Very low	400	Charcoal
Conventional	5-30 min	Low	600	Oil, gas, char
Fast	0.5-5 s	Very high	650	Bio-oil
Flash-liquid	< 1 s	High	<650	Bio-oil
Flash-gas	< 1 s	High	<650	Chemicals, gas
Ultra	< 0.5 s	Very high	1000	Chemicals, gas
Vacuum	2-30 s	Medium	400	Bio-oil
Hydro-pyrolysis	< 10 s	High	<500	Bio-oil
Methano-pyrolysis	< 10 s	High	>700	Chemicals

1.6 Gas cleaning

Gas produced during the pyrolysis process needs to be cleaned in order to remove particulate matter, tar, acid compounds, ammonia, alkali and other compounds. The mineral matter in biomass forms inorganic ash and the unconverted biomass forms char.

[3] Demirbas 2005

These fine particulates are entrained in the syngas stream. They can cause abrasion in internal combustion engines or gas turbines and they can present an emission problem. To clean the gas from particulates, cyclone separators, barrier filters or electrostatic precipitators are used. To remove acid components in the gas, amine-based, physical solvent, liquid phase oxidation or catalytic absorbent processes are used. The type of technology selected largely depends on the system's operating conditions, the sulfur level in the syngas and the desired purity of the treated syngas. Tar in syngas can cause problems when the gas cools below the dew point of tars (370 – 400 °C) and tar deposition occurs in pipes and other equipment. Tar can be removed physically or chemically. Catalytic steam reforming or cracking of tars to lighter gases is the chemical process that can be used. But more often the physical process of cooling the syngas to condense tar into fine droplets and then removing these droplets by wet scrubbing is used. Alkali compounds are also removed by wet scrubbing. Wet scrubbing is the technology most commonly used in small scale applications. It is both cost effective and efficient.

1.6.1 Wet scrubbing

This method is usually used to remove water-soluble contaminants from syngas by absorption into a solvent. The water-soluble tar components can be removed by this method. As was stated before, water scrubbing removes alkali compounds and also particulates, halides, soluble gases and condensable liquids. A commonly used solvent for wet scrubbing is water.

An example of wet scrubbing is the water scrubber at the micro-scale slow pyrolysis rotary kiln laboratory demonstration plant in Perugia, Italy.

At the end of the reactor where the gas exits, the de-ashing device for particulate matter removal is placed. After that the gas is cleaned in a scrubber. Gas enters the scrubber at 500 °C and exits at 50 °C. The cooling of the gas condenses the water vapours and tar. Gas enters the scrubber through an inox pipe that ends at the bottom of the scrubber. The bottom part of the scrubber is filled with clean water to a certain level. Gas exits the pipe into the water. Due to under-pressure created by the suction of the compressor, the gas gurgles through the water. The water cooling coil is placed in that section of the scrubber. The gas cools down and the water vapours and tars are condensed. Then the gas passes three perforated plates that are placed above the water level in the scrubber. Passing these plates, gas is washed with water from a washing nozzle placed on the top of the scrubber. The function of the perforated plates is to increase the surface between gas and water that is sprayed on the gas from above. The light fraction of tar is drained to a separate tank. The heavy tar fraction is discharged from the bottom of the scrubber after the process.

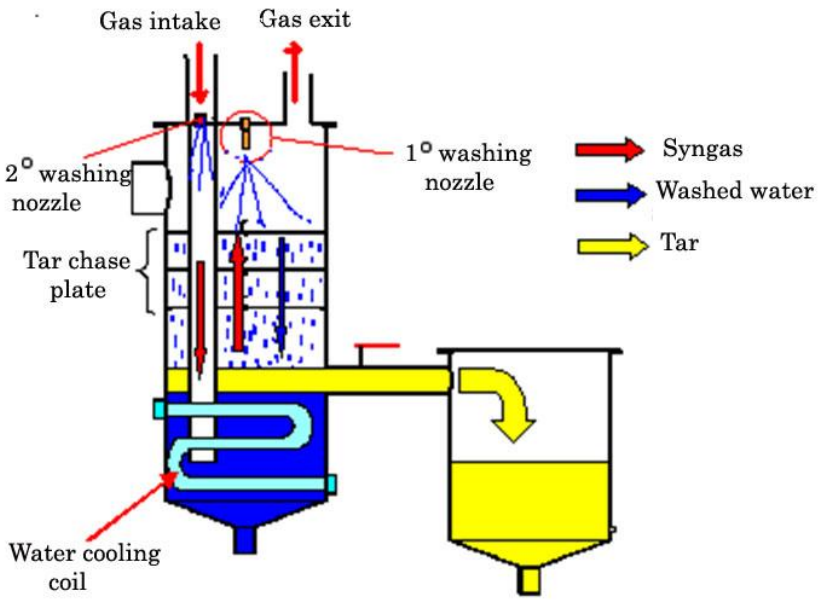


Figure 3: Water scrubber for syngas cleaning – Micro-scale slow pyrolysis rotary kiln in Perugia, Italy.[4]

1.7 Micro-scale slow pyrolysis rotary kiln pyrolyser for syngas and char production in Perugia, Italy – laboratory demonstration plant

A very detailed description of the laboratory demonstration plant in Perugia is to be found in the bachelor thesis by Michele D´Amico (2007). Here only a brief description of the pyrolyser is stated.

The reactor's technology is a rotary kiln that is designed to burn biomass, plastics, tires and RDF (refuse derived fuel). It is designed to operate in a range of temperature from 400 °C to 700 °C, with residence time from 20 to 40 minutes and feed range 15-30 kg/h. Its maximum heat input is 150 kW. The technology used for gas cleaning is quenching – scrubbing (same as in IPRP). The dimensions are 2500x1500x2500 mm. Continuous gas flow and LHV are used for gas metering. For safety reasons the pyrolyser is placed in a fire and leakage free room. Its economics are estimated to be sensible. The rotary kiln is made out of an AISI 303 steel pipe (diameter 325 mm, thickness 30 mm). Four laminar fins are soldered inside to improve the heat transfer rate and the mixing effect caused by rotation. See Figure 5. An electric motor, through a gear and a chain, keeps the kiln rotating on four steel disks placed on two iron skids. One end of the cylinder hosts a flanged hole that holds the terminal part of the feeding section and the sealing system. At the other end, the rotary kiln enters a coaxial stationary cylinder to discharge pyrolysis products. Rotary sealings at both the input and discharge sections are made of 3-4 strand rings of high temperature resisting graphite compressed by a stuffing box flanged ring (Fantozzi & Desideri 2007).

For the exact plant outline with the names of all parts see Table 3 and Figure 6.

[4] D´Amico 2007

Figure 4: Micro-scale slow pyrolysis rotary kiln laboratory demonstration plant

Figure 5: Reactor with four laminar fins

Table 3: List of components of micro-scale slow pyrolysis rotary kiln laboratory demonstration plant[5]

N°	Component	N°	Component
1	Hopper	27	Pressure security regulator
2	Screw conveyor	28	Gas compressor
3	Screw conveyor water cooling circuit	29	Inverter control engine for compressor
4	Electric cooling pump for screw conveyor	30	Pressure security regulator
5	Cooling nozzles circuit of screw conveyor	31	Flow-meter
6	Motor speed reducer	32	Gas flow signal
7	Engine gear of the screw conveyor	33	Safety valves
8	Transmission chain	34	Safety valves
9	Rotary kiln reactor	35	Pressure gas regulator
10	Electrical heaters from ceramic shells	36	Burner
11	Power switch for electrical heater	37	Outlet pipeline safety valve
12	Thermoregulator of electric heater	38	Pilot (methane)
13	Discharge section of char	39	P.I.D. Thermoregulator
14	Char discharged	40	Pressure air regulator
15	Storage for char	41	Blower valve to syngas burner
16	Thermocouple	42	Pressure regulation for the air directed to the burner
17	De-ashing device	43	Flange calibrated measuring air flow
18	Scrubber for cleaning gas and condensation of tars	44	Air flow signal
19	Secondary tank for light tar storage	45	Fan control
20	Tars stockage	46	Computer - PC
21	Cooling radiator	47	I / O interface
22	Electric pump for water cooling circuit of scrubber	48	DAQ equipment
23	Radiator of cooling water for cooling circuit of water Scrubber	49	Temperature measure
24	Filters to remove water in syngas coming from Scrubber	50	Serial Interface
25	Electric pump for water recirculation loop of Scrubber	51	Presetting for safety valve pyrolysed
26	Filter and demister	52	Motor for the screw conveyor

[5] D'Amico 2007

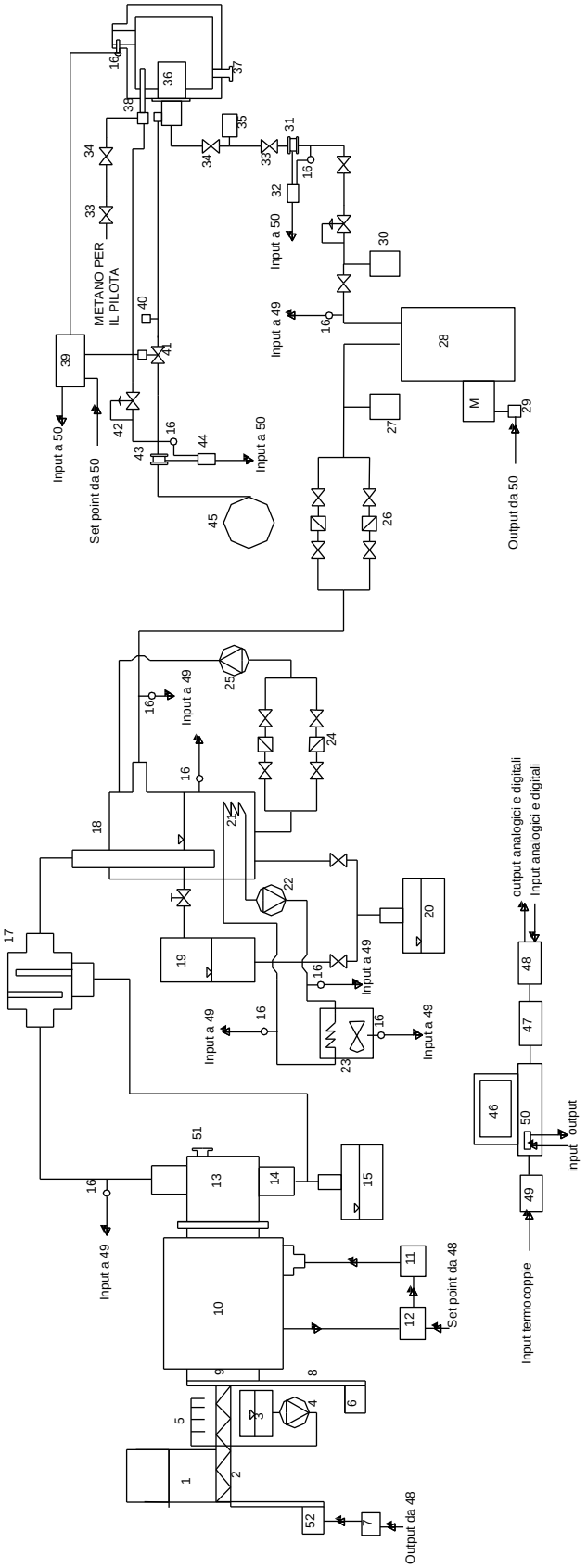


Figure 6: Micro-scale slow pyrolysis rotary kiln laboratory demonstration plant layout.[6]

[6] D'Amico 2007

2 WOODY BIOMASS COMPOSITION

2.1 Cellulose – hemicelluloses – lignin

Cellulose, hemicelluloses and lignin are the three main components of woody biomass. The shares of each differ in each plant species that contains them. It is important to know the approximate chemical composition of these components in order to understand the process of thermal decomposition and the products that are formed from these components.

