

**Long-term Stability, Catalytic Upgrading,
and Application of Pyrolysis Oils -
Improving the Properties
of a Potential Substitute for Fossil Fuels**

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"Where shall I begin, please your Majesty?" he asked.
"Begin at the beginning," the King said,
gravely, "and go on until you come to the end: then stop."

Lewis Carroll, 1832-1898

Alice's Adventures in Wonderland (1865)

1 Introduction

1.1 Demand for renewable energy sources

Fossil fuels constitute the major energy resources of our modern civilization. However, because fossil fuel resources are limited and naturally not replenished on an acceptable time scale, a growing interest in energy research is directed towards renewable energy sources. As presented by Hazlewood (Shell company) on a symposium in 1998 the consumption of fossil fuels will reach a plateau around 2020 (see Figure 1) [Haz98]. According to energy economics and energy policy discussions, solar energy will become of paramount importance in the future. A possible scenario, for instance, is the production of hydrogen from water by solar energy, and subsequently 'burning' the hydrogen in modern fuel cells in the cars of the future. In addition to using solar energy 'as is', wood and other forms of biomass can be regarded as 'stored' solar energy. Biomass resources represent one of the most promising sources of renewable energy, both on the European market and internationally. Compared to other renewable energy sources, biomass possesses the advantage of being less cost intensive [KD97]. Currently, transformation of biomass into energy accounts for more than 15 % to the world energy supply [PFBIO99]. Furthermore, the application of biomass as energy source is highly respected in the public opinion.

In addition to substituting fossil fuels as energy source, renewable energy sources offer considerable advantages with respect to lowering the total emission of exhaust gases responsible for the 'greenhouse effect' and other pollutants being released as a consequence of using fossil fuel oil (e.g. particulates from diesel engines). One of the most important 'greenhouse gases' is carbon dioxide. By using renewable biomass as an energy source, net

CO₂ emission could be drastically decreased. Because CO₂ produced during electrical power production is being re-absorbed during the growth of biomass, this nearly CO₂ neutral procedure has become increasingly important in many developed countries [NL98]. Governments of various countries have initiated special programs to encourage the development of technologies to use biomass as a source of electrical power.

As presented by the European Commission (EC) in its *White Paper* [EC97], the goal desired for the year 2010 is to increase the present bioenergy consumption from 38 Mt/a to 130 Mt/a. Because probably no single company or country is capable of establishing new promising processes for commercial bio fuel operation, intense co-operation between partners from industry and academia all over the world should be sought and are particularly encouraged by the European Union. For this reason the European Commission subsidizes a large amount of research programs in the area of exploiting renewable energy sources.

