ANALYSIS OF THE TOP PHASE FRACTION OF WOOD PYROLYSIS LIQUIDS

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PREFACE

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ABSTRACT

The main purpose of this study (a subproject of the TEKES project) was to develop a suitable fractionation method for the pyrolysis liquid and, on the other hand, to find out potential possibilities to utilize the fractions in the chemical industry. The raw material used was the top phase of wood pyrolysis liquids produced from the Finnish forest residue at the Technical Research Centre of Finland (VTT) in Espoo. The study formally consisted of two parts referring to as Master’s Thesis and Experimental Research Study, which both belong to a syllabus of the Chemistry Department, University of Jyväskylä. The Master’s Thesis (literature review) deals with the chemical composition of wood material, pyrolysis processes of wood, fractionation of products, and possibilities to utilize the product fragments. It was written during the period 1.6.-31.12.2003. The experimental part (reported separately) included the practical laboratory work, was completed by 30.11.2003. The fractionation was carried out by following the practically tested methods of VTT and scientific literature. The main purpose was to separate low-molecular-mass carbohydrate-derived material (aliphatic carboxylic acids, hemicellulose residues, monosaccharides, and anhydrosugars), the extractives and lignin materials (HMM and LMM lignins) using three separate solvent extractions with water, n-hexane and methylenechloride. The separation of the compound groups based on their different solubility. The obtained fractions were analyzed by gel permeation chromatography (GPC), mass spectrometry (MALDI-TOF), $^{13}$C NMR and elemental analysis (CHN) which all provided usable information on the chemical composition of the top phase, its degradation under pyrolysis conditions and the distribution of the high-value compounds.
1 INTRODUCTION

Biomass is the third most common energy source in the world after coal and oil /1/. In the perspective of increase in energy demand, the high costs of fossil fuels and disposal as well as the environmental concern about emission levels of CO$_2$, SO$_2$ and NO$_x$ in the atmosphere, the use of biomass to provide partial substitution of fossil fuels for power generation is of growing significance. Especially developing countries have had a deep interest in the pyrolysis of biomass, since their economics and infrastructure largely base on agriculture and forestry. At the same time thermal conversion of agricultural and forest residues, by means of pyrolysis, combustion, gasification or direct liquefaction, reduces the amount of wastes but allows efficient energy recovery. Considering that resources of fuel oils are limited, the combustion of pyrolysis oil in diesel engines, boilers and gas turbines becomes more and more attractive also in the Northern Europe although the production costs are higher, efficiency is lower (50 %), and the properties of pyrolysis oils are not yet competitive with those of diesel fuels. The quality of pyrolysis oil depends significantly on the temperatures used during the process and storage. However, the knowledge of the chemical composition, toxicity, thermal behaviour, reactivity of biomass fuels and interaction of the constituents under process conditions, and operations of the conversion device is required for development.

Pyrolysis is defined as thermochemical process of decomposition to produce gases, liquids and char /1/. The reactions occur by heat alone in the absence of oxygen. As far as composition of biomass types varies, the distribution of chemical decomposition products is markedly different by wood species or sewage sludge. Wood and other herbaceous biomass consist of cellulose, hemicelluloses and lignin, but contain also small quantities of extractives, water and inorganic matter. Thermal degradation of these constituents takes place through complicated reaction pathways, which are strongly affected by the atmosphere, temperature, pressure, residence time of gases and mass transfer processes.
The pyrolysation process is typically carried out by rapid heating and gas residence times lasting a few seconds to maximise product yield and avoid harmful secondary reactions /1,2/. Pyrolysis under conditions of rapid heating and gas removal produce primarily a high-viscous and single-phase liquid called pyrolysis oil or pyrolysis liquid. Colour of the crude pyrolys is liquid is reddish brown and its elemental composition reflects the character of initial feedstock. For instance, wood pyrolysis oils are consisted of a complex mixture of oxygenated hydrocarbons and solid impurities with a considerable portion of water from the original moisture and reaction product /2/. Source for the complexity arises from the decomposition of cellulose, hemicelluloses, lignin and other organic materials, which are fed to the reactor apparatus. Chemical and physical quality of the liquid from slow pyrolysis is unlike and more tar like than the liquids from fast pyrolysis /3/.

Before establishing pyrolysis oils in the markets an essential quality improvement of these oils must be achieved /1/. In this respect, detailed studies on the composition and aging of pyrolysis oils are of interest. Gas chromatograph equipped with the mass selective detector (GC/MSD) is the most widely used technique to separate and quantify volatile compounds of pyrolysis liquids, though GC/MSD analysis can only detect maximum 40 % of these liquids. For this reason, several parallel analysis techniques are still necessary.

Generally, pyrolysis oils are thermally instable containing mostly non-volatile fractions with variety of oxygenated reactive functional carbonyl and hydroxyl groups such as groups so that they may be infeasible to be fractionated by standard techniques including distillation. However, one effective way to separate compound groups from each other is solvent extraction, in which the dispersion of two non-miscible phases is caused by adding water. In the course of time polar and water-soluble small organic compounds settle on the top while non-polar, water- insoluble extractives and aromatic compounds (MW 400-1500 Da) remain at the bottom. A disadvantage of this phase separation method is the dilution of the aqueous phase when subsequent recovery of water-soluble chemicals can result in the extensive evaporation of water. A gradual selective solvent extraction
of desired substances by ethyl acetate, $n$-hexane or methyl-tert-butyl ether can then be exploited.

In the past decades, the utilisation of biomass pyrolysis oil has focused on fuel applications after partial or comprehensive modification. At the moment pyrolysis products also are considered as potential feedstock for chemicals even if they exhibit interfering properties like instability, acidity and low-heating value of the oils. Due to presence of a large number of constituents, the isolation of all components of the oil is not possible, but specific high value compounds might be fractionated and purified, e.g., for food production or medical purposes.

This thesis concentrates on the structure and the degradation reactions of the wood constituents, the pyrolysis of the wood material and various fractionation methods of the top phase components in the pyrolysis products. Along with fractionation much attention is paid to physical and chemical properties of the oil, since these properties greatly vary according to age, composition of the feedstock or the process and storage conditions. Main parts of the pyrolysis process are thermal decomposition and interaction of wood constituents which determine the operation conditions, the quantities of pyrolysates and the techniques of their further purification and refining.
2 BIOMASS FEEDSTOCKS

2.1 Wood

Wood utilised for biomass conversion mainly consists of waste wood. The term “waste wood” comprises all kinds of wood from working or wood processing which is not considered as the final product of the process or manufacture. For instance, only the forest industry produces annually huge amounts of feasible wood residue such as sawdust, bark, paper pulp, wood chips and paper /4/. Generally wood biomass types are classified as packing wood (pallets, transportation crates, fruit crates), waste wood from processing (blend, sections, thinnings), building site wood (untreated solid wood, timber materials, miscellaneous tree, unwanted wood refuse) and furniture wood.

While harvesting industrial wood from forest plots, it has been as a common manner to gather logs and discharge decomposing residuals to fertilise forest soil /4/. Partially, it would be like deforestation to waste them as far as small wood, branches, tops, green parts (needles) and bark of conifers form a substantial feedstock for thermochemical purposes. For instance, Technical Research Centre of Finland (VTT has carried out laboratory experiments, where they handled forest residues including chips (conifer trees), needles and fairly big proportion of bark by gasification /5/. In another study /6/, the green forestry residue of spruce (40 % wood, 23 % bark and 27 % needles) was utilised for fast pyrolysis and similarly brown residue including about 60 % of stem wood, less than 30 % of bark, and below 10 % of needles, was processed into fuel.

2.2 Other sources

In addition to wood-based feedstocks, there are numerous amounts of other biomass materials, which are suitable for conversion of chemicals and fuels. These biomasses comprise decaying and living plants, or instead they may be synthesised products of nature. The principal sources of other biomass are, e.g., industrial products and leftovers (sludge, residues of food industry), peat,
agricultural residues (sludge, straw, crops, tops, manure), household wastes (food leftovers, paper, plastic) and community wastes (sewage and solids) /4,7,8/. Chemical composition and physical structure of biomass are properly known excluding communal wastes, fertilisers and sewage.

The primary organic components of biomass are cellulose, hemicelluloses and lignin /8/. Many biomass sources contain also different kinds of extractives and they represent for 5 % to 10 % by weight of the dry biomass /8,9/. As far as cellulose is concerned, it is the most common existing carbon hydrate forming the structural framework of plant cell walls. Herbaceous biomass such as wood, hey and straws are renewable, whereas peat is a combination of rotting plant layers and soil so that it matures slower.

3 GENERAL STRUCTURE OF WOOD

3.1 Wood

Structural constituents of wood are root, trunk, branches, top, bark and green parts (leaves or needles) /10/. Structures of trees vary according to species, but from the general point of view they are constructed of fibres and wood cells. Cells are specialised in separate tasks such as offering structural support and transport of nutrients. Composition of cells is considered as heterogeneous and their principal constituents are carbohydrates like cellulose and hemicelluloses, and lignin. These constituents are introduced in the following chapters.

3.2 Bark

Bark is the furthest structural part of wood, which protects tree against microbiological and mechanical damages /11/. Bark consists of two layers, which are called inner core (phloem) and outer core (cork, rhytidome). Cell layers
locating at the narrow inner core are alive, whereas cell tissues of outer core are formed by dead cells seeped out from the inner core. Amount of extractives is significantly high in bark covering 30-40 wt-% of dry wood. On the basis of the fine structure, bark can be divided into fibrous substances, cork cells and refined matter.

4 CHEMICAL CONSTITUENTS OF WOOD AND BARK

Important chemical constituents of wood dry solids are high molecular mass polymers (about 90 % of dry wood), those physical properties and chemical structures differ considerably from another /10/. Carbohydrates, which are found representing for 65-75 wt-%, constitutes about 40 wt-% cellulose. Majority of cellulose locates in the secondary wall (S2) of wood cells. Amount of hemicelluloses in woods vary from 25 to 35 wt-%, though lignin content, depending on the species, is for softwood 25-30 wt-% and hardwood 20-25 wt-%.

4.1 Cellulose

Cellulose is a polymer, which is constructed of β-D-glucopyranose units linked together by (1→4)-glycosidic linkages and it covers around 40-50 % of dry wood. Cellulose molecule is linear (Fig. 1) and it consists of up to 10 000 D-glucose units. Its closest relative polysaccharide is starch, which differs from cellulose only with α-glycosidic linkages.

Due to homogenous feature, attraction to form intramolecular or intermolecular hydrogen bonds as well as high polymerisation degree, cellulose is thermochemically more stable than hemicelluloses /12/. It has a tendency to form tight hydrogen bonds with neighbouring molecules, which makes fibre structure of wood even harder and thus provides mechanical support for wood cells /10/.
Its rigidity arises from overall structure. Amorphous and crystal regions have been identified from ultra structure of cellulose. The extent of these regions alternate irregularly, as also impeding solubility of cellulose in organic solvents and degrading polymer structure by acidic hydrolysis or enzyme-mediated catalysis. Its complete hydrolysis in 40 % aqueous HCl solution produces only D-glucose and disaccharide isolated from partially hydrolysed cellulose is cellobiose.