2.1.1 Cellulose

Cellulose is a long polymer of glucose (β-(1→4)-D-glucopyranose units) without any branches. It has an orderly and strong structure with minimal flexibility and its thermal stability is high. Cellulose provides woods with strength and represents approximately 40 - 50 wt % of dry wood. Glucose anhydride, formed via removal of water from each glucose, is polymerised into long cellulose chains that contain 5000-10000 glucose units. The basic repeating unit of the cellulose polymer consists of two glucose anhydride units, called a cellobiose unit (Mohan et al. 2006). See Figure 7. It is insoluble, crystalline and consists of between 2000 and 14000 residues.

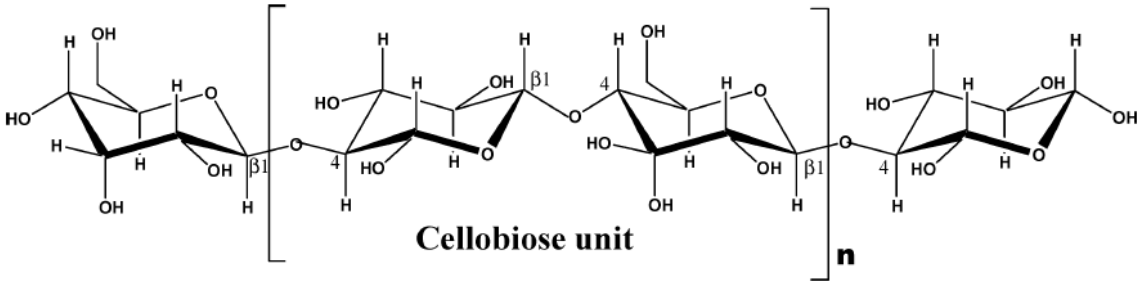


Figure 7: Chemical structure of cellulose[7]

Cellulose forms long chains that are bonded to each other by a long network of hydrogen bonds (Figure 8).

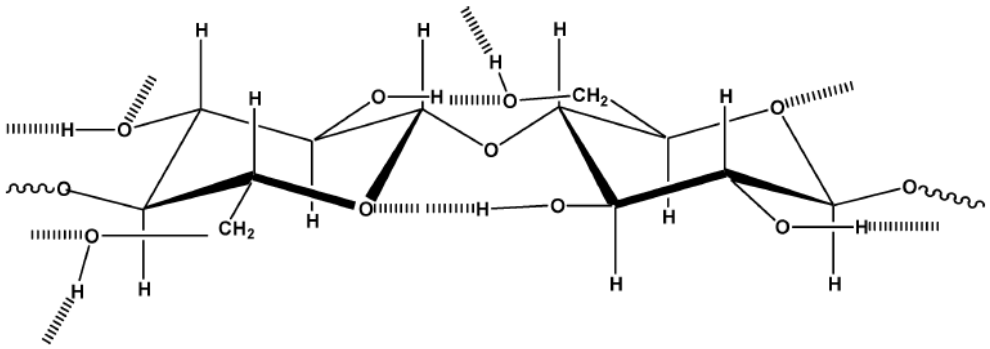


Figure 8: Intrachain and interchain hydrogen-bonded bridging.[8]

[7] Mohan et al. 2006
[8] Mohan et al. 2006

Groups of cellulose chains twist in space to make up the ribbonlike microfibril sheets, which are the basic construction units for a variety of complex fibers.

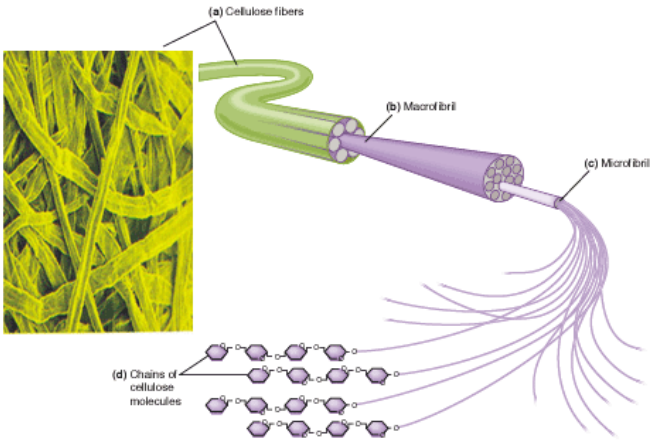


Figure 9: Stucture of cellulose. (a) Cellulose fibers from a ponderosa pine. (b) Macrofibrils compose each fiber. (c) Each macrofibril is composed of bundles of microfibrils. (d) Microfibrils, in turn, are composed of bundles of cellulose chains.[9]

2.1.2 Hemicelluloses

Hemicellulose, known also as polyose, consists of different saccharides, such as xylose, mannose, glucose, galactose, arabinose, 4-*O*-methyl glucuronic acid and galacturonic acid residues.

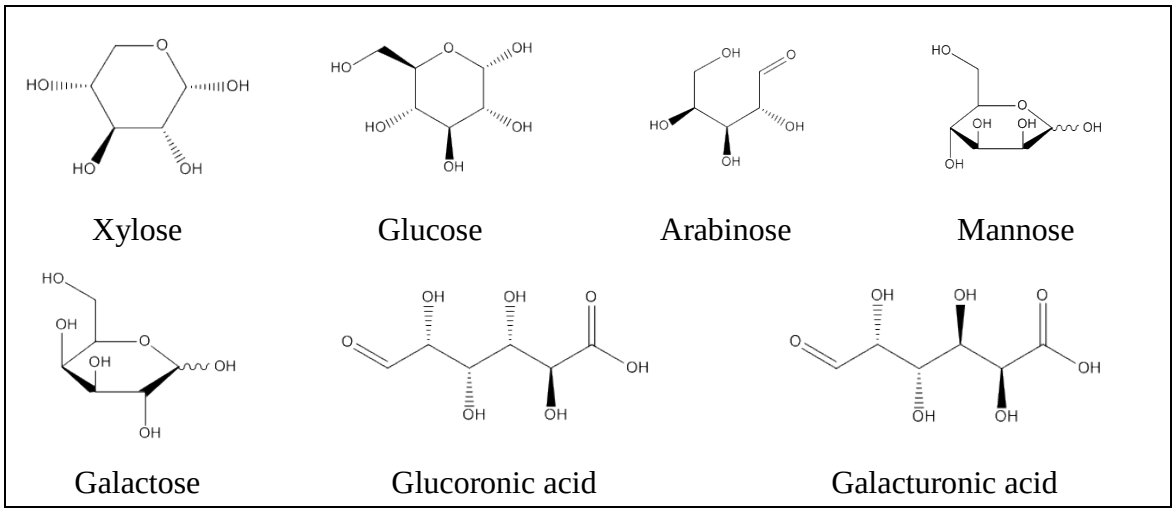


Figure 10: Saccharides that form hemicellulose[10]

A variety of hemicelluloses usually account for 25-35 % of the mass of dry wood, 28 % in softwoods, and 35 % in hardwoods. Hemicelluloses exhibit lower molecular weights than cellulose. The number of repeating saccharide monomers is only around 150, compared to

[9] ‚*Structure of cellulose*‘, http://nutrition.jbpub.com/resources/chemistryreview9.cfm; 17.2.2009
[10] Chemical formulas drawn with ChemBioOffice 2008

the number in cellulose, which is 5000-10000 (Mohan et al. 2006). Its structure is random and amorphous, rich in branches that are easy to remove from the main stem and degrade to volatiles (CO, CO_2, some hydrocarbon...) evolving out at low temperatures. Mohan et al. (2006) further reports that hemicelluloses decompose at 200-260 °C. This gives a rise to more volatiles, less tars and less chars than cellulose. Most hemicelluloses do not yield significant amounts of levoglucosan. Much of the acetic acid liberated from wood during pyrolysis is attributed to deacetylation of the hemicelluloses. Hardwood hemicelluloses are rich in xylan and contain small amounts of glucomannan. Softwood hemicelluloses on the other hand contain a small amount of xylan, and are rich in galacto-glucomannan (Mohan et al. 2006). Thermal decomposition of hemicelluloses occurs at lower temperatures than crystalline cellulose. The loss of hemicellulose occurs in slow pyrolysis of wood in the temperature range of 130-194 °C, with most of this loss occurring above 180 °C.

2.1.3 Lignin

Lignin is the third major component of wood. It represents 23-33 % of mass in softwoods and 16-25 % of the mass in hardwood. As was reported by Mohan et al. (2006) lignin is an amorphous cross-linked resin with no exact structure. It is the main binder of fibrous cellulosic components and it also provides a shield against rapid microbial or fungal destruction of cellulosic fibers. It is a three-dimensional, highly branched, polyphenolic substance which consists of an irregular array of variously bonded hydroxy- and methoxy-substituted phenylpropane units. These three general monomeric phenylpropane units exhibit the *p*-coumaryl, coniferyl and sinapyl structures.

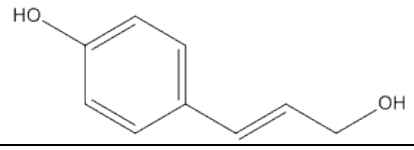
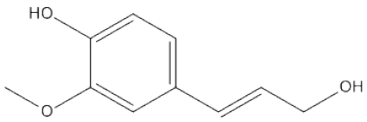
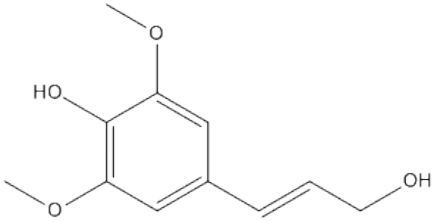
	p-coumaryl alcohol
	Coniferyl alcohol
	Sinapyl alcohol

Figure 11: p-coumaryl, coniferyl and synapyl structures[11]

It is also known that softwood and hardwood lignin is not the same in structure. In softwoods "guaiacyl" lignin is predominantly found. It results from polymerization of a higher fraction of coniferyl phenylpropane units. In many hardwoods "guaiacyl-syringyl" lignin is found. It is a copolymer of coniferyl and sinapyl phenylpropane units where the fraction of sinapyl units is higher than that in softwood lignins (Mohan et al.). Because of

[11] Chemical formulas drawn with ChemBioOffice 2008

lignin's amorphous structure a lot of interlinkages between individual units are possible – radical reactions are nonselective random condensations.