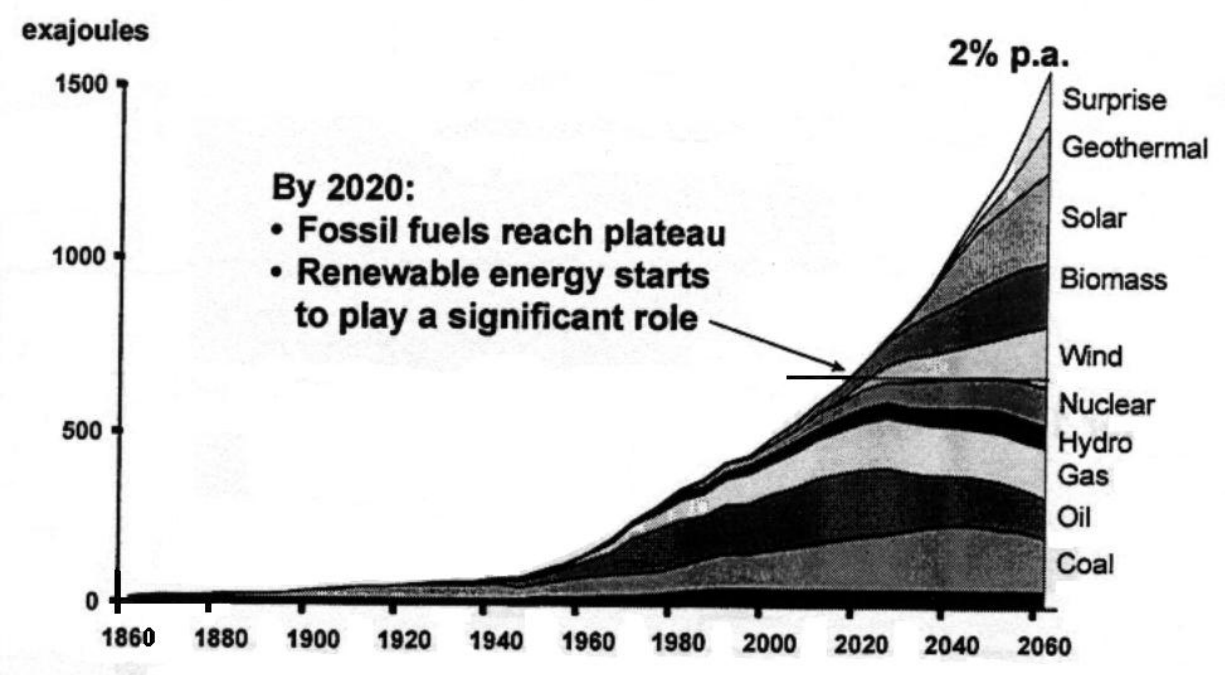


Figure 1: If world energy demand grows by 2 % per annum, renewable energy could contribute up to 50 % by 2050 [Haz98].

Since 1989 various projects are financed by the EC in the framework of JOULE (Joint Opportunities for Unconventional or Long-term Energy). Main topics of this program are both characterization of suitable biomass material and the application of biomass as an energy source. One of the projects supported by the EC was entitled BIO FUEL OIL FOR POWER

PLANTS AND BOILERS (JOR3-CT95-0025) and finalized at the beginning of 1999. Some parts of the work described here were prepared within this EU-project.

1.2 Valorization of raw biomass by pyrolysis

A possible way to transform raw biomass into an even more valuable energy source is by pyrolysis (valorization of biomass, “*Veredelung*”). The word *pyrolysis* is a combination of the Greek words *pyros* (means: fire, heat or warmth) and *lysis* (means dissolving). Since the earliest stage of human civilization, pyrolysis of biomass is well known and has been used extensively. Originally, pyrolysis of biomass was mainly performed to produce gases and char, whereas liquid products were regarded as undesirable by-products. However, since the oil crises in the nineteen seventies, the general interest in the liquid products of the pyrolysis of biomass is increasing steadily. The liquid that is obtained by pyrolysis of biomass has been given a large number of various names such as pyrolysis oil, bio oil, pyrolysis liquid, bio crude, bio fuel oil, wood liquid, or liquid wood. In general, the acronym ‘bio’ is used to indicate the characteristic of being renewable and, hence, environmental friendly. Compared to raw biomass, pyrolysis oil is much easier to transport and possesses a much higher energy density.

In 1985 Chornet and Overend [CO85] coined the following definition of the conversion of biomass into oils by pyrolysis: “To transform a carbonaceous solid material which is originally difficult to handle, bulky, and of low energy concentration, into pumpable oils having physico-chemical characteristics which permit storage, transferability through pumping systems, and further use either in direct combustion furnaces or as feedstocks for hydro treatment leading to specific fuels and chemicals.”

Corresponding to the increased relevance of liquid pyrolysis products, reactors for fast pyrolysis of biomass were developed over the past 20 years in order to maximize the yield of liquid products. Moreover, during that time the number of plants, the capacity of the plants, the number of institutions involved, and the range of applications continuously increased. In addition, possible ways were exploited to make reasonable use of the now by-products gas and charcoal, for instance, to heat the pyrolysis reactor during the process or as filter coal, respectively.