![Chemical structure of cellulose](image)

**Figure 1.** Chemical structure of cellulose /12/.

### 4.2 Hemicelluloses

After cellulose, hemicelluloses are the second prevalent components of cell walls in wood fibres /10/. Their proportion in wood corresponds to 20-30 wt-% of dry wood. Combination of hemicelluloses varies depending on the tree part and wood species (Figs. 2 and 3). In softwoods, the most essential hemicelluloses are galactoglucomannans (15-20 wt-%), in which major chain is built up of β-D-glucopyranose and β-D-mannopyranose units with (1→4)-glycosidic linkages /13/. The second common hemicellulose type of conifers is called arabinogluconoxylan (5-10 %) of the wood dry solids, in which the major chain consists of β-D-xylopyranose units, which are joined with (1→4)-glycosidic bonds, and 4-O-methyl-α-D-glucuronic acid groups act as side groups. In hardwoods, the most often representing hemicellulose type is O-acetyl-4-O-methylglucuronoxylan (25-30 %), in which the main chain is formed of β-D-xylopyranose units ((1→4)-glycosidic linkages) and 4-O-methyl-α-D-glucuronic acid groups as side groups. Glucomannans are found to cover less than 5 % of the solid matter in hardwoods.
Thus, hemicelluloses are structurally heteropolymers constructed of monosaccharide units: D-glucose, D-galactose, D-mannose, D-xylose, L-arabinose and L-ramnose as well as D-galacturonic acid and 4-O-methyl-D-glucuronic acid. Polymerisation degree of hemicelluloses is only 150-200, which is together with amorphousivity one reason for their sensitive degradation and good solubility in water.

**Figure 2.** Hemicelluloses of softwoods /14/.

**Figure 3.** Hemicelluloses of hardwoods /14/.
4.3 Lignin

Lignin is amorphous polymer and the third primary component of wood, in which its proportion of dry solids corresponds to 25-30 % for softwoods and 20-25 % for hardwoods /11/. It provides for wood mechanical strength. Lignin is built up of phenyl propane units, i.e. G:C3 precursors, which have been recognised as \textit{trans}-\textit{p}-coumaryl, \textit{trans}-coniferyl and \textit{trans}-sinapyl alcohols (Fig. 4). These precursors result from complicated enzyme-catalysed biochemical reactions. During biosynthesis the precursors are transformed, through an enzymatic dehydrogenation reactions, to phenoxy radicals, which then are polymerised by forming the final lignin structure.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/4.png}
\caption{C_6C_3 precursors of lignin /4/.
\end{figure}

Bonds connecting lignin precursors together comprise 60-80 % of ether linkages, of which the most common type is \(\beta\)-O-4-bonding. Rest part of linkages have been identified as carbon-carbon bonds and ester bonds. Lignin and hemicelluloses instead are joined to another either by benzyl ether or phenyl glycosidic bonds. Major structures and lignin related linkages are shown in Figure 5.
Along with cellulose, hemicelluloses and lignin solid material of wood includes less than 4 % various extractives which contribute to properties such as colour, taste, smell, decay resistance, density and flammability /13/. Extractives are considered as lipophilic or hydrophilic organic compounds, which can be extracted from a wood sample by using neutral (non-polar) organic solvents (methyl-tert-butyl ether, acetone, tetrahydrofuran) or water, respectively. Water-
soluble extractives are, among others, some carbohydrates and tannins. In contrast lipophilic extractives, containing carbon atoms from 10 to 30, are classified into aliphatic hydrocarbons, fatty alcohols, fatty acids as well as fats and waxes. On top of former substances, wood contains significant amounts of terpenes and terpenoids; resin acids and sterols.

Generally, extractives are divided according to their locations and functions into the following groups: 1) pathological, i.e. ductious sap, which protects conifers against physical and biological damages 2) physical, i.e. parenchyma sap and its function is to restore spare nutrients in softwoods and hardwoods and 3) hardwood sap including phenolic derivatives protects hard wood and bark part of tree /13/. From structural basis, extractives are grouped as aliphatic/acyclic, phenolic and other compounds, those features are detailed in the following.

4.4.1 Aliphatic and acyclic extractives

Aliphatic and acyclic compounds include terpenes, terpenoids, fatty acid esters, alkanes (C22-30 alkanes), fatty acids and alcohols (C18-22). Hundreds of terpenes have been isolated from wood, purified and structurally elucidated. For many decades, they have been refined as perfumes, flavouring agents, waterproofing materials, insect repellents, fungicides and medicines /15/. Terpenes (terpenoids) provide the raw materials for the industrial processes of high-value products. They can be classified on the basis of the number of isopreneunits as mono-, di-, tri-, tetra- and sesquiterpene structures (Fig. 6).
Figure 6. Examples of some feasible terpenes, terpenoids and steroids /16/. There are only small quantities of free fatty acids (30 compounds) in woods, which represent in the form of esters like triglycerides of conifer or hardwood sap. The most often found compound of saturated or unsaturated fatty acids is linolic acid. Unsaturated fatty acids have a tendency to oxidise and form lipophilic soaps with alkali solutions.

4.4.2 Phenolic extractives

Wood contains a large variety of aromatic extractives from simple phenols to multi-substituted polyphenols and their related compounds (Fig. 7) /16/. Most of them can be found in the heartwood (high-molecular-mass extractives), and the rest part which is minor (low-molecular-weight extractives), belongs to sapwood protecting trees against microbes and insects.
This group comprises valuable and convertible compounds such as phenols, stilbenes, lignans, isoflavonoids, flavonoids as well as condensed and hydrolyzable tannins /13/. They can be isolated for industrial purposes by steam distillation, hydrolysation (with acids, bases, enzymes) and solvent extraction.

Figure 7. Some convertible phenolic extractives /16/.

4.4.3 Other extractives

There exist other extractives in wood, which have been identified as diverse /13/: sugars, cyclitones, tropolones, amino acids, alkaloids, coumarines and quinones. As far as sugars are concerned, the variety of saccharides in wood material is large reaching from monosaccharides (glucose, galactose, mannose, arabinose, rhamnose and fructose) to oligosaccharides (saccharose) and polysaccharides (starch and hemicellulose residues).
4.5 Inorganic substances

Inorganic substances cover 0.2–1 wt-% of wood [10,13]. The most common inorganic elements in wood are calcium, potassium and magnesium, while concentrations of other elements such as phosphorous and sodium are minor.

5 CHEMICAL COMPOSITION OF WOOD AND BARK

Cellulose existing in bark is considered to be more amorphous than that of bark-free tree and the fibres are shorter [13]. Amount of extractives is significantly higher in bark (30–40 wt-% of wood) than in other structural parts of wood, of which many are similar to basic wood material. [10]. Bark fibers are particularly rich suberin and polyphenolic substances. Also pectins such as uronic acids and other carbohydrates (glucans, starch) are found to represent high concentrations. In addition to extractives bark is rich source of minerals. Compared to the wood, bark contains smaller proportions of cellulose and hemicelluloses. For softwood species the most common hemicelluloses of bark are galactoglucomannans, whereas in hardwood these are xylan and glucomannans.

Thus far, wood bark has been reinforced mainly as a soil fertiliser or as a combustion feedstock for producing energy, but refining extractives from bark to drugs or chemical fuels could be included. However, processing of bark exhibit practical difficulties as far as bark contains a lot of inorganic impurities (sand), product yield is variable and raw material is laborious to obtain. The bark-free wood material in turn has a large assortment of industrial and other applications.
6 PYROLYSIS OF BIOMASS

Pyrolysis is the degradation of macromolecular materials influenced by heat alone in the absence of oxygen /17-19/. While heating organic polymers, the most sensitive polymers will shatter first due to subsequent cleavage of molecular bonds. Shattering of molecular bonds reminds of depolymerisation reactions, though only insignificant changes have been observed to occur from the structure or physical properties of polymers. As the temperature increases, degradation of a polymer accelerates, since large amount of bonds open, and degradation of polymer to smaller components or from monomers to oligomers occur. Thus reaction products with smaller particle size are more convenient to analyse using chromatographic or spectroscopic techniques.

Pyrolytic conversion of lignocellulose based materials leads in the generation of gas, liquids (tar) and solid char /17/. The products can be exploited as fuels with or without refining, or these are supplied as raw material for chemical plants. Especially the development of advanced pyrolysis for liquid production has paid a lot of attention during the past decades, because they offer an auspicious technique to convert low value wood residue into liquid fuels and other more valuable products. Many pilot scale processes involving the fast vacuum pyrolysis have been established.

Fast pyrolysis is a high temperature process in which biomass is rapidly heated to temperatures about 500 °C in the absence of oxygen /17-21/. As a result biomass decomposes to generate vapours and aerosols. Subsequently, rapid cooling and condensation yield gases, char, and 69-70 % of dry biomass feed off a brown mobile liquid, the pyrolysis oil. Liquid production demands very short vapour residence time (30 to 1500 ms at around 500 °C) to avoid harmful secondary reactions. Considering the future prospects, fast pyrolysis oil would be a noteworthy fuel replacing non-renewable fossil fuels, though its heat value half that of conventional fuel oil.
Vacuum pyrolysis instead means breaking up of complex polymer structures of lignocellulosic material, which aims to a large amount of oxygen-rich primary oil and also good quality char as a side product. Pyrolysis liquids must be either fractionate into simple mixtures of compounds having similar chemical and physical features or refine as other convenient chemicals or intermediates. Proper knowledge of pyrolysis oil composition is a necessity for their utilisation as a chemical feedstock.

6.1 General aspects

Before heavy fuels were applied, refining of chemicals from biomass most often took place by extraction, fermentation and combustion /9/. These days biomass can be transformed to liquids by several thermochemical methods such as pyrolysis, gasification, high pressured liquefaction, catalytic processing or solvolysis /22/. Processing of biomass as liquids, chemical fuels and food constituents requires high temperature conditions and optimised pressure levels, which are attained with hydrogen or nitrogen gases, steam or catalysts /23-26/. Combustion of biomass is practised commercially to provide heat and power. Gasification, in turn, is a technique to produce fuel gas from biomass by partial oxidation to give a mixture of carbon monoxide, carbon dioxide, hydrogen and methane – or by steam or pyrolytic gasification. The reaction occurs in a number of sequential steps including evaporation of moisture from the feedstock, pyrolysis, or partial oxidation of pyrolysis tars, gases and solid char.

6.2 Pyrolysis techniques and equipment

Pyrolysis process consists of several steps following another. At first the feed is dried until moisture content of the material is less than 10 wt-%, so that water residues do not cumulate to the final product /24/. Pre-treatment includes grinding the feedstock. After pre-treatment the grinded particles are lead to the reactor chamber, where heating and pyrolysis reactions occur with the absence of oxygen. Practically, particles have to have extremely small diameter to fulfil
the requirements of rapid heating and to achieve a favourable liquid yield. Char and gas resulting from the thermal decomposing, flow to a cyclone and heat exchangers, where solid material (char), volatile gases and pyrolysis liquid are segregated by taking advantage of gravitation force and cooling. Gaseous compounds are built up of carbon monoxide, carbon dioxide and methane gas, which are condensed to final pyrolysis liquid by rapid cooling /25/. Non-condensable gases in turn are cycled back to the reactor chamber and are possible to utilise in indirect heating. Proceeding of the pyrolysis process is demonstrated in the following scheme (Fig. 8).

**Figure 8. Scheme of pyrolysis pathways /25/.

Reactor is an abundant part of a pyrolysis device, and its costs correspond to about 20% of entire investments of the process /24/. In order to enhance the oil production, the reactor must fulfil many operational requests as far as it must provide high heating rates, precise control of temperatures, rapid cooling of vapours and effective removal of gaseous products.