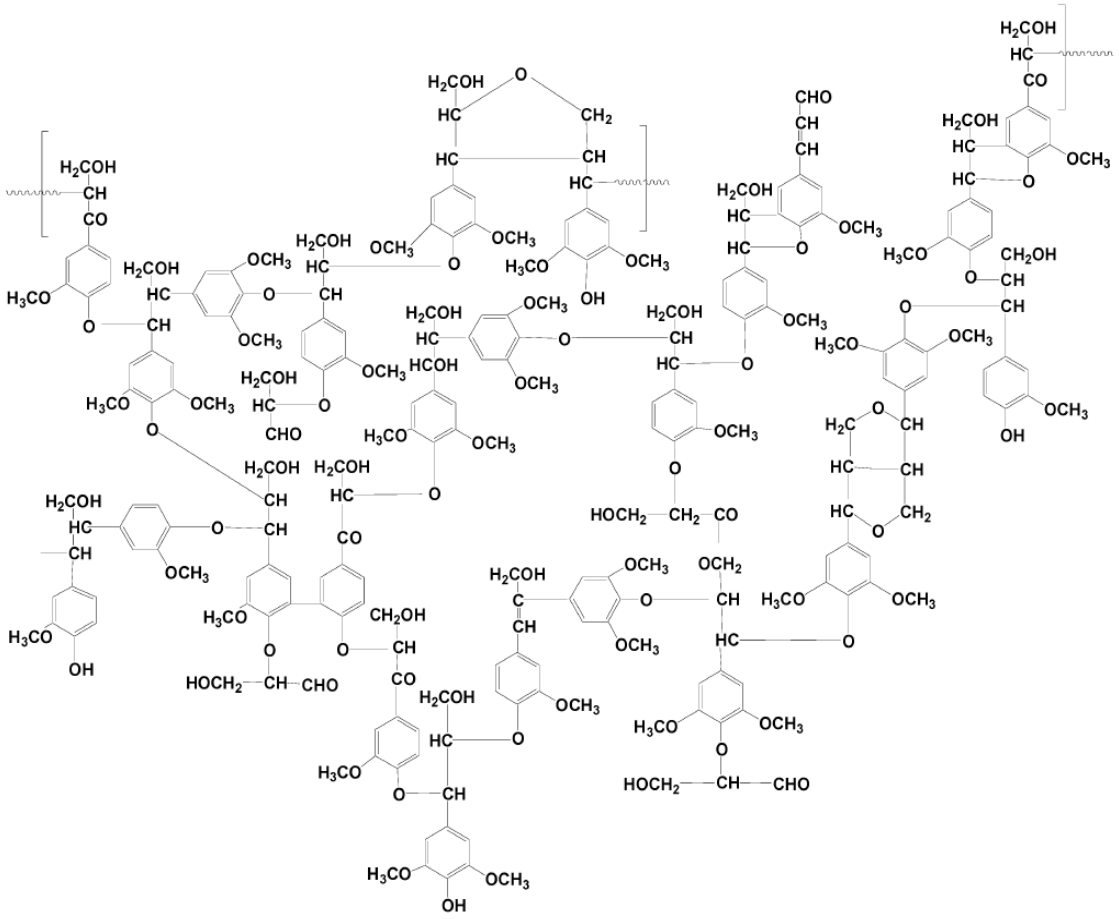


Figure 12: Small section of hardwood (Fagus sylvatica – European beech) lignin polymer with some typical lignin chemical linkages[12]

Mohan et al. (2006) also reports that physical and chemical properties of lignins differ depending on the extraction or isolation technology used to isolate them. Because lignin is inevitably modified and partially degraded during isolation, thermal decomposition studies on separated lignin will not necessarily match the pyrolysis behavior of this component when it is present in the original biomass. Lignin decomposes when heated at 280-500 °C. Lignin pyrolysis yields phenols via the cleavage of ether and carbon-carbon linkages. It is more difficult to dehydrate than cellulose and hemicelluloses. Lignin pyrolysis produces more residual char than does pyrolysis of cellulose.

[12] Mohan et al. 2006

2.2 Characteristics of thermo-chemical decomposition of three main components

According to Mohan et al. (2006) the characteristics of wood pyrolysis products depend on whether a hardwood (angiospermae trees) or softwood (gymnospermae trees) species is pyrolised. Yang et al. (2007) reports on different gas yields coming from cellulose, hemicelluloses and lignin pyrolysis. They observed a higher CO_2 yield of hemicelluloses, cellulose had a higher CO yield and lignin resulted in higher H_2 and CH_4 yields (Figure 14). Lignocellulosic biomass is generally divided into three main components: hemicellulose (20-40 wt.%), cellulose (40-60 wt.%) and lignin (10-25 wt.%). Pyrolysis stages can also be described in order of the main biomass components' decomposition. Moisture evolution comes first, and then hemicellulose, cellulose and lignin follow. Yang et al. (2007) also reports that the three components of biomass most likely consist of alkene, esters, aromatics, ketone and alcohol, with different oxygen-containing functional groups observed, such as OH, C=O, C-O-C, and C-O-(H). Cellulose contains more OH and C-O and hemicellulose more C=O compounds.

Thermal analysis of these three components shows that there are differences among the pyrolysis behaviours of these components (Yang et al. 2007). Decomposition of hemicellulose happens at 220-315 °C and cellulose decomposes at 315-400 °C. See Figure 13. When the temperature is greater than 400 °C almost all cellulose is pyrolysed with a very low solid residue. Lignin is the most difficult one to decompose among the three components. It decomposes slowly in the range from ambient temperature to 900 °C, as reported by Yang et al (2007). The solid residue from lignin is the highest.

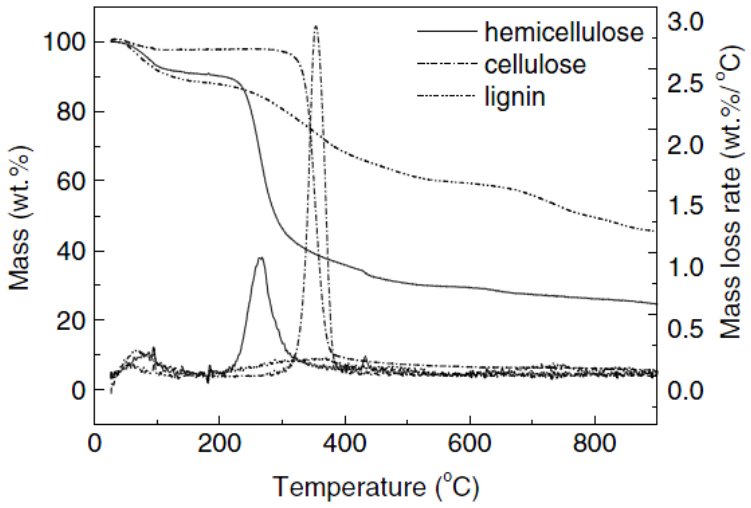


Figure 13: Pyrolysis curves of hemicelluloses, cellulose and lignin in TGA[13]

[13] Yang et al. 2007

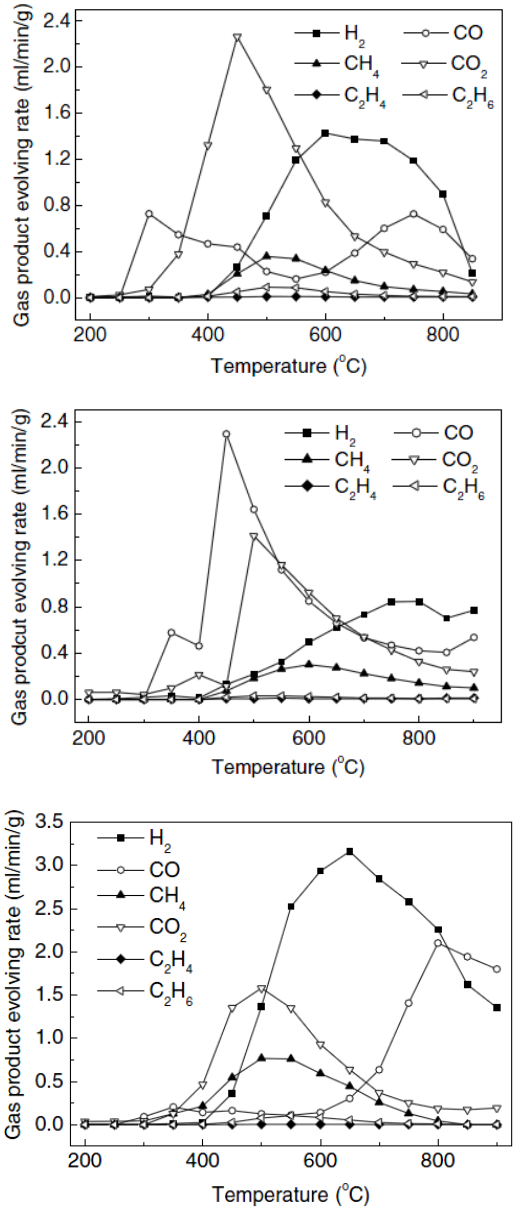


Figure 14: Releasing profile of gas product from lignin pyrolysis in packed bed. Order of graphs from top to bottom: hemicelluloses, cellulose and lignin.[14]

[14] Yang et al. 2007

3 BIO-OIL DERIVED FROM WOODY BIOMASS

As has been said in previous chapters bio-oil is one of the products of the pyrolysis process. It has many synonyms like: pyrolysis oils, pyrolysis liquids, bio-crude oil (BCO), wood liquids, wood oil, liquid smoke, wood distillates, pyroligneous acid, liquid wood, pyrolytic tar, tar. It is dark brown, free-flowing organic liquid that is comprised of highly oxygenated compounds (Mohan et al.). It comes in two fractions: a water soluble fraction and a heavy tar fraction. See Figure 15.

Figure 15: Tar – water soluble fraction and heavy tar fraction.

3.1 Chemical composition of tar

Mohan et al. (2006) reports that pyrolysis liquids are formed by rapidly and simultaneously depolymerizing and fragmenting cellulose, hemicelluloses and lignin with a rapid increase in temperature. Rapid quenching then "freezes in" the intermediate products of the fast degradation of hemicelluloses, cellulose and lignin. Rapid quenching traps many products that would further react (degrade, cleave, or condensate with other molecules) if the residence time at high temperature was extended. Bio-oils contain many reactive species, which contribute to unusual attributes. Chemically, bio-oil is a complex mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isogenol, pyrenes, acetic acid, formic acid, and other carboxylic acids. It also contains other major groups of compounds, including hydroxyaldehydes, hydroxyketons, sugars, carboxylic acids, and phenolics. The exact chemical nature of each bio-oil is dependent on the feedstock and the pyrolysis variables (heating rate, residence time, particle size, temperature). More than 300 compounds were indentified in bio-oils (Mohan et al. 2006).