Since 1994 research in the area of pyrolysis of biomass is performed at the Bundesforschungsanstalt für Forst- und Holzwirtschaft (BFH) in the Institute for Wood

Chemistry (IWC), Hamburg. In the meantime, two pyrolysis plants with 0.2 - 0.5 kg/h and ~ 5 kg/h are under operation, constructed according to the Waterloo Fast Pyrolysis Process (WFPP) and the 'Hamburger Verfahren' [Sim96], respectively.

With the increasing availability of pyrolysis oils and the demand of renewable energy sources, the combustion of pyrolysis oil in diesel engines, boilers, and gas turbines becomes more and more attractive [DB99]. At present, European research funding is aimed at utilizing pyrolysis liquids for heat and power generation at a larger scale. Currently, two institutions, the Finish Research Center Valtion teknillinen tutkimuskeskus (VTT) and the British company Ormrod Diesels, investigate the use of pyrolysis liquids for power generation. Both institutions attempt to burn the liquids in larger diesel engines. Although they possess considerable know-how and experience with the use of fossil fuels, little experience has been made with the application of fast pyrolysis liquids generated from biomass; firstly, because in the past sufficient large amounts of oils were not available for testing purposes and, secondly, reliable information about the physico/chemical properties and the long-term stability of pyrolysis oils were lacking.

However, the production of pyrolysis oil and its utilization as a reliable energy source are still at an early stage of commercialization. In order to establish pyrolysis oil in the market, a substantial quality improvement of the oil must be achieved. The pyrolysis oils obtained under the currently employed conditions seem to exhibit an inferior long-term stability compared to conventional petroleum fuel. Therefore, to improve the usability of bio oils in technical applications, it is important to obtain further information on how storage conditions affect pyrolysis oil properties.

In general, the bio oil obtained by pyrolysis of wood is a dark brown and viscous liquid. Bio oils contain a large number of organic components while many of these components are volatile or contain oxygen in various functional groups. Pyrolysis oil is a chemically complex system and as a result of this complexity, numerous chemical reactions can occur in the oil during storage. Evidently, for utilization as a substitute for fossil fuel and other applications these aging processes are undesirable.

Therefore, in this work various pyrolysis oils were systematically stored and the evolution of the concentration of the most important components in the pyrolysis oils was investigated. In addition, certain physico-chemical properties were monitored as a function of time. The investigations of the aging behavior of pyrolysis oils performed in this work are

divided into three parts according to the various storage conditions of the pyrolysis oils employed. One objective of these investigations was to point out procedures and criteria on how pyrolysis oil should be stored in order to minimize deterioration of the physico-chemical properties of the oils with time.

1.3 Upgrading of pyrolysis oils

In addition to investigations of the long-term stability of pyrolysis oils, tailoring of certain physico-chemical properties of bio oil already during or immediately after the production process has attracted increasing interest. This improvement of desired properties of the oil is often referred to as 'upgrading'. Different procedures can be envisaged for the upgrading of pyrolysis oils. First, heterogeneous catalysts can be employed during the pyrolysis process in order to modify the vapor composition of the oil before cooling down. Second, pyrolysis oils can be hydrogenated after the production in order to modify the type and amount of functional groups in the oils.

The objective of the investigations performed in this work with respect to the upgrading of bio oils was to obtain pyrolysis oils, which can be stored without significant changes in their physico-chemical properties. Furthermore, pyrolysis oils with a low viscosity and a high heating value are desirable because these properties determine the applicability of the oils in diesel engines and boiler combustion.

1.4 Pyrolysis liquids as a source of fine chemicals

In addition to using bio oils as a fuel in diesel engines and boilers, pyrolysis oils constitute a viable source of more than 200 organic chemicals. Pyrolysis oils can be effectively fractionated by adding water in order to precipitate lignin derived hydrophobic compounds, the so-called pyrolytic lignin. At present there are only few reports in the literature on the production and the characteristics of pyrolytic lignin [Cze94, MS97, SKFO98, SM01]. Basically two mechanisms for the formation of the oligomeric compounds present in the pyrolytic lignin have been proposed. On the one hand, the organic polymers in the biomass can be cracked to yield single monomers, followed by recombination of the monomers and formation of the pyrolytic lignin [EM87]. On the other hand, oligomers (i.e. the building blocks of the pyrolytic lignin) can be directly 'ejected' from the polymers in the wood particles [LDPP99, PMR99]. It is assumed that pyrolytic lignin contributes significantly to the