Usually pyrolysis processes are named according to the reactor configuration and adjusting operations /9/. At the moment there are three primary device types and methods being suitable for fast pyrolysis:
1. Ablative pyrolysis in which large wood particles are pressed against a heated surface and rapidly moved while wood is melting at high temperature and generates an oil film that evaporates. Ablative pyrolysis processes were first reported by Diebold and Lédé [27].

2. Bubbling fluid bed and circulating fluid bed flash pyrolysis, which shift heat from a condenser to small wood particles (smaller than 3 mm) by a combination of convection and conduction. The required gas flow depends on the size and mass of the fluidising material. The flash pyrolysis reactors developed in the University of Waterloo, Canada, yield pyrolysis liquid up to 75 wt-% from fry feed.

3. Vacuum pyrolysis where heating occurs deliberately but the reactor removes pyrolysis products as quickly as previous systems. One of the most commonly used vacuum system was built at the Institute of Pyrovac in Sainte-Foy, Canada. In this system a molten salt acts as heating medium. The molten salt flows through heating plates in the reactor to indirectly heat the feedstock conveyed over the heating plates. Compared to rotating cones and the two techniques mentioned above, pyrolysis in vacuum employs a much lower heating rate and therefore liquids yield (60-65 %) remains smaller. The dominant pyrolysis techniques are illustrated in Figures 9, 10 and 11 [25].
Figure 9. Conceptual fluid bed fast pyrolysis process, in which the feedstock is at first dried, grinded and then fed to the reactor /25/. The process involves an efficient heat control and separation of condensable gases from char.

Figure 10. Continuous ablative process, in which the raw material is treated with nitrogen before feeding to the reactor /25/.
6.3 Influence of process conditions on the products

Conversion of biomass in pyrolysis and the compounds resulting from the degradation reactions are strongly affected by physical factors /28,29/. For instance, increasing pressure, use of additives, ash content of biomass and subsequent decrease of the pyrolysis temperature reduce the yield of volatile substances but at the same time more char is formed. The yields of pyrolysis oils and their chemical distribution is typically in the respect to initial wood composition, heating rate, pressure, moisture content, participation of catalysts in the reaction, particle size of feedstock, pyrolsation mechanism (secondary cracking) and other environmental parameters.
6.3.1 Raw material

Wood degradation reactions are also affected by various interactions occurring between the chemical constituents. The requirements of heat transfer rate set limitations for the particle size of feed in some reactors /27,30/. The process conditions favour smaller particles, in which volatilisation is more efficient. Smaller particles (d < 0.8 mm) warm up more rapidly from the centre, but for bigger particles (d > 0.8 mm) heat flux from the surface to inner layers is slower and more char is formed. Smaller mass and particle size has also an effect on the composition of gas and it contributes to the cracking of hydrocarbons by increasing hydrogen yield. Gas transfer is faster from a small particle than from a large one, so that gas residence time in the reactor delays and cracking proceeds.

Before feeding, raw material is dried to remove overall moisture, which affects the heat transfer rate through the solids and the variation in the thermal properties. Moisture content of fed biomass must be less than 10 % of dry weight, though more water is always generated in flash pyrolysis /31/.

Roy et al. /32/ have noticed that decreased extractive content in aspen polar wood results higher yield of pyrolysis oils, whereas cellulose content has a controversial effect. While comparing oil production for ordinary wood and extractive-free wood, they also found that extractive-free wood yields more oils than ordinary one, although higher amounts of charcoal was obtained. At the temperatures from 250 to 350 °C influence of extractives on oil yield was defined to be negative. At the same time, the formation of formic and acetic acid from polysaccharides reduced.

In the further experiments, Roy et al. /32/ investigated sugars and measured levoglucosan contents from wood, extractive-free wood and holocellulose pyrolysis oils at separate degradation temperatures. The highest levoglucosan yields were obtained from extractive-free wood as far as extractives act as inhibiting agents.
Extractives were removed from tree material by water and alcohol extraction, in which wood polysaccharide chains were pushed apart as wood swelled and fibre orientation took place. Wood was further soaked in cold water, which reduced around 1% of extractives containing material.

6.3.2 Temperature

Pyrolysis oils exhibit considerable changes in their chemical composition with time and temperature. Particularly heating rate, temperature, reaction heat, cooling and heat capacity affect abundantly transformation of biomass into pyrolysis products /33/. The inner part of bigger particles warm up slower than their surface and hence outer layer is soon covered by char layer. As the temperature increases the amounts of oxygen and solid residual and the relative amount of carbon to hydrogen raise. This way pyrolysis occurring at a higher temperature results in more tar containing high levels of benzopyrene, polycyclic aromatic hydrocarbons and other gaseous compounds /34/. On the other hand, with lower temperatures or slow heating rates char production is predominant /35/. The higher temperature is adjusted, the greater is secretion of pyrolysis oil, but formation of char will be declined. For fast pyrolysis, the lowest temperature limit of wood decomposition is about 435 °C for producing sufficient liquid yields: at least 50% with low reaction times /27/. Thereby longer residence time decreases yield of oil fractions with temperature, even if it has been demonstrated that residence had only little influence on the formation of certain products /36/. Ordinarily, the maximum yield is obtained at the temperature scale from 500 to 520 °C for most wood biomass species. The detailed pyrolysis reactions of lignocellulosic material occurring at different temperatures are described in Table 1 /9,25/.
Table 1. Pyrolysis reactions at different temperatures /9,25/

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Reactions</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 300 °C</td>
<td>• Free radical initiation</td>
<td>• Carbonyl and carboxyl compounds</td>
</tr>
<tr>
<td></td>
<td>• Elimination of water and depolymerisation</td>
<td>• CO and CO\textsubscript{2} and a charred residue</td>
</tr>
<tr>
<td>300-450 °C</td>
<td>• Breaking of glycosidic linkages of polysaccharide</td>
<td>• Mixture of levoglucosan, anhydrides and oligosaccharides mostly in the form of a tar fraction</td>
</tr>
<tr>
<td>450–500 °C</td>
<td>• Dehydration, rearrangement and fission of sugar units</td>
<td>• Carbonyl compounds such as acetaldehyde, glyoxal and acrolein which evaporate easily</td>
</tr>
<tr>
<td>Above 500 °C</td>
<td>• A mixture of all above processes</td>
<td>• A mixture of all above products</td>
</tr>
<tr>
<td>Condensation</td>
<td>• Unsaturated products condense and cleave to the char</td>
<td>• A highly reactive char residue containing trapped free radicals</td>
</tr>
</tbody>
</table>

6.3.3 Pressure

Hydrogen pressure effects on product yields in thermal conversion /37,38/. By increasing the pressure a remarkable increase (even 30 wt-% of dry feed) in lighter oil fractions can be obtained. At the same time amount of char decreases significantly. While studying the effect of pressure on tar hydropyrolysis Güell et al. /38/ reported that increasing pressure (>1 bar) does not particularly diminish tar yield from pine at 400 °C, but with higher pressures and temperatures formation of volatiles (methane) is more effective.
Adjaye et al. /39/ have found that pyrolysis liquid produced from the high-pressure liquefaction of aspen poplar produces a more complex mixture of acids, alcohols, aldehydes, ketones, aromatic and aliphatic hydrocarbons, furans, ethers and phenols. Also Elliott /33/ came to similar results using high pressures, as their liquefaction products had a very complex aromatic and viscous nature. His high pressure liquefaction products exhibited higher boiling point and limited water solubility than the low pressure ones, which resulted from the oxygenated and aromatic character of the substances.

6.3.4 Catalysts

Even little amounts of inorganic substances may influence on thermal behaviour of cellulose in pyrolysis conditions and interfere the process /41,42/. For example Meier /41/ has optimised process parameters of semi-continuous catalytic hydropyrolysis of lignin. His experiments proved that using a mixture of nickel oxide and chromium oxide additives supported on aluminium or silicon oxide as catalyst in high pressured conditions, higher amount of phenols is generated. At the same time the H/C ratio was seen to raise notable. Although the composition of these high-value phenols is simpler than without a catalytic treatment. As aromatic compounds are desired, the H/C ratio is shown to be a useful indicator of the aromatic character of the product. Saturation of the aromatic components under pyrolysis conditions has a strong effect on the octane and heating value of the product.

Roy et al. /32/ have made catalytic hydropyrolysis in batch and semicontinuous reactors to evaluate, how the different catalyst concentrations affected on yield and properties of the generated oils. As more quantities of catalyst were added, the oxygen content of oil substances reduced by 10 %, the average molecular mass decreased and high molecules become middle-sized. The composition of the oils was simpler and higher amounts of lignin-based monophenols were obtained meaning the improved physical properties and feasibility of the oil.
Similar kind of experiences and results have been acquired in another research /43/, in which the liquefaction process was carried out by palladium mediated hydropyrolysis as far as oil yields from lignin, containing to some extent woody material, increased. The formation of solid char in turn diminished. The results of iron-based liquefaction process (atmospheric pressure) have also been promising, since the oil yield increased of 1.5 times /44/.

For this reason characteristics of hydropyrolysis oils depend on concentration of catalysts and degradation rate into lignin products, although the quality, chemical composition and yield of charcoal varies according to feedstock.

7 THERMOCHEMICAL DEGRADATION OF WOOD CONSTITUENTS

As a result of heating, wood decomposes into char, pyrolysis oil and gases. Compounds generated in pyrolysis are merely similar as in the original wood or organic biomass, although their shares are different. Wood material starts to lose mechanical strength at temperatures reaching above 100 °C, when intramolecular and intermolecular linkages slightly break up /45/. As soon as temperature passes 200 °C polymer construction of cellulose goes through a smaller metamorphosis by generating tar and flammable evaporating compounds.

Between 200 and 280 °C endothermic dehydration reactions become frequent on wood surface /46/. The reactions begin with evaporation of water and result in carbon monoxide, carbon dioxide, formic acid, acetic acid and glyoxal as primary products. At temperature zones from 280 to 500 °C reactions become exothermic and heat energy is released from wood, while temperature inside the reactor raises rapidly.
Combustion of wood yields gas (carbon monoxide and carbon dioxide), formaldehyde, formic acid and acetic acid, methanol and after deliberation of hydrogen also some charcoal. Harmful secondary reactions, which generate plenty of charcoal, become dominant whenever temperature exceeds 500 °C.

At normal pressure, degradation of wood starts with evaporation of free water from the surface. Murwanashyaka et al. /47/ have noticed, that degradation of wood and biooil formation activate at 275–350 °C, because relatively higher proportions of phenols (4.9 % of dry wood) were detected there.

### 7.1 Cellulose

The destructive reaction of cellulose begins at temperatures lower than 252 °C and is characterised by a decreasing degree of polymerisation and mechanical strength. With in a respect to pyrolysis, its polymer structure starts subsequently to disperse from random sites in the chain. Later on, cellulose-containing wood material breaks up in pyrolysis circumstances into three primary products, which are volatile small-molecular-mass compounds (e.g., methanol, carbon monoxide, carbon dioxide and acetaldehyde), tars and coal /48,49/. When the wood material is heated, glycosidic bonds between glucose units commence to break at the same time with inter- and intramolecular hydrogen bonds /45/. Degradation proceeds through three types of reactions competing with one another and their frequency varies according to temperature scale, heating rate and crystallinity of molecular cellulose /42/.