As written by Mohan et al. (2006), wood pyrolysis causes bond cleavage and produces fragments of the original polymers (cellulose, hemicellulose, and lignin). Most of the

original oxygen is retained in fragments that collectively comprise bio-oil. A small amount of CO_2 and CO is formed, along with a substantial amount of water. Bio-oil contains 45 - 50 wt % oxygen, but the oxygen content is dependent on the bio-oil´s water content. Proximate analysis of bio-oil gives a chemical formula of $CH_{1.9}O_{0.7}$, which corresponds to ~ 46 wt % oxygen (versus ~ 42 wt % oxygen in wood). The difference in oxygen content present in the feed versus that in the bio-oil is related to the oxygen content in the gases and the amount present as water in the oil. Oxygen is present in most of more than 300 compounds that have been indentified in bio-oil. The compounds found in bio-oil have been classified into the following five broad categories: hydroxyaldehydes, hydroxyketones, sugars and dehydrosugars, carboxylic acids, phenolic compounds. A more detailed classification organizes compounds under the following categories: acids, alcohols, aldehydes, esters, ketones, phenols, guaiacols, syringols, sugars, furans, alkenes, aromatics, nitrogen compounds, and miscellaneous oxygenates. The highest concentration of any single chemical compound (besides water) is hydroxyacetaldehyde (at levels up to 10 wt %), followed by acetic and formic acids (at ~ 5 wt % and ~ 3 wt % respectively). This accounts for the acidic pH of 2.0-3.0 that is exhibited in bio-oil. The relationship of products and the temperature to which the vapors are exposed before quenching can be described as shown in Figure 16. As temperature is increased, alkyl groups cleave from aromatic compounds. Eventually, the aromatic compounds condense into polycyclic aromatic hydrocarbons (PAHs) at higher temperatures.

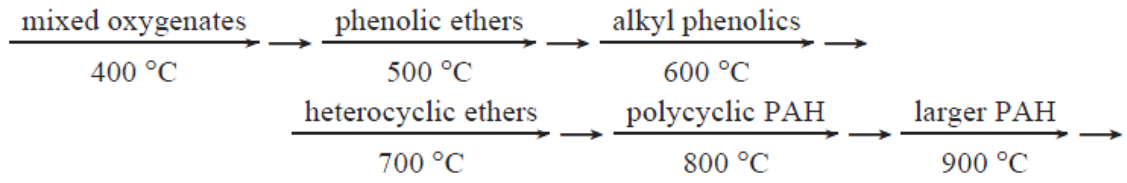


Figure 16: Relationship between products and temperature to which vapors are exposed before quenching[15]

[15] Mohan et al. 2006

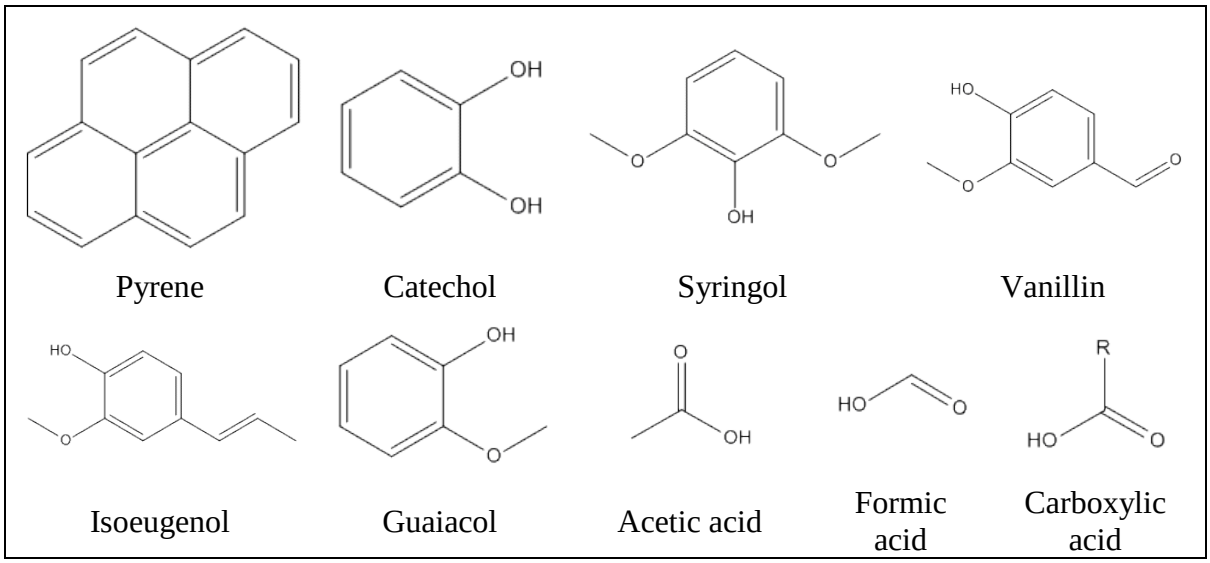


Figure 17: Some of the main components of tar

Guaiacol

Guaiacol is the methyl ether of pyrocatechol. It is a main constituent of creosote obtained from wood tar (mainly beech) by distillation mostly between 203 and 220 °C. It is synthesized from anisole also. The dimethyl ether of pyrocatechol is called veratrol. They and their derivatives are used as an external antiseptic, expectorant, gastric sedative, deodorant, and as a parasiticide. Methoxyphenols are used in manufacturing stabilizers and antioxidants for plastics and rubbers. They are also used in analgesics, local anesthetic, flavorings, biocides, antiseptics. 2-Methoxyphenol is used in manufacturing vanillin and other flavorings. Pyrocatechol monomethyl ether; Pyroguaiac acid; 1-hydroxy-2-methoxybenzene; o-Hydroxyanisole; 2-Methoxyphenol; o-Methylcatechol; Catechol monomethyl ether; Guaicol; Methyl Catechol; Hydroxy-2-methoxybenzene are all synonyms for guaiacol (*Guaiacol*, n.a.).

Catechol

Catechol is a combustible compound also known as Pyrocatechol, 1,2-Benzenediol, 1,2-Dihydroxybenzene, and its molecular formula can also be written as $C_6H_6O_2$. When inhaled it can cause a burning sensation, cough and labored breathing. It can also be absorbed through skin and cause redness; the same appears on eyes along with pain and the possibility of severe deep burns. If digested it causes abdominal pain, diarrhea and vomiting. Catechol is not allowed to be disposed in to the environment. When in storage it should be kept in the dark and separated from strong oxidants, food and feedstuffs. This substance is toxic to aquatic organisms. Its boiling point is 245.5 °C, its melting point is 105°C, its relative density (water = 1) is 1.3, and its solubility in water 43 g/100 ml (*Catechol*, n.a.).

Table 4: Application of some valuable phenols[16]

Compounds	*Applications*
Catechol	Antiseptic, pothography and dyes, electroplanting, antioxidant and speciality inks
Guaiacol	Sweet aroma, burnt aroma, smokey odor used in synthetic flavors and fragrances and pharmaceutical
4-methylguaiacol	Smokey aroma, smokey test, used in food (candy and baked goods)
4-ethylguaiacol	Soya sauce flavor, used in non-alcoholic beverages, ice cream, gelatins and puddings
Syringol	Woody, medicinal and smoky aroma used in food (in meat, soups and sefood), pharmaceutical (platelet aggregation, anti-dermatophyte activity)

3.2 Chemical characterization methods

Different methods of determining the chemical characterization of bio-oil are mentioned in various scientific articles. As was stated by Mohan et al (2006) the complete chemical characterization of bio-oil is difficult (or impossible). The bio-oil contains higher-molecular-weight species, including degradation products of pentoses, hexsoses, and lignin. Only a portion of bio-oil can be detected via GC (gas chromatography), even using robust columns and high-temperature programs. In addition, the bio-oil contains polar, nonvolatile components that are only accessible by HPLC (High pressure liquid chromatography) or GPC (Gel Permeation Chromatography) analysis. Whole pyrolysis liquids can be analyzed by GC-MS (Gas Chromatography – Mass Spectrometry) (volatile compounds), HPLC and HPLC/electrospray MS (nonvolatile compounds), Fourier transform infrared (FTIR) spectroscopy (functional groups), gel permeation spectroscopy (GPC) (molecular weight distributions), and nuclear magnetic resonance (NMR) (types of hydrogens or carbons in specific structural groups, bonds, area integrations). Analysis is especially difficult because complex phenolic species from lignin decomposition can have molecular weights as high as ~ 5000 amu (atomic mass unit). A variety of these fragmented oligomeric products exist with varying numbers of acidic phenolic and carboxylic acid hydroxyl groups as well as aldehyde, alcohol and ether functions. They exist in a variety of hydrogen-bonded aggregates, micelles, droplets, gels, etc., thus GPC analysis can overestimate the molecular weights because of aggregation. During HPLC analysis the combination of polarity differences and molecular-weight differences interact to produce broadened envelopes of peaks that are difficult to analyze by subsequent MS analysis.

[16] Murwanashyaka et al. 2001

Table 5: Analytical methods for wood-based pyrolysis liquids[17]

Analysis	*Method*	*Sample size*
Water content (wt %)	ASTM 203	1 g
Solids content (wt %)	Ethanol insolubles	30 g
	Methanol-dichloromethane insolubles	30 g
Particle size distribution	Microscopy + particle counter	1 g
Conradson carbon residue content (wt %)	ASTM D189	2-4 g
Ash content (wt %)	EN 7	40 ml
CHN content (wt %)	ASTM D5291	1 ml
Sulfur and chlorine content (wt %)	Capillary electrophoresis	2-10 ml
Alkali metals content (wt %)	AAS	50 ml
Metals content (wt %)	ICP, AAS	50 ml
Density, at 15°C (kg/dm^3)	ASTM D4052	4 ml
Viscosity, at 20 at 40°C (cSt)	ASTM D445	80 ML
Viscosity (mPa s)	Rotational viscometry	40 ml
Pour point (°C)	ASTM D97	80 ml
Heating value (MJ/kg)		
Calorimetric value, HMV	DIN 51900	1 ml
Effective value, LHV	DIN 51900	1 ml
Flash point (°C)	ASTM D93	150 ml
pH	pH meter	50 ml
Water insolubles content (wt %)	Water addition	5 ml
stability	80°C for 24 h	200 ml
	40°C for 1 week	

[17] Mohan et al. 2006

Table 6: Typical properties and characteristics of wood derived crude bio-oil[18]

Property	*Characteristics*
Appearance	From almost black or dark red-brown to dark green, depending on the initial feedstock and the mode of fast pyrolysis
Miscibility	Varying quantities of water exist, ranging from ~ 15 wt% to an upper limit of ~ 30-50 wt% water, depending on production and collection
	Pyrolysis liquids can tolerate the addition of some water before phase separation occurs
	Bio-oil cannot be dissolved in water
	Miscible with polar solvents such as methanol, acetone, ect., but totally immiscible with petroleum derived fuels
Density	Bio-oil density is ~ 1.2 kg/L, compared to ~ 0.85 kg/L for light fuel oil
Viscosity	Viscosity (of as produced bio-oil) varies from as low as 25 cSt to as high as 1000 cSt (measured at 40°C) depending on the feedstock, the water content of the oil, the mount of light ends that have collected, the pyrolysis process used, and the extent to which the oil has been aged
Distillation	It cannot be completely vaporized after initial condensation from the vapor phase
	At 100 °C or more, it rapidly reacts and eventually produces a solid residue from ~ 50 wt % of the original liquid
	It is chemically unstable, and the instability increases with heating
	It is always preferable to store the liquid at or below room temperature; changes do occur at room temperature, but much more slowly and they can be accommodated in a commercial application
Ageing of pyrolysis liquid	Causes unusual time-dependant behavior
	Properties such as viscosity increase, volatility decreases, phase separation, and deposition of gums change with time

Bio-oil is a wanted product in flash or vacuum pyrolysis. The quantity of it in those types of pyrolysis is big enough that further distillation and purification of components is done. An example of bio-oil distillation products is shown in the Apendix.