instability of pyrolysis liquids. Hence, identification of the composition and the structure of pyrolytic lignin may help to identify and eventually prevent the chemical reaction that result in the undesired aging of bio oils during storage. In this work pyrolytic lignins were obtained from different pyrolysis oils and their physico-chemical properties were systematically investigated. Furthermore, a well-characterized pyrolytic lignin may promote the commercial application of bio oil, for instance, as adhesive for the wood based panel industry [HGG00, CRWRLC00].

By convention there is color, by convention
sweetness, by convention bitterness,
but in reality there are atoms and space.

Democritus, 460-370 v. Chr.

2 Pyrolysis of Biomass

2.1 Historical development

Using wood for the production of charcoal by thermal conversion with low heating rates and long residence time in the reaction chamber is an ancient process. In addition to charcoal the original manufacturing method yields products such as methanol, acetic acid, wood vinegar, wood tar, and acetone. However, originally all volatile products were lost because the process was carried out in pits. Wood tar was used for medical purposes, as lubricant, and for the production of colors and inks. In the middle of the 19th century the carbonization process was optimized and the extraction of a number of by-products was possible. Until 1922 the pyrolysis of wood was the most utilized methanol source. In 1922 the technical methanol production from synthesis gas was introduced [Knö94]. After the Second World War the use of charcoal decreased rapidly in Europe. To date, the coal consumption is mainly limited to activated carbon and coal for barbecues.

First ideas of fast pyrolysis and ablative pyrolysis of biomass were presented on the 'Specialist's Workshop of Fast Pyrolysis of Biomass' in 1980 [SER80]. In 1982 Scott and Piskorz [SP82, SP83] extended the ideas first presented in 1980. They demonstrated that pyrolysis of biomass in a fluid bed yields above 60 % of a viscous liquid product, the so-called pyrolysis oil. In the following years the process was studied and continuously improved, for example, at the university of Waterloo (Canada) and attracted a steadily increasing attention. Development of suitable pyrolysis technology has also been pursued by the U.S. Department of Energy's Biomass Power Program.

For the production of electrical power from biomass three thermal conversion technologies are envisioned:

- Direct combustion
- Gasification
- Pyrolysis, with condensation of the devolatilized organic vapor to yield a potential fuel [SH99].

Recent investigations were made on the basis of the increasing interest in environmental protection capabilities. Wehlte et al. [WMMF97] demonstrated that pyrolysis of wood treated with inorganic, heavy metal, wood preservatives results in a clean oil. The heavy metals were found to remain in the char.

2.2 Composition and properties of wood

2.2.1 Introduction

Plant cell walls must be capable of enduring osmotic pressure variances up to 20 bar between the extracellular and intracellular spaces. Cellulose is the primary constituent of cell walls. Hemicelluloses and lignin are other major components in wood. Because regular lignin is compared to the pyrolytic lignin investigated in this work, it is described in detail in the following. In total these three components build up about 95 to 97 wt. % of dried wood [Sjö81]. Cellulose is present in all types of plant materials whereas the content of lignin and hemicelluloses differs in hardwood (angiosperms) and softwood (gymnosperms). About 42 % of the mass of both types of wood, based on their dry substance, consists of cellulose. Wood contains lignin and hemicelluloses in corresponding amounts. Wood, which contains high lignin amounts, has low hemicelluloses contents. Hardwood and softwood consist of 16-24 % and 24-33 % lignin, respectively [Hil85].

The energy content of biomass is lower than that of conventional hydrocarbon fuel. Because biomass possesses high oxygen content, the low heating value (LHV) is between 16 and 18 MJ/kg (based on dry biomass), compared to hydrocarbon fuels, whose LHVs are in the range between 40 and 44 MJ/kg [GB79].