There are many theories explaining the process of thermal depolymerisation of cellulose. The two foremost depolymerisation mechanisms are decay of cellulose molecule by the homolytic process with the formation of free radicals or by the heterolytic process with the formation of intermediate carbonium ions and anhydrosaccharides /44/.
Lomax et al. /50/ have confirmed by mass-spectrometric techniques that under rapid pyrolysis cellulose chains tend to be unstable and to undergo ring cleavage through three competitive mechanisms. The prevalent decomposing mechanisms are: 1) transglycosylation 2) cycloconversion and 3) E1-elimination. Cellulose degradates to various $\beta$-(1→4) linked oligosaccharides, which contain the glycosidically bound 1,6-anhydroglycosyl or ethanal structures that arise from the top C_1 of the glucopyranose ring /45/.

Other popular concepts describing formation mechanism of small molecules from cellulose are homolytic fragmentation pathways through radical intermediates, reverse aldol reactions, heterolytic involving cathionic or anionic intermediates and Diels-Adler aldolisation reactions such as cycloconversion of glucopyranose ring to three different glucoaldehydes /51/. Hydroxyacetaldehyde developed in aldolisation is the second most common pyrolysate of cellulose. Reversal Diels-Adler reaction often signifies the rearrangement of double bonds and the formation of dienes, alkenes or carbonyl compounds from cyclic structures. The decomposition of cellulose is illustrated in Figures 12 and 13 /45,52/, and the fragmentation pathways in Figure 14 /49/.

Major component of tar fraction is levoglucosan, i.e. 1,6-anhydro-$\beta$-D-glucopyranose (4 wt-% of softwood). Using low pyrolysis temperatures or slow heating, dehydration is more likely reaction compared to depolymerisation. But still, whenever temperature rises significantly, more levoglucosan is obtained and the yield grows up to 60 wt-% of the dry solid wood /1,52/. Along with anhydrosugars, decomposition of cellulose generates high concentrations of hydroxylacetaldehyde (from oxidation) and small-molecular-mass compounds such as carbonyls and furans.

Synthesis of levoglucosan proceeds through depolymerisation that involves the intramolecular transfer of the chain. In practice, inside the cellulose molecule occurs displacement of the C_1-O–glycosidic linkage by nucleophilic S_n2 reaction with the C_4 oxygen within the same unit, i.e. the homolytic breaking of the 1,4-glycosidic bond between C_1 atom and oxygens O_4,O_6.
The C₆ hydroxyl is then able to attack C₁ by cationic addition reaction, displacing a C₁-C₂ bridge and forming a bridge between C₁-C₆ /46/.

Splitting up of the polymer of cellulose structure is more effective whenever acids, bases, water or oxygen are present, because oxygen, for example, is able to intrude on the amorphous region of the molecule. Under 300 °C fibre structure of cellulose begins to transform due to contribution of polymerisation, dehydration and decarboxylation reactions. It subsequently loses mechanical strength and provides, among others, char and carbon monoxide /46/. By raising pyrolysis temperature above 300 °C, decomposition of cellulose produces mostly tar and gaseous components through pathways which were introduced before.

Figure 12. Mechanism of the fast thermal degradation of cellulose /52/. 
Figure 13. Thermal degradation of cellulose via a) transglycosylation, b) (2+2+2) cycloconversion pathway and c) E1- elimination pathway /45/.

Figure 14. Thermal decomposition mechanism of cellulose /49/. The main reaction pathways are decarbonylation and depolymerisation yielding principally levoglucosan and other anhydrosugars.
7.2 Hemicelluloses

Hemicelluloses are thermally the least instable components of wood and evolve more non-combustible gases and less tar /45,48,53/. Most hemicelluloses do not yield significant amounts of levoglucosan but instead levoglucosenone. Much of the acetic acid liberated from wood pyrolysis is attributed to deacetylation of the hemicelluloses. Degradation and dehydration reactions of hemicelluloses are most effective at temperatures between 200 and 260 °C. At 400 °C the most valuable product is levoglucosenone, but as far as temperature exceeds 400 °C notable proportions of anhydrosugar derivatives of D-glucose, D-mannose and D-galactose are formed. At higher temperatures beginning from 800 °C there are some residuals of aliphatic hydrocarbons, alkyl benzenes and phenolic and polyphenonolic hydrocarbons.

Under thermal pyrolysis conditions softwood hemicelluloses such as glucomannans release compounds which are classified as follows: 1) small-molecular-weight volatile compounds, i.e. carbon monoxide, carbon dioxide, formic acid and acetic acid, 2) anhydroglucopyranoses, i.e. levoglucosan, 3) other anhydroglucoses, i.e. 1,6-anhydro-β-D-glucofuranose, 4) other anhydrohexoses, i.e. 1,6-anhydro-β-D-mannopyranose 5) levoglucosenone, i.e. 1,6-anhydro-3,4-dideoxy-β-D-glycero-hex-1-enopyranos-2-ulose 6) furans, i.e. 2-furaldehyde and other similar compounds. As compared to cellulose, the formation of tar from decomposing hemicelluloses occurs only in a minor scale, whereas tar formation of gaseous products is active /45,48/.

Hardwood hemicelluloses are rich in xylan but contain a small amount of glucomannan /10/. Softwood hemicelluloses comprises a small amount of xylan and are rich of galactoglucomannans. Xylan is the least thermally stable of hemicelluloses, because pentosans are most susceptible to hydrolysis and dehydration reactions.
### 7.3 Lignin

During pyrolysis lignin has a tendency to swell and degrade into smaller fractions in the temperature range 200-600 °C /54/. The reactions of lignin are then very rapid, because of the pressure and heat transfer on the molecules. Gradually, the structure of lignin undergoes softening, evaporation of volatiles, melting and decomposition during free radical reactions.

Due to cleavage of ether and carbon-carbon bonds, lignin splits up to smaller monomeric phenols, methyl ethers and alkyl derivatives such as o-cresols, guaiacols and vanillin and also to numerous oligomers, whose sizes vary from small-weight-molecules (MW less than 500 Da) to heavy molecules (MW more than 1000 Da) /53/. According to the used pressure, the thermal degradation of lignin structure produces also a lot of char. The structure of lignin has been investigated using mass spectrometry in order to determine various pyrolytic stages. Dehydration reactions around 200 °C are primarily responsible for the thermal degradation of lignin. Between 150 and 300 °C, the cleavage of α and β aryl-alkyl-ether linkages occurs. Around 300 °C aliphatic side chains begin to split off from the aromatic ring. Finally, the carbon-carbon linkages between the precursor units are cleaved at 370-400 °C.

Comparing the thermal behaviour of lignin to that of carbohydrates, Bridgwater et al. /19/ observed that decomposition of lignin needs a broader temperature scale than the previous ones and produces more char. Thermal degradation of lignin is an exothermic reaction with peaks occurring between 225 and 450 °C. Scholze et al. /45/ have proved that main products from softwood lignin pyrolysis are guaiacyls comparing to 90 % of the total products, whereas in hardwood liquids syringyls are the most common products (60–80 %). The degradation pathway of lignin is described in Figure 15.
Figure 15. Degradation pathways of lignin on heating through the cleavage of ether bonds and formation of radicals /45/.

7.4 Extractives

Extractives are not included in structural components of wood, and many of them undergo structural transformations and evaporate during heating /45,55/. In turn, at low temperatures many non-structural components remain almost unchanged.
Roy et al. /32/ have found that fatty and resin acids whenever linked with aromatic or steroid structures, withstand better temperatures between 200-550 °C than many other extractives, though fatty acids existed in their free forms (e.g., linoleic acid and oleic acid). During heating the acids liberate from glyceridic structures and decompose into carboxylic acids, hydrocarbons or olefins. Degradation of aromatic extractives, such as lignans, remind of lignin complexes.

Abbot et al. /56/ have investigated the thermal behaviour of specific steroids (cholestanone) during heating and recognised the cleavage of carbon-carbon bonds in the ring system and dehydrogenation to occur, but also more water was formed. Expecting that oxygen is generated in the reactors, six-membered rings containing one or two double bonds undergo dehydrogenation and rearrangement to form aromatic derivatives. McGraw et al. /55/ have noticed this when studying formation of \( p \)-cymene and thymol structures from \( \alpha \)-terpinene and limonene by GC/MS and NMR. The second reaction observed was the oxidative cleavage of carbon-carbon double bonds, which caused the formation of two keto aldehydes from \( \alpha \)-terpinene. The third common reaction in thermal conditions was epoxide formation.

### 8 PYROLYSIS PRODUCTS

Pyrolysis products can be grouped as volatile (boiling point under 100 °C), evaporating volatile and weakly volatile substances (boiling point above 100 °C) /44,57,58/. The first mentioned group comprises mainly alcohols (methanol), aldehydes (formaldehyde), ketones (acetone), ethers (dimethyl ether) and esters (methyl acetate and ethyl acetate). The second group is formed by atseotropic gas mixtures. The third group consists of alcohols (allyl and furfuryl alcohols), aldehydes (furfural based compounds) and some phenols.
Generally, the pyrolysis products are classified into a liquid phase (oil, moisture from feedstock and pyrolytical water), a solid phase (char coal) and non-condensable gas phase /59/. The accurate product distribution is shown in Figure 16. The compound yields, expressed as percents of the total liquid mass in regard to reaction temperature, are shown in Figure 17 /60/.

\[ \begin{align*}
\text{Condensate} & \quad \text{Floating oils} \\
\text{Oil-water} & \quad \text{Sedimental oil} \\
\text{Volatile products} & \quad \text{Vapours with vapour} \\
& \quad (\text{homo- and heteroazeotropic mixtures}) \\
\text{Soluble oil} & \quad \text{Oils with vapour} \\
\text{Non-volatile products} & \quad (t \text{ boiling} > 100 \text{ C}) \\
\text{Ether-soluble products} & \quad \text{Ether-insoluble products} \\
\text{Neutral substances} & \quad \text{Phenols} \\
& \quad \text{Carboxylic acids}
\end{align*} \]

*Figure* 16. Distribution of liquid products of pyrolysis /59/. Condensed degradation products yield sedimental and floating oils as well as liquid consisting of oil and water. The latter product can be fractionated and refined to commercial feedstock by means of solvent extraction.
8.1 Pyrolysis oil

Wood pyrolysis produces a dark brown and viscous liquid, which may be used as a fuel or a chemical feedstock /60/. The formed pyrolysis oil consists of different sized molecules as a result of fragmentation reactions of cellulose, hemicelluloses and lignin polymers. However, the oils are highly oxygenated, viscous, corrosive, acidic, relatively unstable and chemically very complex. The direct substitution of wood-derived pyrolysis oil for fossil fuels or chemical feedstock may therefore be reduced.

8.1.1 Chemical composition

There exist variable data on pyrolysis oils according to the process type and conditions, but some prevailing compound groups of wood pyrolysis oils are summarised in Table 2 /44/. This table informs that the oils comprise mainly water, carboxylic acids, carbohydrates and lignin-derived substances. Comparing the identical wood materials can be noticed that higher moisture content of the feed increases water content in the end product but decreases the yields of other substances.
8.1.2 Top and bottom phases

Pyrolysis oil usually forms only a single phase, in which solid content is affected by feedstock, pyrolysis process and collection method of the product /61-63/. Pyrolysis oils have limited miscibility with water so that phase separation takes place when water content of pyrolysis oil exceeds 35-40 %. Increasing water content results in an increasing pH value but simultaneously in low heating value and viscosity.