Those products are later used as valuable chemicals in various industry processes. The proportion of tar in conventional pyrolysis is too small to have any significant industrial meaning. Thus tar can be degraded in secondary reactions, resulting in higher yields of gas

[18] Mohan et al. 2006

and char, or it is completely considered a waste product. As such it needs a lot of attention in disposal. It is treated as chemical waste because of all of the previous described components. These components are not necessarily dangerous or hazardous in small quantities, but if highly concentrated they can cause myriad environmental and health problems.

There is a possibility to use tar acquired during pyrolysis and mix it with other fuels, such as char, into a combustible slurry. In the case of slow pyrolysis the proportion of light fraction of tar is too great to make an adequate mixture for combustion.

Disposal as chemical waste, use as chemical base material, tar combustion for heat production, and tar recycling to the gasifier for increased biomass conversion to produce gas (only possible in gasification process) are the possibilities of tar degradation in use so far.

Another option is possible though: bioremediation with the use of different fungi species to degrade tar derived from a slow pyrolysis process. This option is being investigated because the cost for chemical waste disposal is too high and not economical for small- and micro-scale applications.

4 TAR DEGRADATION BY FUNGI

As was written in the previous chapter tar comes in two fractions – heavy tar and a water soluble fraction. Both fractions include considerable amounts of phenols, which are among the most common and harmful toxicants. Microorganisms of various taxonomic groups, largely bacteria and micromycetes, are the major agents for natural water self-cleaning from pollutants. Micromycete have a more potent enzyme system, which allows them to utilize a wide range of organic compounds, including toxicants (Karetnikova & Zhirkova 2005).

Karetnikova and Zhirkova (2005) conducted a study about the fungal degradation of phenols created during lignin pyrolysis. The water soluble fraction (WSF) of tar was produced by lignin pyrolysis at 300-500 °C under laboratory conditions. The yield of WSF was 7.5 g per 29 g of lignin. The concentration of phenols in WSF was 6.2 mg/ml and pH was 3.6. The fungal strains were isolated from the Khor and Amur rivers. Degradation of phenols was studied in batch cultures in a mineral medium containing WSF at 0.5, 1 and 2 %. Suspension of fungal conidia (2 ml) grown on agar was added to 100 ml volumetric flasks containing 50 ml of the medium in a thermostat room at 24 °C with shaking at 160 rpm. Micromycete cultures completely utilized phenol and the creosol-xylenol fraction. *Penicillium* strains demonstrated a more active growth on media containing phenol, p-cresol, or guaiacum tar as the source of carbon as compared to *Trichoderma*. m-Cresol and m-xylenol in micromycete growth media containing products of lignin pyrolysis seem to be utilized by co-oxidation.

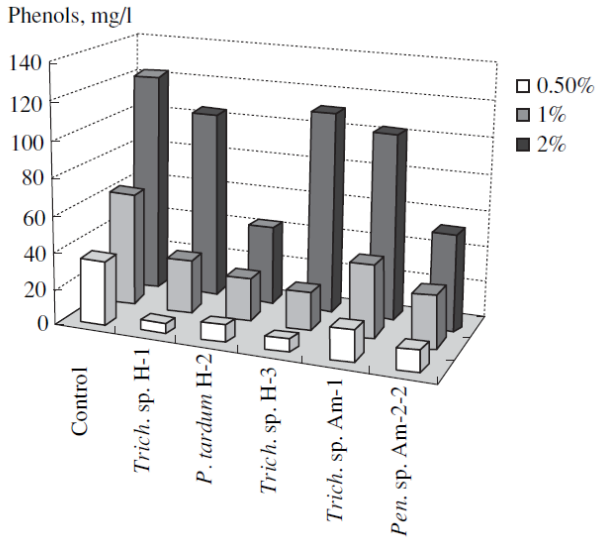


Figure 18: Utilization of phenols by micromycetes Trichoderma and Penicillium at different WSF concentration in the medium[19]

Phenol, cresols and m-xylenol were indentified among liquid products of lignin pyrolysis. An analysis of changes in the composition of phenols after the growth of micromycetes *Trichoderma* sp. H-1 and *Penicillium tardum* H-2 (at 0.5 % WSF in the medium) demonstrated the disappearance of phenol and cresols after 2 days of incubation.

[19] Karetnikova & Zhirkova 2005

Phenol utilization was determined by the changes in absorption spectra from 200 to 500 nm recorded on a UV spectrophotometer.

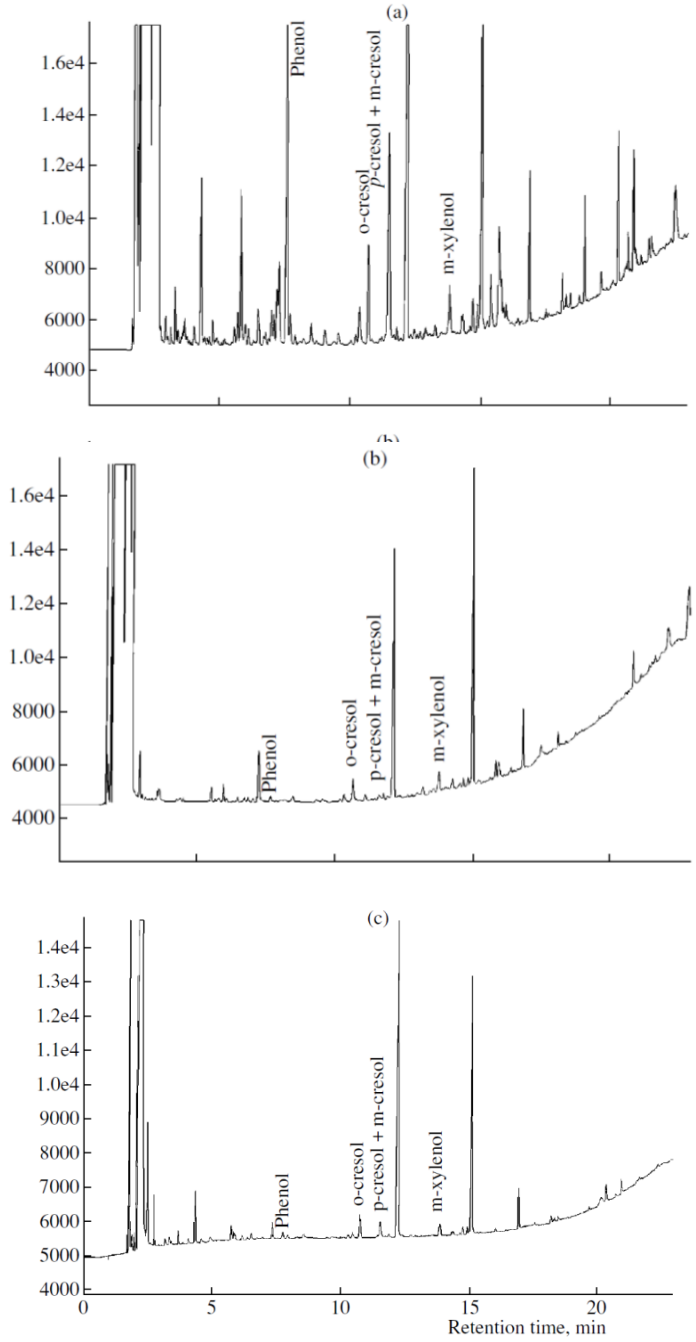


Figure 19: Changes in qualitative composition of WSF phenols after microbial degradation: chromatogram of control sample (a); chromatograms of samples after 48 h growth of Penicillium tardum H-2 (b) and Trichoderma sp. H-1 (c). [20]

[20] Karetnikova & Zhirkova 2005

Table 7: Growth of microfungi on phenols with different structure[21]

Carbon source	*Growth rate*				
	Trichoderma sp. (H-1)	*Trichoderma* sp. (H-3)	*Trichoderma* sp. (Am-1)	*Penicilluium* sp. (H-2)	*Penicillium* sp. (Am-2-2)
Pyrocatechin	+++	+++	+++	+++	+++
Phenol	+	+	+	++	++
Vanillin	+	+	+	++	+
o-Cresol	+	+	+	+	+
m-Cresol	-	-	-	-	-
p-Cresol	+	+	+	++	++
m-Xylenol	+	+	+	+	+
Guaiacum tar	++	+	+	++	++

'+' corresponds to slow growth yielding small colonies

In this study it was also written that since liquid products of lignin pyrolysis have low pH, their neutralization is an essential stage in wastewater treatment. And at the same time neutralizing the liquid favors the transfer of phenols from the heavy tar to the aqueous phase. The fraction of tar separated from WSF, washed with distilled water and adjusted to pH 6 from 3.6 with NaOH, gave rise to a water-soluble fraction (WSF-T) with phenol concentration of 13.7 mg/ml. Both micromycetes utilized 70 – 80 % phenols irrespective of WSF-T content in the medium.

According to UV spectrophotometry, *Penicillium* isolates completely utilized phenol and considerably decreased the concentrations of p-cresol and guaiacum tar in 10 days. Neither of the isolated fungi utilized the meta-derivates of phenol that were used as the carbon source. Degradation of these compounds in the medium with WSF seems to be due to co-oxidation processes.