Gaur and Reed [GR95] published thermal gravimetric analysis (TGA) data of biomass in 1995. The authors showed that only a minor mass loss of biomass occurred up to a

temperature of 150 °C. The main mass loss was observed in the range between 200 °C and 380 °C.

2.2.2 Cellulose

More than half of the entire carbon in the biosphere is fixed in biomass cellulose. About 10^{12} tons of cellulose are estimated to be synthesized and degraded annually [VV95, Str98]. Cellulose, a so-called polysaccharide, is a linear polymer of D-Glucose units linked by β -(1 \rightarrow 4) glucosidic bonds. Cellulose molecules contain between 2000 and 15000 β -D-Glucose monomers, rotated by 180 ° with respect to each other. The cellulose polymers orient parallel to each other, held together by hydrogen bridges. This results in a band-like structure of cellulose polymers up to 8 μ m. The accumulated cellulose polymers possess diameters between 5 nm and 30 nm and a nearly crystalline long-range order. Because of this high long-range order these molecules are extremely tear proof. A cellulose band of 1 mm is capable of tolerate more than 60 kg. This corresponds to 80 % of the tensile strength of steel [Str98].

2.2.3 Hemicelluloses

Hemicelluloses molecules are combined and branched polysaccharides. Main components are pentosanes and hexosanes. Pentosanes contain different pentose units, mainly D-xylose and L-arabinose. Combination of hexoses, predominantly D-mannose, D-galactose, and D-glucose, results in hexosanes. Hemicelluloses are X-ray amorphous. Hemicelluloses possess a polymerization degree of about 200 monomers.

2.2.4 Lignin

2.2.4.1 Structural features of lignin

After cellulose, lignin is the second dominating organic compound in the biosphere. Already as early as 1920 Klason [Kla20] suggested that lignin contains a large number of compounds with carbonyl groups. More than 20 years later the presence of carbonyl groups in spruce lignin was proven by Adler et al. [ABH48 and AE48]. During the following decades a number of authors sought to define the structure of lignin in plants as well as in an isolated form. Today, lignin structure and morphology are considered to be sufficiently determined. To date, lignin is regarded as a heterogeneous amorphous polymer, which contains minor amounts of

extractives and inorganic materials. In contrast to cellulose and hemicellulose (carbon content less than 50 wt. %, oxygen content about 50 wt. %) lignin consists of 60 wt. % carbon and 30 wt. % oxygen. In plants, lignin is synthesized from p-hydroxy cinnamyl alcohol precursors by polymerization [Gla85]. The resulting basic constituent units of lignin are p-hydroxyphenylpropane (H), guaiacylpropane (G), and syringylpropane (S), which are derivatives from trans-p-cumaralcohol, trans-coniferylalcohol, and trans-sinapalcohol, respectively (see Figure 2).

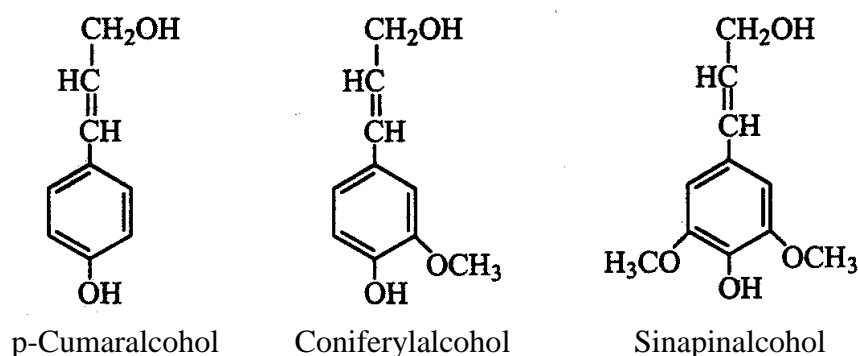


Figure 2: Main preliminary compounds of lignin.

The different phenylpropane units are preponderant linked by ether bonds and C-C-bonds and, hence, build up the three-dimensional lignin macromolecule, which eventually forms an amorphous solid. Because of the many different types of linkages between the phenylpropane units lignin is chemically complex.