Proportion of the top phase in the forest residue pyrolysis oil may reach up to 20 wt-% of dry wood and the quantity of bottom phase varies between 80-90 % /63/. The volume of the top phase depends on the composition of raw material and process conditions. Major compound groups belonging to the top phase are degradation products of lignin (30 %) and extractives. Moreover, the phase is made of water soluble compounds, i.e. water, sugars and carboxylic acids (40 wt-%). The extractives, which represent often in the forest residue pyrolysis oil, are resin acids, fatty alcohols, fatty acids, triglycerides and hydroxy carboxylic acids.
Pakdel et al. /57/ have found by GC/MS that the forest residue pyrolysis oil contains the similar unsaturated or saturated fatty acids which are typical for conifers: palmitic acid (C_{16}), stearic acid (C_{18:0}), oleic acid (C_{18:1}), linoleic acid (C_{18:2}) and linolenic acid (C_{18:3}). Furthermore, the most noteworthy resin acids are abietic acid, pimaric acid, levopimaric, palustic, dehydroabietic and neoabietic acids. Chemical composition of the bottom phase is quite similar between bark-free and forest residue pyrolysis liquids.

In the forest residue pyrolysis liquid, separation of phases is caused by variable oxygen content and high contents of water and extractives /6/. The newly formed top phase possesses lower polarity but higher viscosity and heat value than the bottom phase. The biggest difference between the top and bottom phases is the chemical composition, since top phase contains more phenolic compounds, i.e. high-molecular-mass lignin derivatives and water-insoluble extractives (35-50 %).

During aging chemical reactions such as esterification occur and change the polarity of the pyrolysis liquid components /64/. Due to esterification, highly polar organic acid and alcohol molecules are converted to esters with fairly low polarity. The formation of acetals increases the water content through hydration, while the polarity of organic matter decreases and thereby phase partition is induced. It is also supposed that joining of larger molecules improves their solubility and leads to degradation of a light, highly polar aqueous phase and a less polar heavy organic phase. In the course of time, the molecule groups have a tendency to form micelles. The low-polar molecules such as aromatics may attach to char particles on the top and expand as an emulsion.

Artificially phase separation can be achieved by adding water to the pyrolysis liquid when it separates into an aqueous and an organic phase /64,65/. The latter is more brownish and contains high-molecular-mass compounds of decomposed lignin and some extractives. Piskorz et al. /31/ have deduced this from the $^{13}$C NMR spectra in which signals of pyrolytic lignin and milled wood lignin reminds of each other, though units of pyrolytic lignin are more decomposed.

8.2 Stability properties
Wood-derived pyrolysis liquids are physically and chemically instable in time and depending on storage conditions /39,65,66/. Viscosity of these biooils varies from medium to high, but the liquids are also corrosive, contain plenty of oxygen and alter for changes in chemical composition. Along with the changes in the composition, there occurs continuous polyaddition, polymerisation and condensation reactions since carbon-carbon bonds in aldehydes, ketones and carboxyl acids activate. It has been noticed that the viscosity of pyrolysis oils increase if the concentration of high-molecular-mass compounds increases. Due to raised viscosity, the flow characteristics of biooils weaken. The longer storage time of oil is, the lower are total concentrations of oxygenates and hydrocarbon fractions. At the same time, the total concentrations of aromatic hydrocarbons and phenols increase while the aldehydes and ketones formation decreases. Also the presence of alkali has been shown to facilitate formation of liquids with lower oxygen content and better stability.

Pyrolysis liquefaction products become instable when temperature exceeds 50 °C /64-66/. Instability of oils is mainly caused by easily volatile and degradable carbonyl and carboxyl compounds with low boiling points, which are exposed to temperature and pH by resulting high oxygen content in pyrolysis. Instability may be seen as evaporation of volatile compounds from biooil into air, increased viscosity, oil separation into two phases and as accelerated depolymerisation. With respect to the temperature, oil subsequently becomes thicker, while increased water content (30 wt-% of dry solids) separates heavy water-insoluble phase and water-soluble phase from each other. As the temperature rise the heavy lignin containing phase becomes a gum-like substance and forms a solid residue.
During storage, there occur some important chemical reactions, which are caused by carbonyls and impair the oil quality /64/:

- Organic acids form esters and water with alcohols.
- Aldehydes and water form hydrates.
- Aldehydes and alcohols form hemiacetals, or acetals and water.
- Aldehydes form oligomers and resins.
- Unsaturated compounds form polyolefins.
- Air oxidation produces more acids and reactive peroxides that catalyse the polymerisation of unsaturated compounds.

9 CATALYTIC UPGRADEING

Thermal liquefaction products can be utilised directly in energy applications, but might also be refined to chemical feedstock or more feasible liquid hydrocarbon fuels by catalytic upgrading /67/. The upgrading of pyrolytic oils is a necessary process before they can be used as a regular fuel and it involves the removal of oxygen. Accordingly, upgrading diminishes the undesirable properties, instability and high viscosity, which are induced by phenolic and ether (methoxy) groups. It has been proposed to convert phenols into aryl ethers via catalytic processes. Currently exist mainly two upgrading techniques comprising 1) modified conventional hydrotreating to naphtha-like product and 2) zeolite cracking to a highly aromatic product. The first method is a typical catalytic hydrotreating with hydrogen or hydrogen and carbon monoxide under high pressure or in the presence of hydrogen donor solvents. Alternatively, upgrading can be carried out using cracking catalysts such as zeolite, zinc dioxide, silica-alumina and molecular sieves. The procedure occurs at atmospheric pressure in the absence of hydrogen. The products obtained from the reactions depend on the characteristics of the catalyst used in upgrading.
9.1 Hydrotreating

Hydrotreatment is a two stage process, which begins with an initial stabilisation at 250-275 °C followed by conventional catalytic hydrotreating at 350 – 400 °C using high pressures of 70 to 200 bars /67-69/. Some successful results have been obtained with cobalt, molybdenum and other hydrotreating catalysts including Ni, Co and Mo in oxide and sulphite since oxygen content was greatly reduced and simultaneously the density of the reaction products decreased. On the other hand, in the case of fast pyrolysis lignin, a non-isothermal hydrotreating with sulfided Co-Mo catalyst was seen to yield 61 % to 64 % of light organic liquids /68/.

Hydrotreatment comprises of reactions like hydrogenation, deoxygenation and reforming /69/. For example, if single ring phenolics are present in the wood pyrolysis oils they can be upgraded through deoxygenation to hydrocarbons in the gasoline and diesel with certain boiling point ranges. Higher-molecular-weight extractives like polycyclic aromatic compounds must also be hydrocracked by partial ring saturation. The major concern in hydrotreating has been the maintenance of the aromatic character of the biomass oil in order to minimise hydrogen consumption and to produce a higher octane gasoline blending stock.

9.2 Zeolites and other catalysts

When upgrading of the pyrolysis liquid is carried out with acidic ZSM-5 zeolite catalysts the liquid fraction consists of two easily separable layers /69-71/: organic phase and aqueous phase. It has been suggested that acidic zeolites induce partial cracking of the heavy organics to light organics and partially cumulate on the catalyst top where they act as a coke precursors. The light oxygenated organics are further cracked, deoxygenated, decarboxylated and decarbonylated. Through carbonium ion mechanism, oligomerisation of the cracked fragments being followed by alkylation, isomerisation, cyclisation and aromatisation together produce a mixture of light aliphatic (C₁–C₆) and aromatic
(C₆–C₁₀) hydrocarbons /70,71/. When the H-Y zeolite and silica–alumina are used, a single phase is formed. It consists of aliphatic hydrocarbons of which the organic compounds are either dispersed or dissolved in water. The oxygen in the oxygenated compounds of wood pyrolysis oils is primarily converted to CO, CO₂ and H₂O as far as the yield of hydrocarbons tend to remain low because of the high yields of char, coke and tar.

10 FRACTIONATION METHODS OF PYROLYSIS OILS

Fractionation facilitates separation of pyrolysis oil into groups of compounds, which are possible to refine or analyse individually by the means of modern quantitative techniques. Fractionation usually takes places by liquid extraction and chemical adsorption. Size exclusion chromatography and ultra filtration have been exploited as well. The purpose of using fractionation methods for pyrolysis oils is mainly to isolate the high value aromatic compounds from the water-soluble bottom phase.

In practise, fractionation of the top phase could begin with extracting the pyrolysis oil with water into water-soluble and water-insoluble fractions /37/. Also liquid chromatography could be an efficient technique for the separation of the water-insoluble and phenolic-rich top phase, but high consumption of solvents and regeneration of adsorbents render the procedure tedious and uneconomic. There exist two feasible methods to isolate water-insoluble substances such as lignin and extractives from water-soluble carbohydrates: 1) the addition of water to the oil and 2) slow addition of pyrolysis liquid with stirring into distilled water in 1:10 ratio. Especially the second method is advocated for analytical studies, since blending pyrolysis oil with water leads to the precipitation of lignin-like hydrophobic components. The water-insoluble fraction might be then isolated by filtration (0.1 µm filters) while the remaining water-soluble fraction is discharged and used for other purposes.
After filtration and stirring for couple of hours desired water-insoluble fraction is washed with water, dried in a vacuum oven (<40 °C) overnight and then weighed after cooling in a desiccator. During vacuum drying the biggest part of water residue must evaporate from water-insoluble fraction.

Figure 18 shows how the fractionation of water-insoluble compounds could proceed in the case of wood residue pyrolysis oils. The methods are developed by Scholze et al. /72/ and Holmbom et al. /8/.

**Figure 18.** Fractionation scheme to isolate the top phase from wood pyrolysis oils /8,72/.
10.1 Technical principles

Complexity of pyrolysis oils makes their analysis a demanding task so that careful sample preparation is usually needed. Pre-fractionation is mostly necessary, although it includes many procedures and it is tedious. After separation, oil fractions are suitable for analysis by chromatographic (GC/MS, Py-GC/MS) or spectroscopic techniques, where the results from the top phase are compared with CHN data on whole oil and lignin model compounds.

Generally, pyrolysis liquids are at first separated to water soluble and water-insoluble or other kind of fractions according to polarity. The following steps depend on the feedstock, wood species and part of wood used in pyrolysis. For example, the forest residue top fraction contains more extractives than that of bark-free tree. For this reason, extraction solvents and pH must be suitable for lignin pyrolysates as well as for extractives. A difficulties associated with extraction pH is that pyrolysed resin and fatty acids may become bound to lignin residues at acidic pH. The conditions must be alkaline. While investigating dissolved and colloidal wood components in kraft pulp effluents, particular researchers have extracted water-insolubles using, e.g., methyl-tert-butyl ether (MTBE) as solvent. In the extraction lipophilic extractives and lignans remain with MTBE on the top while lignin components remain in water phase on the bottom /8/. Dissolved lignin and lignin-like substances were subsequently quantified from the UV absorption region at 280 nm of the extracted water sample, whereas lipophilic extractives and lignan were determined by GC.