[21] Karetnikova & Zhirkova 2005

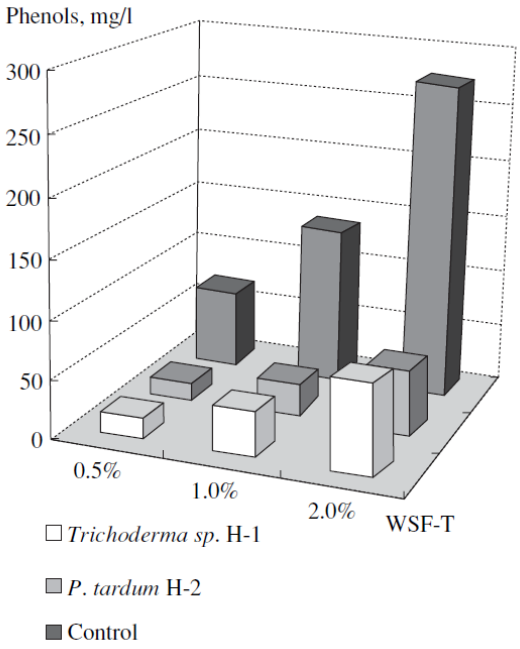


Figure 20: Utilization of phenols transferred to the aquatic phase from the tar (WSF-T).[22]

4.1 Pathway of phenols degradation by fungi

Santos and Linardi (2004) state that although the microbial metabolism of aromatic compounds has been extensively studied, most of the knowledge of the metabolic pathways of aromatic degradation comes from studies with bacteria. Some studies have shown that mycelial fungi can exert an important role in recycling aromatic compounds in the biosphere, among them the phenols. *Fusarium flocciferum* and *Aspergillus fumigatus* have been cited for their potential for phenol degradation. In all of these studies, phenol was metabolized by the β-ketoadipate pathway, through ortho fission of the catechol. It is important to study and select strains that can potentially be used as biocatalysts in the detoxification of these compounds in the environment.

Furthermore they report that a general comparison of the major pathways for catabolism of aromatic compounds in bacteria, and possibly in fungi, has revealed that the initial conversion steps are carried out by different enzymes but that the compounds are transformed into a limited number of central intermediates, such as protocatechuate and (substituted) catechols. These dihydroxylated intermediates are channeled into the *ortho* cleavage pathway (also termed β-ketoadipate pathway) or *meta* cleavage pathway, although only the former route has been demonstrated in fungi. Both types of pathways lead to intermediates of central metabolic routes, such as the tricarboxylic acid cycle. See Figure 21 and Figure 22. This generalized scheme of catabolic pathways for aromatic compounds suggests that microorganisms have extended their substrate range by developing peripheral enzymes which are able to transform initial substrates into one of the central intermediates. This mechanism may contribute to the metabolic adaptation of ubiquitous fungus found in nature, commonly isolated from soil, plant debris, and indoor

[22] Karetnikova & Zhirkova 2005

air environment, such as *Graphium, Aspergillus, Fusarium* and *Penicillium*, exposed to xenobiotic and aromatic compounds. The genera *Graphium* that presented the highest phenol degradation rates have been shown to degrade gaseous n-alkanes. The potential for phenol degradation was demonstrated there. The *Graphium* sp. FIB4 strain will be further studied for possible utilization in industrial effluent treatment and decontamination of natural areas (Santos & Linardi 2004).

Atagana (2004) also reports on a positive result of growth of fungal isolates on solid media spiked with phenols.

Table 8: Growth of fungal isolates on soil media spiked with phenols[23]

Organism	*Phenol*	*o-Cresol*	*m-Cresol*	*p-Cresol*
Aspergillus	+++	++	++	++
Cladosporium	++	+++	++	++
Fusarium	+	++	++	++
Candida	++	++	++	-
Monicillium	++	+	+	++
Trichoderma	++	++	-	+
Penicillium	++	++	+	+++
Pleurotus	+	+	+	-
Phaneochaete	+++	-	+	+

An issue also addressed there (Atagana 2004) is the slower reduction in concentration of *m*-cresol and *p*-cresol compared to phenol and *o*-cresol, which could be a function of methylation, which reduces the solubility of phenol as the methyl position increases from *ortho* through *meta* to *para*, thus rendering the phenol less available for fungal attack. Some changes in pH were also reported, but that did not affect the growth of the fungi and the removal of the phenols.

[23] Atagana 2004

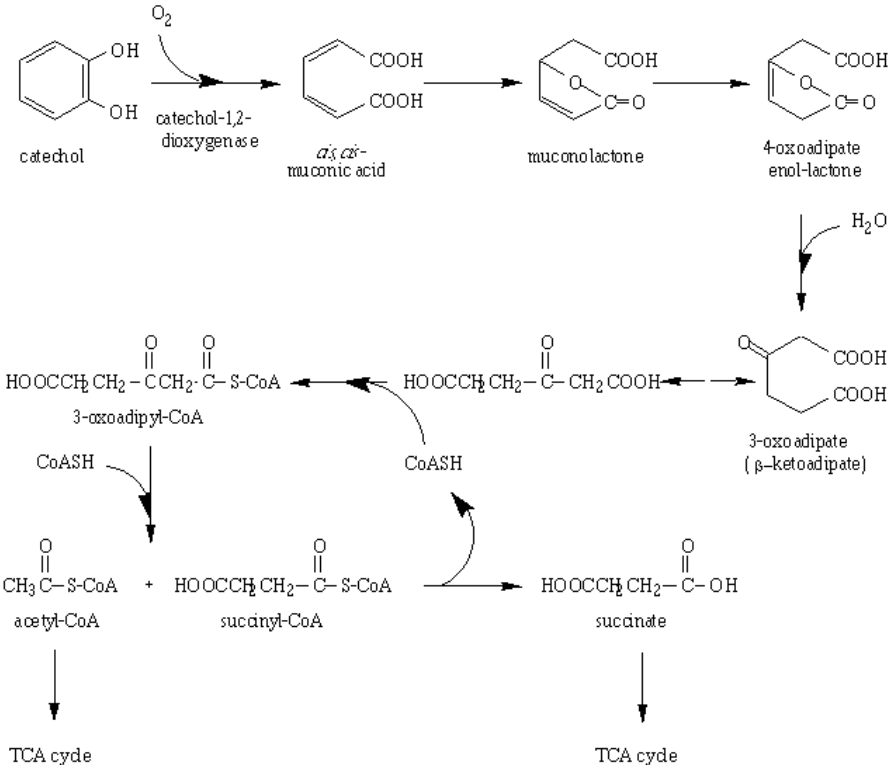


Figure 21: Ortho- *cleavage pathway for catabolism of catechol*[24]

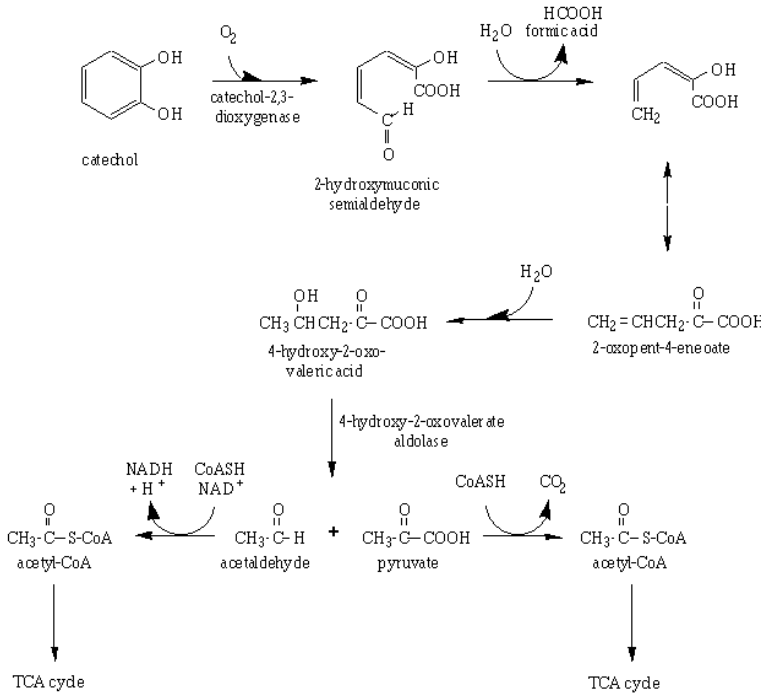


Figure 22: Meta- *cleavage pathway for catechol catabolism*[25]

[24] http://www.ence.umd.edu/~eseagren/bioAHC97.htm; 18.2.2009
[25] http://www.ence.umd.edu/~eseagren/bioAHC97.htm; 18.2.2009

Claussen and Schmidt (1998) report in their work a possible catabolism pathway of phenol and *p*-cresol for hypomycete *Scedosporium apiospermum*. Phenol can also be degraded by bacteria via catechol and *p*-cresol can be catabolised via 4-methylcatechol or via protocatechuate pathway.

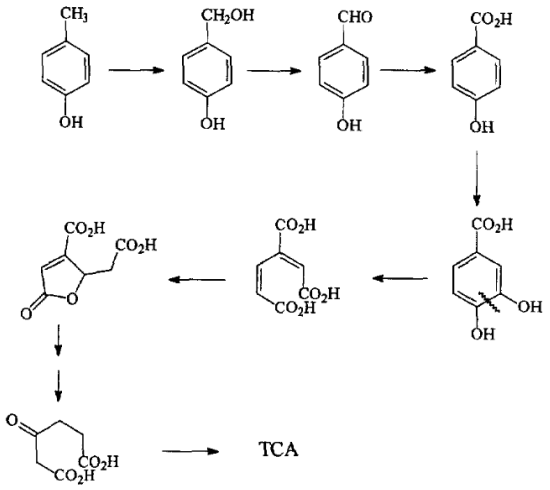


Figure 23: Proposed pathway for the degradation of p-cresol by S. apiospermum[26]

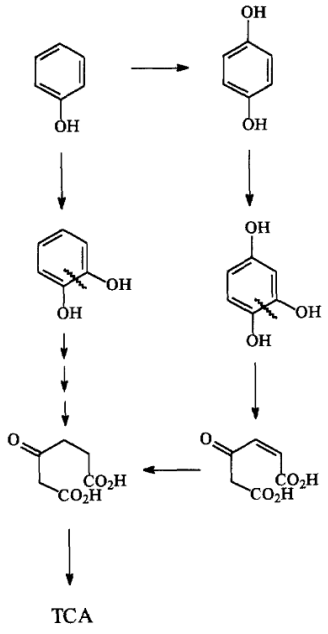


Figure 24: Catabolism of phenol via two possible routes in S. apiospermum[27]

[26] Claussen & Schmidt 1998
[27] Same as above

5 POSSIBLE APPLICATION FOR MICRO-SCALE SLOW PYROLYSIS ROTARY KILN

5.1 Differences in research work and real life situation

Before doing the mass and energy balance of any system and pre-dimensioning of a tank for fungi tar degradation, it should be stressed that a lot of work on a test bench level is needed because a number of factors influence the slow pyrolysis process and products at the end. There are literature data available on woody biomass composition regarding cellulose-hemicellulose-lignin composition and the thermo-chemical decomposition of these components. But these data are not necessarily compatible with our own experimental data acquired. That is because most publications report results done on "pure" feedstock material. It is a known fact that purifying components from natural material can change their chemical composition to a certain extent. That is why contradictory literature data from various authors can be found. A basic requirement is also a chemical analysis of tar that needs to be degraded. Every biomass gives different tar composition. And again most of the available literature data deals with "pure" samples of tar components and their degradation.