Models, such as those proposed for spruce lignin by Freudenberg [Fre68] or for beech lignin by Nimz [Nim74], attempt to describe the structure of lignin. The structural model of beech lignin presented by Nimz [Nim74] is depicted in Figure 3. Nevertheless, these models depict only the types and linkage modes of the structural units and estimate the ratios of these units, which are expected to occur in lignin [DL92]. In softwood only phenylpropane units of the guaiacyl type build up the lignin molecules. In contrast, hardwood lignin, e.g. beech, consists of phenylpropane units of the syringyl and the guaiacyl type. Therefore, hardwood and softwood lignins are often named as guaiacyl-syringyl lignins and guaiacyl lignins, respectively. In addition to the structural variability of lignin in hard- and softwood with respect to the morphological location in the plant, lignin is also known to be different within one plant [Gor81]. Glasser [Gla85] suggested that lignin formation and lignin structure of a plant is affected by environmental influences.

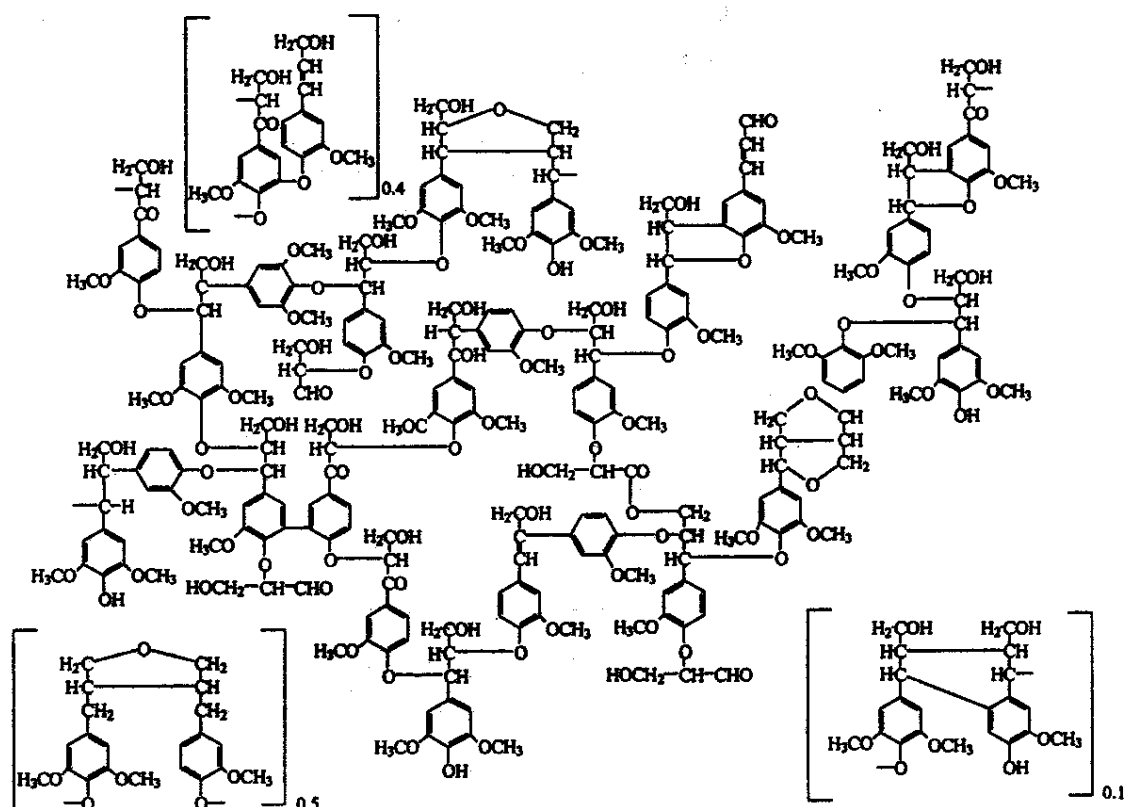


Figure 3: Model of beech lignin by Nimz [Nim74].