At first pyrolysis oils have been analysed by simple solvation experiments and fractionating the samples with liquid extractions using solvents in different polarities /72–74/. Fractions obtained from extraction have been distinguished to acidic, neutral and basic substances. A remarkable breakthrough in oil analyses was achieved when GC/MS was introduced as far as the measurements could be carried out quantitatively and repetitively.
Chromatographic methods, focusing especially on gas chromatography and liquid chromatography are feasible methods to measure oil fractions and to determine the occurred variables during storage. Infrared spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR) in turn are suitable for whole oil analyses. Fourier transform infrared spectroscopy (FTIR) is a practical tool to determine concentrations of hydroxyl groups and procentual proportions of oxygen in pyrolysis oil. Naturally, aromaticity or structural parameters of the oil samples could also be determined by NMR.

10.2 Homogenisation and sampling

Homogeneity of pyrolysis oils is the most critical factor for an accurate analysis. The pyrolysis liquid samples are usually homogenised by mixing, but a fresh single-phase sample with lower viscosity remains homogenous, according to storage temperature and other conditions up to half a year without any mixing /66/. In the course of time, solid particles, however, sink to the bottom. If necessary, char-like solid matter can be filtered or removed by centrifugation /73/. For an aged phase-separated pyrolysis oil the only possibility is homogenisation by adding polar solvents such as water or alcohol, i.e. ethanol and methanol.

10.3 Extraction

Liquid-liquid extraction (LLE) is the traditional, but a laborious sample separation and upgrading method, which is carried out manually in the funnel or as continuous process by using agitable steam extractor. Continuous extraction is recommended for soluble and small sample quantities in order to avoid contamination of the sample, carcinogenic solvents or to find an efficient extraction technique. However, formation of a dispersed emulsion, volatile substances or reactions of lignin-originated aromatic “solvents” (phenols, benzene) may disturb the formation of equilibrium in LLE extraction. Manual
extraction instead is suitable for water-insoluble samples with a large volume. LLE tower includes a thermal bath, extraction chambers and a condenser.

Carbohydrate-free lignin and lignin originated phenolic compounds can be fractionated efficiently extracting the oil sample with dioxane-water solution (100:4), diluting with pyridine-acetic acid-water solution (9:1:4), and re-extracting the samples twice with chloroform /75/. Phenolic compounds have also been extracted with basic aqueous solutions of 8–15 % by weight of NaOH in soluble polar organic solvent media such as ethyl acetate and methyl isobutyl ketone. Hyötyläinen et al. /76/ have succeeded to extract phenols in pine pyrolysis oil by microporous membrane LLE. The oil was diluted with tetrahydrofuran and dichloromethane (0.1 % w/w), filtrated and extracted through a dichloromethane-wetted PTFE membrane. The extract was then purified by solid phase extraction using water-methanol as an eluent (80:20 % v/v).

However, many practical applications include the extraction of phenols from pyrolysis oil such as the separation of phenols in polar and non-polar phases and precipitation between the organic phases. High-molecular-mass extractives are insoluble in water, but dissolve in solvents, i.e. methanol, THF and n-hexane.

An interesting point of view concerning extraction was reported by Yokoi et al. /77/ since they had succeeded to analyse phenolic acids and fatty acids replacing complicated pre-treatments including solvent extraction by Py-GC in the presence of organic alkalis like tetramethylammonium acetate.

Soxhlet extraction device can be modified for the sample in the proportion of the phase sample, though some standard instructions recommend extraction of 10 g of solid sample in the extractors using about 250 ml of solvent /78/. In the case of lignin, lipophilic resins including wood soaps (alkaline salts of fatty and resin acids), acetone-water solvent (9:1) has turned out effective as far as it is at the same time less harmful and easy to evaporate from sample solutions, although acetone may extract unwanted hydrophilic compounds like sugars. The second practical pre-treatment method is to handle water-soluble sample with diethylether (1:1 v/v) after water fractionation (1:1 v/v), pyrolyse and analyse the
obtained two fractions along with water-insoluble fraction by Py-GC/MS at the temperatures from 400 to 700 °C /37,58/. Water-insoluble fraction can be determined by IR and CHN.

In the case of minority compounds, like extractives, the separation of water-insoluble compounds from aspen poplar (*Populus tremuloides*) has been carried out according to the standards ASTM D 1105-56 or TAPPI T 12 M-45, but the instructions are also suitable for other wood species /79/. The distillation procedures have occurred in a Soxhlet apparatus with pre-distilled ethanol-benzene (1:2 v/v) for 4 hours and followed by ethanol extraction. The wood samples were then extracted with distilled water at 100 °C for 1 hour.

### 10.4 Distillation

The physical and chemical properties of wood-derived pyrolysis liquids such as complex composition and thermal instability make their distillation less unsuitable and thereby extraction techniques are preferred. However, in industry distillation is the most common physical separation technique of petroleum components, which is performed as atmospheric or vacuum distillation /29/. The products refined by distillation are, among others, naphtha, gasoline, kerosene, diesel/heating oil, light gas oils and lubricating oil.

Each compound of pyrolysis liquid has a specific steam pressure, which is in the respect to separate bonding strengths, particle size and particle mass. The phenomena, in which steam pressure of the compounds differ according to used temperatures, is utilised in their separation by steam distillation. Typically, steam or atmospheric distillation is used as a tool to separate a small amount of a volatile fraction from a large amount of non-volatile phenols or other heat-sensitive materials.

Steam distillation is important in petrochemical industry, where it is applied during steam flooding of light oils /47/. Saturated steam in contact with pyrolysis liquid provides heat to the oil, decreasing the viscosity and causing the
vaporization of a portion of the oil into the vapor phase, which will be subsequently transferred with steam. The light phenol components, for instance, may thereby be neutralised by mild NaOH and then extracted with dichloromethane. Murwanashyaka et al. have carried out the distillation of pyrolysis liquid by using steam (100 °C) and flow rate of 5 ml/min for water. During distillation the oil sample was held in 130 °C oil bath, while distillate was collected to a glass container. Then water-soluble phase was extracted with an equal volume (1:1) of ethyl acetate and again with a half volume of ethyl acetate. Solvate was evaporated and oils were combined with the oil distillate in a glass bottle.

As far as the desired top phase of pyrolysis liquid includes volatile substances such as benzene and phenols, vacuum distillation may be preferred. Distillation facilitates fractionation of such compounds, which otherwise would react at atmospheric pressure or degrade below their characteristic boiling points. Vacuum is created by steam ejectors and it permits heavier hydrocarbon to vaporise from the liquid inter phase without thermal cracking below the normal boiling points.

11 ANALYSIS OF THE TOP PHASE

11.1 Stability and aging measurements of pyrolysis oils

Process development requires valid data on the physical and chemical properties of the pyrolysis oils /39,66,80/. The essential properties which are usually measured include: density, viscosity, pour point, cloud point, flash point, heating value, thermal and electrical conductivity, ignition temperature, solid content, carbon residue, ash content, particle size, lubricity and variation with temperature, time, exposure to air/oxygen and history. The information obtained from measurements are valuable in the handling, evaluation of transport units and sizing the process device, for instance in diesel engines, turbines and combustors.
The changes in the oil quality and composition are seen by comparing the samples stored in different conditions. The typical physical characteristics, which contribute to pyrolysis oil quality are listed in Tables 3 and 4.

Table 3. Physical characteristics of pyrolysis oil /66,80/

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>15 – 30 %</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.20</td>
</tr>
<tr>
<td>Elemental analysis, dry basis</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>56.4%</td>
</tr>
<tr>
<td>H</td>
<td>6.2%</td>
</tr>
<tr>
<td>O</td>
<td>37.3 % (by difference)</td>
</tr>
<tr>
<td>N</td>
<td>0.1%</td>
</tr>
<tr>
<td>Ash</td>
<td>0.1%</td>
</tr>
<tr>
<td>HHV as produced (depends on moisture)</td>
<td>16–19 MJ/kg</td>
</tr>
<tr>
<td>Viscosity (at 40 ºC and 25 % water)</td>
<td>40–100 cp</td>
</tr>
<tr>
<td>Solids (char)</td>
<td>0.5 %</td>
</tr>
<tr>
<td>Distillation</td>
<td>max. 50 % as liquid degrades</td>
</tr>
</tbody>
</table>

♦ Liquid fuel.
♦ Does not mix with hydrocarbon fuels.
♦ Heating value is about 40 wt-%% than fuel oil or diesel

♦ Not as stable as fossil fuels.
♦ Easy substitution for conventional fuels in boilers, engines and turbines.

Table 4 introduces effects of harmful oil properties and methods for modification. As can be seen, careful material selection or development and adjusting of the process operations may partially prevent interferences in the apparatus.
Table 4. Effects of biooil properties and methods for modification /67/

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Effect</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended char</td>
<td>Erosion, equipment blockage, high CO emissions</td>
<td>Filtration of vapour and liquid, char modification</td>
</tr>
<tr>
<td>Alkali metals</td>
<td>Deposition of solids in combustion and damage to turbines</td>
<td>Hot vapour filtration, feedstock pre-treatment</td>
</tr>
<tr>
<td>Low pH</td>
<td>Corrosion of vessels and pipework</td>
<td>Careful materials selection</td>
</tr>
<tr>
<td>Incompatibility</td>
<td>Destruction of seals and gaskets</td>
<td>Careful materials selection</td>
</tr>
<tr>
<td>Temperature</td>
<td>Decomposition on hot surfaces, adhesion of droplets on surfaces below 400 °C</td>
<td>Identification of problem and sufficient cooling facilities, avoiding hot surfaces</td>
</tr>
<tr>
<td>sensitivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High viscosity</td>
<td>High pressure drops can give higher cost equipment, leakage or rupture</td>
<td>Careful low temperature heating or water addition</td>
</tr>
<tr>
<td>Water content</td>
<td>Complex effect on viscosity, heating value, density, stability, pH, etc.</td>
<td>Problem identification, optimisation of the process</td>
</tr>
<tr>
<td>In-homogeneity</td>
<td>Layering or partial separation of phases, filtration problems</td>
<td>Process modification, changing the feedstock to low lignin, additives, controlling of water content</td>
</tr>
</tbody>
</table>

11.1.1 Density

Density of pyrolysis liquids are high, locating typically between 1.11-1.28 g/cm³ /7,66/. Although, the value may decrease in the top phase of aging liquid since water-soluble compounds have settled on the bottom.

Peacocke et al. /80/ have determined the density of unfiltered pyrolysis liquids using two water-calibrated 5 ml pycnometers at the temperatures from 25 to 70 °C. VTT has carried out the measurements according to the standard ASTM D 4052 by a digital density meter at 15 °C /63/.
11.1.2 Viscosity

Level of viscosity determines storage and handling conditions of the oil samples. It increases due long storage time and lower content of water by leading to instability /65,81,82/. In addition to water quantity, the level of viscosity is significantly dependent on the temperature and characteristics of the oil /63/. Usually the selected measuring techniques base on kinematic or dynamic viscosity as far as it is internal friction which hinders flowing of substances. Peacocke et al. /80/ have made the dynamic viscosity measurements at the temperatures reaching from 25 to 70 °C using a cylinder-shaped viscometer, which rotates in a fluid and converts the signals of mechanical movement to resistances. VTT instead has observed kinematic viscosity of oils by glass capillars and this method obeyed largely the standard ASTM D 445. Viscosity properties of pyrolysis oil resemble the behaviour of non-Newtonian liquids under atmospheric conditions.