During our work in Italy on a micro-scale slow pyrolysis rotary kiln pyrolyser few issues occurred that need to be addressed and taken into consideration before dimensioning a tank for fungi tar degradation.

5.2 Biomass preparation

We started with grinding fresh biomass – black locust (*Accacia pseudorobinia*) short rotation coppice (SRC).

Figure 25: Black locust (Accacia pseudorobinia)

We obtained inhomogeneous biomass that we tried to dry in the pyrolyser. Because the biomass was too humid when it was ground, it caused clogging in the discharge section of the reactor. Very high humidity content of biomass resulted in the formation of lumps whenever an obstacle was reached. A simple solution is to air dry the biomass before grinding. Using a different type of grinding machine could result in more homogeneous biomass. We used a grinder that works on the principle of hammers and a sieve at the bottom.

Figure 26: Ground biomass

Figure 27: Clogged reactor because of inappropriate preparation of biomass

Figure 28: Grinding machine, the hammers that crush biomass and the sieve that determines the particle size.

The biomass that was later used for our experiments was brought from Slovenia. It was pure wood (no bark) woodchips from spruce (*Picea abia*) and beech (*Fagus sylvatica*) made by a farmer that prepares and uses these woodchips for house heating.

Not only can too humid biomass cause problems with clogging in the reactor, it also needs a substantial energy input for drying before the pyrolysis reaction can occur, thus affecting the mass and energy balance in a negative way. For drying biomass (drying tests) in the pyrolyser a different discharge section would be needed. Bigger dimensions and a different double shutter system are required.

Figure 29: Picea abia woodchips

5.3 Sealing system of the plant

Efficient sealing and stuffing material is needed to prevent air coming into the system. Pyrolysis is a process that is conducted in the absence of oxygen, which is why it is important to keep air out of the system; otherwise combustion occurs. The main problem that we encountered in this section was the graphite stuffing that closes the section between reactor and the screw conveyer. During the test, smoke was coming out of the hopper which indicates bad sealing quality in that section. It is particularly hard to make an efficient air barrier in that section. Also for the laboratory scale cheaper material is used than in industrial scale - that lowers the cost of building but has a negative impact on result quality.

Figure 30: Graphite stuffing between reactor and screw conveyer

Another sealing material was utilized. The back of the reactor and the de-ashing device were sealed with fiberglass, which was later changed for “BARLAN” - incombustible inorganic fiber cardboard sealing. The fiberglass can endure the high temperature standard required, but is not adequate to block the gas shifting. The inorganic cardboard sealing “BARLAN” proved to be better than fiberglass but, same as the previous sealing, needed to be changed after every one or two tests. Figure 33 and Figure 34 show the considerable difference in soot residue at the back of the reactor and the state of the sealing after the test.

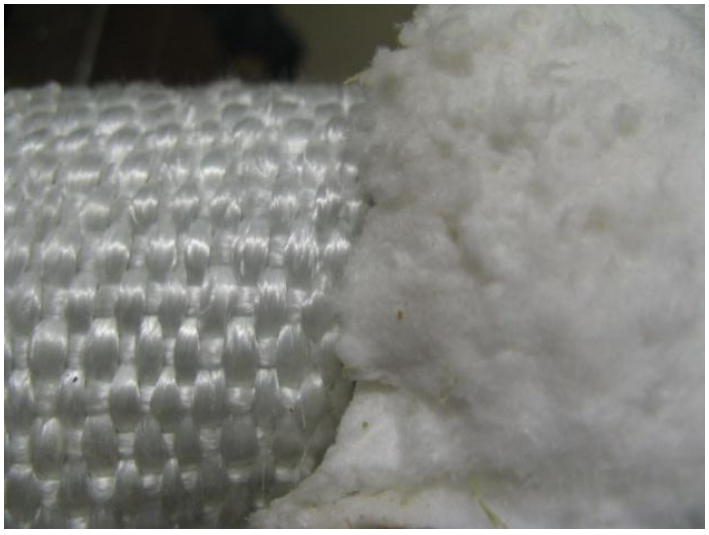


Figure 31: Fiberglass sealing used at the back of the reactor and at the de-ashing device.

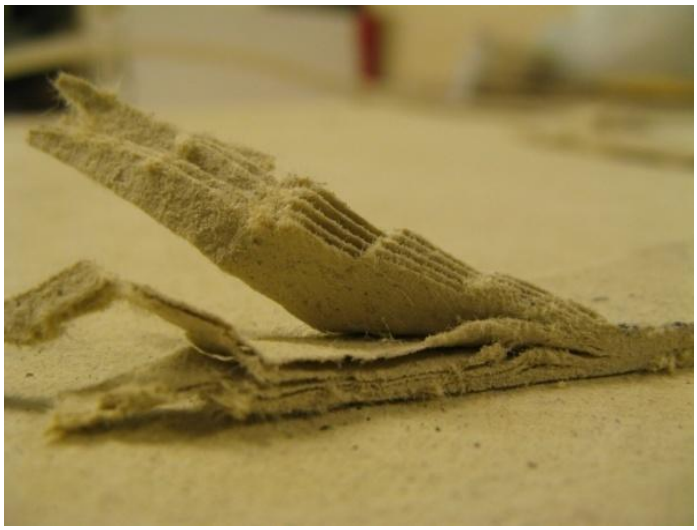


Figure 32: “BARLAN” inorganic fibers cardboard sealing that replaced fiberglass sealing.

Figure 33: "BARLAN" sealing after two pyrolysis tests

Figure 34: Fiberglass sealing at the back of the reactor after one test and soot residue.

5.4 Retention time

Retention time, or the time that biomass stays in the reactor at a certain temperature, is also one of the factors that are very important for the overall process of slow pyrolysis. At the test bench pyrolyser in Perugia an engine through a gear and chain runs the reactor at constant 3 rpm. Even with the reduced speed of the screw conveyer that feeds the biomass to the reactor, biomass failed to stay in the reactor long enough for all the reactions to take place. The solution for this problem was manually stopping the reactor every 30 seconds during our last test. That gave much better results in pyrogas acquired. An inverter that will automatically stop and run the reactor is being installed now to eliminate the need for manually stopping the reactor. Also a barrier at the end of the reactor, before the char

discharge section, is being set up. A better retention time is also possible to achieve with welding additional laminar fins to the inside of the reactor.

Figure 35: Inside of the reactor

5.5 Scrubber cleaning

After every test the scrubber needs to be cleaned. For every test the scrubber section must not contain any residues from previous tests in order to obtain correct data from the chemical analysis of tar samples. As was said in previous chapters, each biomass forms different tar in addition to changing the pyrolysis parameters, which also greatly affects the pyrolysis process. Usually when the test is over, the contaminated water with tar is discharged from the bottom of the scrubber. The scrubber section is than washed with fresh water so long that "clean" water comes out the discharge section. Because of the combustion that occurred briefly due to poor sealing, some soot entered the scrubber through the de-ashing device with the gas. That and the heavy tar clogged the bottom section of the scrubber. Opening of the scrubber and manual cleaning with alcohol followed. After cleaning with alcohol the scrubber was washed with water several times.

It is also very important for the scrubber to be clean to get a realistic evaluation of tar formed during individual tests.

Figure 36: Scrubber cleaning – washing with water.

Figure 37: Interior of the scrubber – bottom part clogged with heavy tar and soot.

5.6 Pre-design of a tank for fungi tar degradation

The micro-scale slow pyrolysis rotary kiln test bench plant has a limitation of intake of 20 kg of biomass feed per experiment. That is because of the char discharge section with

limited storage capacity. The wood chips that we used were beech and spruce woodchips. The initial water put to the scrubber was 18.7 kg, and the water with tar discharged at the end of the experiment was 25.5 kg. So this means that the 6.8 kg in weight difference represents condensed water vapors and tar. The TGA (thermo-gravimetric analysis) results for Norway spruce are in Table 9. It is hard to believe that moisture level of 6.92 % was reached by only one round of biomass drying. Nevertheless all the contaminated water needs to be treated before disposal. This means that a water tank with an intake of approximately 30 kg of contaminated water is needed for this test bench plant.

Table 9: TGA analysis of Norway spruce woodchips

Norway spruce – woodchips, TGA	*WOOD CHIPS – before pyrolysis (1x dried) (%)*	*CHAR - after pyrolysis (%)*
moisture	6.92	2.34
volatile (db)	90.12	49.75
ash (db)	0.38	1.34
fixed carbon (db)	9.49	48.91

It is impossible to determine the exact compounds of the tar produced and their concentration without any chemical analysis results. Thus it is hard or impossible to say which fungi would be the most appropriate to use for degrading tar. A combination of multiple fungi that excrete different enzymes that degrade tar would contribute to faster tar degradation.

It would be good to set up a vessel that can take 30 kg of contaminated water for the test bench plant in Perugia. More experimental work would be needed to determine best conditions for fungi optimal growth and tar degradation. Parameters such as pH, temperature, etc. should be considered. My suggestion is to have the vessel separate from the plant simply because there is no room for it in the current arrangement. Also, the room in which the pyrolyser is set is too cold for efficient fungi growth – at least room temperature is needed. In other small-scale applications the vessel could be attached to the scrubber discharge section directly with the possibility to easily dismount and separate it from there.

6 CONCLUSIONS

As slow pyrolysis yields approximately 35 % of char and gas and 30 % of tar it is not economical to do a tar distillation for acquiring useful chemical components. Another issue is that tar comes in two fractions – water soluble and heavy tar. The water soluble fraction has too much water content to be used in co-firing with other fuels, for instance char. And the heavy tar fraction is very dense and not a sufficient amount for direct combustion as fuel. In slow pyrolysis tar is acquired by gas cleaning. In small scale applications water scrubbing (quenching) is most commonly used. That is because it is efficient and the most economical option. The condensed water vapors and tar together with rest of the water from the scrubber needs to be disposed properly after the pyrolysis process. To treat and dispose of this contaminated water as chemical waste is very expensive. That is why bioremediation methods with microorganisms or fungi are considered. By claims of Karetnikova and Zhirkova (2005) fungi have a more potent enzyme system then bacteria. Atagana (2004) also reports about similar conclusions. That is why fungi tar degradation is considered to be a good option for tar degradation.

After three months of working with the micro-scale slow pyrolysis rotary kiln test bench pyrolyser in Perugia, Italy, we came to the following conclusions. Biomass preparation and the method of grinding it is a very important step in the overall process. It saves a lot of time and unnecessary cleaning and disassembling of the pyrolyser if the biomass is prepared correctly. The next step to a successful pyrolysis is a good sealing system of the plant. If air comes into the reactor, combustion occurs instead of pyrolysis. That is why all sealing materials should be selected carefully. Longer retention time proved to give better results – i.e. favourable gas composition. The importance of scrubber cleaning comes to light when the tar contaminated water needs to be disposed. So far this has been done via chemical waste treatment. But for a small scale plant like the one in Perugia, that is too expensive. Fungi tar degradation is a good option for small-scale slow pyrolysis applications. Further tests and analysis will have to be conducted in order to dimension the vessel for fungi tar degradation correctly in a plant with continuous operation. We expect that such an addition will reduce costs of disposal and benefit the mass and energy balance of the plant and that it will contribute to a cleaner environment. Atagana (2004) reports that before a successful large scale application of fungi in bioremediation, problems of the production of large amounts of inocula and their long term storage in viable conditions need to be addressed. It should be noted that, regardless of any kind of results acquired at the test bench pyrolysis plant, scaling up and mass reproduction of fungi might not react in the same way as in small scale applications.