11.1.3 Pour point

Pour point is defined as the lowest temperature (-23- -33°C) at which pyrolysis oil is still noticed to move or it can be pumped /66,83/. As mentioned before, raw pyrolysis oils are non-Newtonian and contain to some extent wax kind of substance, which can crystallise during processing or handling, achieving the grown viscosity by several orders of magnitude, and oil gelation. At lower temperatures crystals of wax may form impermeable cakes, which can block tubing and, eventually, lead into engine failure. The upper pour point limit recommended for fuels is about 600 cSt.

The measurement can be made using, for instance, the calorimetric standard method ASTM D 97-87, in which sample is preheated and cooled with a certain rate, and flowing is observed according to the temperature /81/. Another feasible option is to resort to X-ray diffraction method.
11.1.4 Heating value

Specific heat capacity of pyrolysis liquids depends mainly on elemental composition of raw material /66,81/. Because high water content reduces the heating value, they are reported as higher (HHV) and lower (LHV) ones. The difference between these two heating values is equal to the heat vaporisation from water formed by combustion of the fuel. HHV and LHV can be measured by a bomb calorimeter. Heating value of forest residue liquid ranges only up to 33 wt-%, since the water content increases and phases are separated. The value remains higher at the top phase.

11.1.5 Solubility

Pyrolysis oils have low solubility in water, but as temperature increases, the solubility improves /64/. When water content of pyrolysis oil exceeds the certain limit, the polar compounds segregate from non-polar ones to form micelles and may then adsorb on char particles. The insoluble phase in oil represents /66/: for forest residues and softwoods 32-35 wt-%, for hardwoods 34-35 wt-% and for straw 17-28 wt-%. The phase is largely made up of pyrolytic lignin, a smaller amount of lipophilic extractives, which are soluble in dichloromethane and neutral solvents, i.e. THF, n-hexane and toluene /84/. The biggest part of lignin is extractable and soluble in diethyl ether, whereas dichloromethane dissolves only the part of lignin with greater molecular mass. Water-soluble phase contains polar small molecular compounds such as anhydrosugars, aldehydes, ketones and carboxylic acids.

11.1.6 Water content

Since pyrolysis oils contain several volatile compounds, the water content is not appropriate to measure by any drying method which uses specific temperatures. Therefore, the water content is often determined by the Karl-Fischer titration /25, 66,81/. The Karl-Fischer solution contains sulphur dioxide and iodine, which react with water yielding sulphuric acid and hydrogen iodide.
The determined water content of wood pyrolysis liquids locates often between 16 - 32 wt-% according to wood species.

11.1.7 Solids content

The solid content refers to the heavy and insoluble material in the pyrolysis liquid, which does not dissolve in the organic solvents like ethanol, methanol and acetone /65,84/. The solid substance is collected by solvent wash and filtration (0.1-10 µm filter), which afterwards are dried and weighed. Oasmaa et al. /65,66/ have discovered that the procedure with a sample size of 1-3 g and a sample to solvent ratio of 1:100 produces repetitive and precise results.

11.1.8 Elemental analysis

Elemental analysis of carbon, hydrogen and nitrogen included in the pyrolysis oils are typically performed by a CHN-analyser /25,81/. Because of pyrolysis mechanism and feedstock used, the oxygen content in the oils may be very high. The content determines the chemical reactivity and stability properties of the oils, which have been described before. The equipment does not directly measure oxygen quantity. Oxygen quantities are calculated as a difference of carbon, hydrogen and nitrogen amounts from the total sample mass, paying attention for water content. If the water content in oil varies significantly, the elemental analysis is better to be done on a water free basis too.

11.2 Gas chromatography

Chromatographic techniques can be considered as a separation process involving mass transfer between stationary and gaseous mobile phases. Gas chromatography (GC) is the most common method to analyse pyrolysis liquids, where samples are injected to the column through split injector or on-column, as already separated groups of compounds, i.e. phenols, hydroxyl acids and
terpenoids /85/. Along with column, an important part of a GC device is a detector. To detect lignin-pyrolysis products a flame ionisation detector (FID) and a mass selective detector (MSD) can be exploited /86/. Fractionation of oil components for GC detection is possible to carry out with solvent or solid extraction. So far, GC has facilitated separation of more than 200 constituents from pyrolysis liquids, since it provides quantitative data and possesses high resolution. However, whole oil samples are impossible to drive with a GC device, because of their wide-extended molecular distribution and different polarity. There are also some weakly volatile, thermally instable or obstructing substances in top phase samples, demanding derivatisation or parallel measurement by NMR, FTIR or HPLC.

In order to analyse weakly volatile compounds of top phase by connected GC/MSD, they must be derivatised. One of the derivatisation methods is silylation of non-pyrolysed lignin, terpenes and alcohols as trimethylsilyl ethers using a combination of the reagents $N,O$-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS), and heating for 20 minutes at 70 °C /78/. Lignin may require a derivatisation by acidolysis with weak HCl in dioxane-water (9:1 v/v) or alternatively with acetyl bromide followed by dissolvation in dioxane / acetic acid / water solution (5:4:1 v/v/v) /14,87/.

Sipilä et al. /58/ have performed Py-GC/MSD analysis for water-insoluble fractions in a quartz tube, at temperatures 400, 500, 600 and 700 °C by using silica columns and helium as the carrier gas to avoid explosion. Their results of diethyl ether-insoluble and water-insoluble fractions proved that hardwood pyrolysis oils comprise more water-insoluble (lignin-derived) substance than pine and straw, respectively. It seems that remarkable part of pine pyrolysis oil is composed of ether-insolubles, which dissolve in water.

Bocchini et al. /88/ have made some other investigations with wheat lignin pyrolysis fragments using Py-GC/MSD, in which they compared the formed products with easily vaporising internal standards such as: 1,3,5-tri-tert-butyl benzene, 1,2,4-benzene tricarboxylic acid trimethyl ester and 1,3,5-
trimethoxybenzene. As external standards, vanillin-like phenolic compounds were used to calculate quantities. The results yielded large variety of substituted hydroxyphenyl, guaiacyl and syringyl compounds, which originate in different sites of the phenylpropanoid structure of lignin, and are also characteristic for wood lignocellulosic pyrolysis patterns.

Vasalos et al. /7/ have examined fragments of lignin pyrolysates by GC using alkylphenols and anisole as internal standards. Their aim was to design a pyrolysis process, which maximises the volume of phenolic liquids. The sample fractions extracted from the oil by \( n \)-hexane/toluene and analysed by GC were aromatic. The results of Vasalos et al. /7/ and some other research teams have indicated that phenolic fractions were brought about at 500 °C.

11.3 Liquid chromatography

High-performance liquid chromatography (HPLC) is a technique, which utilises a liquid phase to separate the components of a mixture. As a pre-treatment, the samples are first dissolved in a specific solvent and then forced to flow through a chromatographic column under high pressure. Separation of the compounds depends on the extent of interaction between the solute components and the stationary phase and the mechanism. One possible separation mechanism is adsorption, in which polar stationary phase retains the molecules with a similar charge by dipole- dipole interaction.

HPLC have also been used for simultaneous analysis of extractives in both size-exclusion (SE) and reversed-phase (RP) applications /89/. Wood resins have been separated successfully by applying SE technique. The analysis device was equipped with a cross-linked polystyrene resin column and tetrahydrofuran (THF) was used as a solvent, though some problems, resulted from overlapping of sterols with fatty acids, occur. HPLC- analysis of extractives can be carried out without derivatisation of weakly volatile substances, but still methylation is commonly performed improve the separation of fatty and resin acids. An advantage of HPLC is ability to detect easily evaporating or weak non-resistible
organic compounds, which may be lost in GC under thermal measurement conditions. Fractions provided by the combined GPC and HPLC equipment, are feasible for further isolations or detailed studies of single compounds, even in smaller volumes.

The second applicable and repetitive procedure is multidimensional liquid chromatography (LC-LC) with GPC device, which Andersson et al. /89/ have developed in order to analyse phenols in pyrolysis oils. They dissolved the whole oil sample in THF before pre-fractionation in GPC column or liquid-liquid apparatus. As for HPLC standards, the lignin precursor-like phenols such as m-cresol, vanillin, guaiacol and 2,6-dimethyl phenol were prepared in experiment.

11.4 Gel permeation chromatography

Gel permeation chromatography (GPC or SEC) is used for analysis and quantitative detection of phenolic compounds in pyrolysis oils, but also to study chemical compositions of tar and coal /89,90/. The sample molecules are separated according to their molecular mass, shape and ability to enter through a porous chromatography gel. The speed of penetration depends primarily on the size of the molecules and hydrodynamic volumes. Bigger molecules move faster than small ones, which fit inside the pores. The GPC-HPLC system with differential refractometer detectors can be utilised to analyse pyrolysis oils obtained from different sources and to compare their molecular mass distributions under the same measurement conditions. High-molecular-mass extractives are difficult to vaporise and may degrade in high temperatures used in GC. Solvents, in which the oil-derived samples can be dissolved are, for instance, THF, acetone and methanol. Using GPC, the average molecular mass of pyrolytic lignin has been determined to be between 650 and 1300 Da /72/.
11.5. Mass spectroscopy

Mass spectrometry is a modern instrumental technique which generates, separates and discerns ions in the gas phase. Thermally degraded water-insoluble compounds, i.e. lignin and extractives are made up of small fragments, which are separated by GC and identified with mass spectrometry. The sample pretreatment is not necessary, however, in the case of non-pyrolysed lignin samples homogenisation or derivatisation is often needed. During analytical pyrolysis the sample is rapidly heated to the maximum temperature to obtain thermal fragmentation and secondary reactions /86,90/. In this respect, a Curie-point pyrolyser has proved to be a helpful pre-tool.

Typically, mass spectrometer operates as a detector and records the mass spectrum of each compound eluting from a gas chromatography column. The most prevalent ionisation technique is electron impact (EI) at the mode of 70 eV, which produces ordinary fragment ions from lignin, comprising the p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) propane units /86/. The peaks are recognised by comparing characteristic masses of standards and known compounds or milled wood lignin with unknown samples /72/. For instance, simple phenol possesses the mass/potential value 94 Da, guaiacol 124 Da and syringyl 154 Da. At the most currently there is a specific demand for mass spectrometric Maldi analysis that are measuring the average molecular mass of lignin-originated degradation products.

11.6 $^{13}$C and $^1$H NMR

NMR is a phenomenon which occurs, when certain substances are inserted in a static magnetic field and exposed to a second oscillating magnetic field /91,92/. $^1$H NMR is a practical tool for the determination of aliphatic hydroxyl, phenolic hydroxyl or benzyl alcohol groups from lignin or aromatic extractives by comparing their signals with the spectra of propionate derivatives. In the $^1$H NMR of the water insoluble fraction, the signals of aromatic protons are found in
the region from 6.5 to 10 ppm, the aliphatic compounds from 1.5 to 3.5 ppm and the methoxy groups from 3.0 to 4.2 ppm.

The determination of benzyl alcohol and phenolic hydroxyl groups could also be carried out by $^{13}$C NMR, which bases on the signals from the carbonyl carbon in the acetate groups. Signals of aromatic carbon structures are found in the 110 to 148 ppm region and a stronger methoxy peak at 55.6 ppm. Thus, practical way of approaching the water-insoluble phase is to scrutinise particularly signals from carboxyls of acetyl groups (68-171 ppm). The traces derived from aromatic carbons can be divided further into quaternary (125-160 ppm), methine carbons (110-125 ppm) and side-chain carbons (50-90 ppm) /92/. Exceptional signals of aliphatic carbons are seen in the aromatic region attributed to $\alpha$ (134-135 ppm) and $\beta$ (122-124 ppm) carbons of unsaturated coniferyl alcohol end groups. Other strong signals are located at 56-57 ppm due to methoxyl groups. Before NMR analysis, the water-insoluble oil sample can be pre-treated by dissolved in 15-20 % DMSO-d$_6$ solution /72/.

While studying pyrolytic lignins by $^{13}$C NMR at 100.6 MHz and 60 °C, Scholze et al. /72/ have found that the amount of guaiacyl units for softwood samples cover more than 90 % which is roughly the same as the value of pine MWL. The values of syringyl and guaiacyl units of hardwood pyrolytic lignin samples corresponded to the range 58-79 % and 21-41 %, respectively. According to methoxyl groups, the main signal of pyrolytic lignin and MWL appeared at 55 ppm. Other notable signals of pyrolytic lignin were noticed in the overlapping aromatic region between 155 and 100 ppm. They were assumed to indicate fundamental structural changes and possible new C-C bonds.

Considering the water-insoluble fraction of the fast pyrolysis oils, Scott et al. /93/ have explored the detailed composition by $^{13}$C NMR using 9 % pyrolytic lignin of poplar wood in DMSO-d$_6$ at 63.9 MHz and 50 °C with broad-band proton decoupling. They noticed, that NMR spectrum of pyrolytic lignin reminded that
of steam exploded lignin and found the two major peak groups from 20-90 ppm, and 105 ppm. The previous one responds to aliphatic chains and the latter is typical for aromatic carbons, and olefinic side chains.

Composition of hydrophobic extractives such as fatty and resin acids, triglycerides, and fatty acids esters of top phase can be detected by $^{13}$C NMR technique according to functional groups /15,37/. Measurements base on carbonyl signals in the region (170-200 ppm) of fatty and resin acids or fatty acid esters or the glycerol signals from triglycerides (55-75 ppm). Vanillin has been utilised as internal standard. The disadvantages of NMR are its complexity, long measurement time and requirements for extractive volumes.

11.7 IR spectroscopy

Fourier transform infrared (FT-IR) and FT near infrared (FT-NIR) spectroscopy are feasible and rapid analysis techniques of wood-derived substances, which base on the fact that molecules are able to absorb infrared light /94/. Covalent bonds have a tendency for vibrations, stretching and bending resulting in the absorption at the specific frequencies in the infrared region of the light. As FT-IR and FT-NIR spectra originate in characteristic molecular vibrations, these can be applied to gather information about molecular structure and composition of the oil fractions. The FT-IR bands obtained from the sample are verified by comparison with the spectra of known lignins, model compounds and related substances.

The frequency scales, corresponding to the adsorption energy, are given in units of reciprocal centimetres (cm$^{-1}$), which mean the number of wave cycles in one centimetre. Wavelength units, in turn, are given in micrometers. The accurate frequency, at which a vibration of the molecule occurs, is determined by the strengths of the involved bonds and the mass of component atoms. Stretching frequencies are higher than bending frequencies. Covalent bonds to hydrogen, for instance, have higher stretching frequencies than those to heavier atoms. Double bonds have higher frequencies than single bonds.
The patterns of water-insoluble compounds, having bending vibrations in the region between 600 to 1450 cm\(^{-1}\), form absorption bands in the fingerprint region, while compounds, having stretching vibrations of diatomic units in the 1450 to 4000 cm\(^{-1}\), form absorption bands in the group frequency region. When Maggi et al. \cite{95} analyzed the composition of oak pyrolysis oils by FT-IR, they noticed two valuable signal regions, which might be utilised for top phase fractions. They identified particularly strong bonds referring to O-H stretching between 3200-3600 cm\(^{-1}\) and, in addition, signals associating with OH, and COH stretching around 1237 cm\(^{-1}\). Stretching of C-H, CH\(_2\) and CH\(_3\), and aromatic rings were also recorded to interferograms.

11.8 Thin layer chromatography

Thin layer chromatography (TLC) is mainly considered as a qualitative, but inaccurate technique, which can be utilised for experimental study of the separation between surface and bottom phases, determination concentrations of individual compounds in a complex mixture, identifying or purifying small amounts of any substance from the top phase. Churin et al. \cite{96} have isolated and determined paraffin, olefin and aromatic hydrocarbons (C\(_{10}\)-C\(_{30}\)) of the olive oil-derived pyrolysis liquids using TLC along with GC/MSD. TLC is also practical to optimise the separation conditions in HPLC.

The principle of TLC is quite simple: due to capillary forces, mobile phase streams with the sample upwards on silica plate. Many extractives of forest residual oil may not be easy to notice, but still part of them are colourless substances, which have ability to emit fluorescence and, thereby, they could be seen by UV source. Instead, some organic compounds are noticed as dark spots from wet combustion, the others must be stained before detection.

Polar and non-polar compounds move with different speed and distance on the plate in respect to mobile phase. As far as solid phase has a polar charge, non-polar phase (lipophilic fatty and resin acids) moves more rapidly with the mobile phase. Mobility of compounds is ordinarily displayed with Rf values, which
inform about the distance migrated by the single compound in respect to the position of solvent. TLC separation of fatty and resin acids can be carried out using a solvent system containing dichloromethane, methanol and ammonia (80: 19:1 by volume) /8/.

12 APPLICATIONS FOR THE SURFACE FRACTION OF WOOD PYROLYSIS OIL

12.1 Lignocellulosic pyrolysates

Wood pyrolysis oils contain numerous classes of chemical compounds with different quantities, i.e. alcohols, aldehydes, ketones, carboxylic acids, esters, furans, lactones and phenols /44/. Their volumes depend on the process type and conditions, but still many of them are potential sources of chemical raw material. At the moment, industrial manufacture of pyrolysis oils base on processing feasible chemicals other than fuels /96/. Some hydroxy acids, for example, can be achieved from lignin matrix by combined precipitation, vacuum distillation or partition chromatographic techniques /97/. Aromatic degradation products of the wood oil can be utilised as a high value chemical feedstock.

Specific phenols have anti-diarrhoea and anti-motility properties, germicidal activity and herbicidal and antiseptic properties /98/. They have been used in tanning into leather, as staining agents, as thermal insulating material and as food additives. Pyrolysis oils, when refined, can be used as a substitute for fossil fuels to generate heat, power and chemicals. For instance, there exists a large range of chemicals that can be extracted, adsorbed or refined from pyrolysis liquid matrices comprising specialities, food flavourings, resins, agri-chemicals, fertilisers, emission control agents and packing materials. Levoglucosan, for instance, formed in cellulose degradation, can be a source of pharmaceutical and pesticides, herbicides and plant growth regulators, oligosaccharides via saccharification and fermentation, glycosidic surfactants, dextrines, stereoregular
polymers, biocompatible polymers (i.e. methacrylate), liquid-crystals, non-
hydrolysable glucose polymers and epoxies /1/.

Short-term applications are boilers and furnaces (including power stations),
whereas turbines and diesel engines may become available on, somewhat, longer
term /99/. Upgrading of the pyrolysis oil to a transportation fuel is technically
feasible, but needs further development. The fuels, such as methanol, can be
derived from the pyrolysis oil through synthesis gas processes.

VTT and some other institutes have carried out laboratory tests from diesel
engines to large size modified dual fuel ones /99/. Test results have turned out to
be positive as long as the engines operated smoothly. Nevertheless, quite many
problems need to be solved to use pyrolysis oil instead of diesel fuels, particularly
if the acidic pH of the oil and its tendency for soot formation, and polymerisation
are considered. Pyrolysis oils contain plenty of organic acids, which cause
corrosion and decrease pH of the oil. The use of pyrolysis oil requires
modification of several parts of the engine. Thermal stability, contaminants and
low pH prevent also oil combustion in gas turbines.

Along with lignocellulosic material, wood pyrolysates comprise small amounts of
decomposed extractives. The fractionation may not be economical; there exist
less knowledge of their thermal behaviour. However, to some extent, pulp
industry converts cooked and gasified extractives, i.e. terpenes as a tar /10/. Resin
and fatty acids, in turn, form wood soaps, which are distilled to pine oils.

12.2 Pyrolytic lignin

The physico-chemical properties of water insoluble surface fraction in pyrolysis
oils and pyrolytic lignin, have not yet been fully explored. Pyrolysis conditions
could be developed to increase amount of phenolic compounds and, thereby,
higher value of the source oil might be achieved /100/. The pyrolytic lignin,
derived from vacuum pyrolysis, is highly phenolic from the nature and, as a
result, it could be a good source of phenolic compounds in phenol-formaldehyde formulation.

Pulp mills generate huge amounts of lignin as a residue and prefer combustion as a fuel. Certainly, there are a few other purposes for pyrolytic lignins, which are detailed in forthcoming chapter. Figure 19 displays the exploitation of entire lignin and lignin sulphonates, which are obtained from the pulp mills. The sulphonates are modified as dispersgents in oil drilling and adhesives in animal foodstuffs or synthesised for cement, concrete, ceramics, bricks, antioxidants, fertilisers, and even as a filling of batteries. Fragmentation pathway might be counted for lignin pyrolysates as well.

**Figure 19.** Potential use of lignin /100/.

Aromatic compounds such as vanillin, cresols and simple phenols are accomplished by selective hydrotreating, in which oxygen-containing functional groups are preserved while carbon-carbon bonds are cleaved /101/. The
hydrogenation step is followed by etherification to yield aromatic ethers that could perform as commercial oxygenated fuel additives or other substitutes in organic chemical industry.

Vanillin or 3-methoxy-4-hydroxybenzaldehyde, in general, has been a very popular as aromatic flavour, but it is also used in the synthesis of perfumes and drugs. One of these pharmaceuticals is antihypertensive drug called Aldomet (1-3-(3,4-dihydroxy phenyl)-2-methylalanine) /101/. In the North America they have utilised wood-derived vanillin as petrochemical raw material, although environmental impacts of the separation process are a matter of concern.

Traditionally cresols, i.e. p-cresol, have been utilised for antioxidants, dyes, pesticides and resins, but have found also a variety of other purposes including solvents, disinfectants or intermediates in the preparation of chemical specialities such as motor fuels and rubber polymers.

Phenols exhibit corrosive and hazardous properties, which partially limits the industrial exploitation. Phenols play an important role in the industry, since they have been sources of certain artificial epoxy or phenol formaldehyde resins and are used as a starting material in synthesis of many drugs (ear and nose drops), dyes, insecticides, nylon and explosives /101/.

However, several organisations, i.e. National Renewable Energy Laboratory (NREL) and Fortum, have been interested in the possibility to extract pyrolytic lignin from wood pyrolysis liquids as far as they are intending to manufacture bio-based resins /102/. Before resin is cooked, the pyrolysis oil requires modification into wood glue, where fillers, extenders and other additives are added. Intricate problems in resin cook are caused by acidic nature and lower reactivity of pyrolysis oils, as the oils demand fairly more sodium hydroxide in regard to phenol than a standard phenol formaldehyde resins. Finally, pyrolytic lignin might partly substitute phenol in phenol-formaldehyde novellas and resoles, although the current resins contain only 35-45 % of novellas and resoles. In the future pyrolysis oil-based formulation products, i.e. resins, will be promising and long-lasting materials in building industry.
13 REFERENCES


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