REFERENCES

Atagana, HI 2004, 'Biodegradation of phenol, o-cresol, m-cresol and p-cresol by indigenous soil fungi in soil contaminated with creosote', *World Journal of Microbiology & Biotechnology*, vol. 20, no. 8, pp. 851-858.

Catechol, <http://www.ilo.org/safework_bookshelf/english?print&nd=857171729&nh=0> viewed 17 February 2009

Claussen, M, Schmidt, S 1998, 'Biodegradation of phenol and p-cresol by the hyphomycete *Scedosporium apiospermum*', *Research in Microbiology*, vol. 149, no. 6, pp. 399-406.

D'Amico, M 2007, 'Pirolisi lenta in un reattore a tamburo rotante: Ottimizzazione dell'impianto e prova sperimentale', BSc thesis, University of Perugia, Faculty of Engineering, Department of Industrial Engineering, Italy.

Demirbas, A 2005, 'Pyrolysis of ground beech wood in irregular heating rate conditions', *Journal of Analytical and Applied Pyrolysis*, vol. 73, no. 1, pp. 39-43.

Elliott, DC 2004, 'Chemicals from Biomass', in Cleveland CJ (ed.), *Encyclopedia of Energy*, Volume 1, Elsevier Inc., Boston University, Boston, Massachusetts USA, pp. 163-174.

Fantozzi, F 2008, 'Biomass Pyrolysis' (lecture material), Perugia, Faculty of Engineering, (material distributed at lectures BIO 608 in Akureyri, Iceland, RES| the school for Renewable Energy Science).

Fantozzi, F, Desideri, U 2007, 'Microscale slow pyrolysis rotary kiln for syngas and char production from biomass and waste – Design and construction of a reactor test bench', poster, University of Perugia, Faculty of Engineering, Department for Mechanical Engineering, Italy.

Guaiacol, <http://www.chemicalland21.com/lifescience/foco/GUAIACOL.htm>, viewed 17 February 2009.

Karetnikova, EA, Zhirkova, AD 2005, 'Degradation of Phenols Formed during Lignin Pyrolysis by Microfungi of Genera *Trichoderma* and *Penicillium*', *Biology Bulletin*, vol. 32, no. 5, pp. 445-449. Translated from Izvestiya Akademii Nauk, Seriya Biologicheskaya, no. 5, 2005, pp. 539-544.

Mohan, D, Pittman, CU, Steele, PH 2006, 'Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review', *Energy & Fuels*, vol. 20, no. 3, pp. 848-889

Murwanashyaka, JN, Pakdel, H, Roy, C 2001, 'Separation of syringol from birch wood-derived vacuum pyrolysis oil', *Separation and Purification Technology*, vol. 24, no. 3, pp. 155-165.

Santos, VL, Linardi VR 2004, 'Biodegradation of phenol by a filamentous fungi isolated from industrial effluents - identification and degradation potential', *Process Biochemistry*, vol. 39, no. 8, pp. 1001-1006

Shafizadeh, F, Chin, PPS 1977, 'Thermal deterioration of wood', ACS Symposium Ser.,.

Structure of cellulose, <http://nutrition.jbpub.com/resources/chemistryreview9.cfm>, viewed 17 February 2009.

Wrenn, BA 1998, 'Biodegradation of Aromatic Hydrocarbons', <http://www.ence.umd.edu/~eseagren/bioAHC97.htm>, viewed 18 February 2009.

Yang, H, Yan, R, Chen, H, Lee, HD, Zheng, C 2007, 'Characteristics of hemicelluloses, cellulose and lignin pyrolysis', *Fuel*, vol.86, no. 13-13, pp. 1781-1788.

APPENDIX A

Table A1: Phenolic compounds distribution in the fractional vacuum distillates (wt.% in the distillate); (Murwanashyaka et al. 2001)

Fraction number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Temperature cut (°C)	25–45	45–55	55–60	60–65	65–70	70–80	80–85	85–90	90–95	95–100	100–105	105–110	110–115	115–120	120–130	130–135
Phenol	13.34	12.09	3.24	–	–	–	–	–	–	–	–	–	–	–	–	–
o-cresol	3.98	7.60	3.47	0.54	–	–	–	–	–	–	–	–	–	–	–	–
m-cresol	–	5.43	7.67	5.40	0.68	–	–	–	–	–	–	–	–	–	–	–
p-cresol	0.41	10.47	14.30	9.77	1.09	–	–	–	–	–	–	–	–	–	–	–
2,4-xylenol	10.11	1.53	0.71	–	–	–	–	–	–	–	–	–	–	–	–	–
2-ethylphenol	–	1.30	1.17	0.80	–	–	–	–	–	–	–	–	–	–	–	–
2,5-xylenol	–	0.55	1.73	3.13	0.59	–	–	–	–	–	–	–	–	–	–	–
2,3-xylenol	–	1.11	4.72	9.71	2.24	0.44	–	–	–	–	–	–	–	–	–	–
3-ethylphenol	–	–	–	0.49	3.13	1.07	–	–	–	–	–	–	–	–	–	–
4-ethylphenol	–	–	–	2.11	15.02	5.28	0.43	–	–	–	–	–	–	–	–	–
Guaiacol	10.41	9.92	3.79	0.18	–	–	–	–	–	–	–	–	–	–	–	–
3,5-xylenol	–	–	–	2.06	1.47	–	–	–	–	–	–	–	–	–	–	–
3,4-xylenol	–	–	–	–	1.53	2.51	0.30	–	–	–	–	–	–	–	–	–
Trimethylphenol	–	–	1.25	1.59	0.33	1.33	–	–	–	–	–	–	–	–	–	–
Trimethylphenol (isomer)	–	–	–	0.47	1.84	3.31	–	–	–	–	–	–	–	–	–	–
Methylguaicol	03.6	0.79	0.39	0.44	–	–	–	–	–	–	–	–	–	–	–	–
4-propenylphenol	–	–	–	–	–	1.59	0.86	–	–	–	–	–	–	–	–	–
Trimethylphenol	–	–	–	–	–	0.96	0.38	–	–	–	–	–	–	–	–	–
4-propylphenol	–	–	–	–	–	–	1.72	0.61	–	–	–	–	–	–	–	–
Methylguaicol (isomer)	–	–	0.47	0.82	–	–	0.45	–	–	–	–	–	–	–	–	–
Trimethylphenol (isomer)	–	–	–	–	1.78	–	–	–	–	–	–	–	–	–	–	–
4-methylguaicol	–	8.21	14.95	14.10	3.00	0.82	–	–	–	–	–	–	–	–	–	–
4-allyphenol	–	–	–	–	–	0.50	0.75	–	–	0.53	–	–	–	–	–	–
Catechol	–	–	–	–	–	3.27	16.46	35.33	19.82	12.94	0.71	–	–	–	–	–
Trimethylphenol (isomer)	–	–	–	–	–	–	–	–	–	–	–	–	0.51	0.52	0.26	–
Rersorcinol	–	-	-	-	-	-	-	-	-	-	-	-	4.37	3.68	0.80	
4-ethylguaiacol	–	–	0.62	3.52	9.78	4.72	0.31	–	–	–	–	–	–	–	–	–
3-methylcatechol	–	–	–	–	–	–	1.58	4.50	7.58	9.23	1.31	0.22	0.17	–	0.31	–
Syringol	–	–	–	–	–	–	–	0.93	11.40	33.72	12.09	0.26	–	–	–	–
4-methylcatechol	–	–	–	–	–	–	–	–	0.92	0.75	16.72	14.19	0.65	–	–	–
Methylresorcinol	–	–	–	–	–	–	–	–	–	–	–	–	1.30	1.39	0.49	–
Eugenol	–	–	–	–	–	3.68	3.17	1.64	–	0.66	0.47	–	0.13	0.31	0.35	–
Propylguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	0.18	–	–	–
4-ethylcatechol	–	–	–	–	–	–	–	–	–	–	–	5.23	0.49	–	–	–
Ethylcatechol (isomer)	–	–	–	–	–	–	–	–	–	–	–	2.32	6.84	4.29	0.82	–
Isoeugenol	–	–	–	–	–	–	2.23	2.61	9.00	0.62	–	–	–	–	–	–
4-methylsyringol	–	–	–	–	–	–	–	–	–	–	14.48	25.92	1.50	0.35	–	–
Methoxycatechol	–	–	–	–	–	–	4.68	10.18	–	1.63	-	1.74	–	–	–	–
Dimethylresorcinol	–	–	–	–	–	–	–	–	–	–	–	–	0.60	–	0.19	–
Dimethylresorcinol (isomer)	–	–	–	–	–	–	–	–	–	–	–	–	2.00	1.64	0.44	–
Propenylmethoxyphenol	–	–	–	–	–	–	–	–	–	–	2.26	–	–	–	–	–
Trimethylresorcinol	–	–	–	–	–	–	–	–	–	–	–	–	0.64	0.57	–	–
Trimethylresorcinol (isomer)	–	–	–	–	–	–	–	–	–	–	–	–	0.81	0.46	–	0.27
Isopropylguaiacol	–	–	–	–	–	–	–	–	–	–	–	–	3.76	3.97	1.43	–
Trimethylresorcinol (isomer)	–	–	–	–	–	–	–	–	–	–	–	–	2.94	2.14	0.61	–
Methylmethoxycatechol	–	–	–	–	–	–	–	0.2	0.78	0.55	–	–	4.80	1.95	0.22	–
Propylbenzenediol	–	–	–	–	–	–	–	–	–	–	–	–	1.0	1.5	1.3	0.0
Allylsyringol	–	–	–	–	–	–	–	–	–	–	–	–	8.7	7.6	2.7	0.0
Propylsyringol	–	–	–	–	–	–	–	–	–	–	–	–	0.4	0.1	0.1	–
Dimethylmethoxyresorcinol	–	–	–	–	–	–	–	–	–	–	–	–	2.8	1.2	0.7	–
Isopropylsyringol	–	–	–	–	–	–	–	–	–	–	–	–	1.1	1.5	1.7	–
Propenylsyringol	–	–	–	–	–	–	–	–	–	–	–	–	2.8	4.9	6.2	1.0
Total phenols in distillate	29.61	58.99	58.47	55.14	40.71	33.00	32.21	55.71	49.49	60.63	48.04	49.89	48.96	38.15	18.99	2.87
Distillate yields[a]	13.91	9.59	9.60	5.05	4.54	5.85	4.56	4.53	6.60	6.95	2.68	5.50	4.71	3.05	2.08	1.88