2.2.4.2 Determination methods of lignin

Because of mechanically or chemically degradation, to date it is not possible to isolate lignin quantitatively from plant materials. Dence and Lin [DL92] presented a detailed description of different characterization methods for lignin. Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR-spectroscopy) are examples for spectroscopic methods. The latter can be used to determine the ratio of syringyl/guaiacyl units in lignin [LMN87 and Man87]. The assignment of all the important signals in the ^{13}C -NMR spectrum of milled wood lignin from beech was adopted from Lüdemann and Nimz, and Robert [LN74, Rob92]. As a result of the various lignin structures, the content of methoxyl groups in hardwood and softwood lignin is different. Quantification of methoxyl groups of milled wood lignin (MWL) from hardwood and softwood is presented by Fengel and Wegner [FW84] to be 18-22 % and 12-16 %, respectively. Lignins can also be characterized by elemental analysis. For an isolated lignin sample a so-called C_{900} chemical formula can be derived (e.g. $\text{C}_{900}\text{H}_x\text{O}_y(\text{OCH}_3)_z$). This formula is calculated from a combined elemental and

methoxyl group analysis. A more detailed and descriptive formula can be determined if hydroxyl and carbonyl group data are available. Usually, this formula is reported on a C₉-basis because basic lignin units consist of C₉ carbon skeletons. Dence and Lin [DL92] presented C₉ formulas for typical softwood and hardwood MWL as C₉H_{8.3}O_{2.7}(OCH₃)_{0.97} and C₉H_{8.7}O_{2.9}(OCH₃)_{1.58}, respectively. However, the authors pointed out that in cases where the propyl side chain is degraded, a formula on a C₉ basis might not be justified anymore.

In addition to quantify hydroxyl groups and methoxyl groups in lignin, different methods for carbonyl group determination were developed as summarized by Dence and Lin. Already in 1953 different methods for carbonyl group measurements were published by Heuser [Heu53]. In 1935 Bryant and Smith [BS35] developed a method for determining carbonyl groups by oximation using hydroxylamin hydrochloride with an additional amount of pyridine. In 1955 Adler and Gierer [AG55] presented carbonyl content of lignin preparation utilizing hydroxylamin hydrochloride as the reagent.

In 1992 Chen [Che92] published carbonyl group data for milled wood lignin (MWL) obtained by the same method. Additionally, Chen presented an overview of different methods that can be used to determine carbonyl groups in lignins. A comparison of different techniques revealed that the procedure based on reaction of hydroxylamin hydrochloride with carbonyl groups is the most effective and convenient method. In addition, different wet chemical analysis methods have been established (e.g. oxidative degradation methods [GL84]) to describe the structure of lignin.

2.3 Production of liquids by flash pyrolysis

2.3.1 Introduction

In the last 20 years several studies have shown, that high heating rates and short reaction times in the pyrolysis process afford high yields of liquid products. These processes are known as fast or flash pyrolysis. Here, biomass is rapidly heated to temperatures of about 500 °C in the absence of oxygen, which results in decomposition of the biomass into a mixture of vapors and aerosols. Subsequently, rapid cooling and condensation yield gases, char, and about 60-70 wt. % (based on dry biomass feed) of a brown mobile liquid, the pyrolysis oil. Yields of gases, liquids, and solid products obtained from pyrolysis processes depend strongly on reaction parameters such as physical and chemical nature of the feedstock, and time and

temperature of the reaction system during the process. The total volume of gases, chars, and liquids is considerably increased compared to the volume of biomass feedstock. The obtained by-products gas and charcoal can be used to dry the feedstock and to preheat the reactor.

2.3.2 Mechanism and kinetics of the pyrolysis of wood

The amount of pyrolysis oil, gas, and coal obtained by pyrolysis of wood depends on the chosen pyrolysis conditions. In 1991 Radlein et al. [RPS91] presented a simple kinetic model for the pyrolysis of biomass as shown in Figure 4.

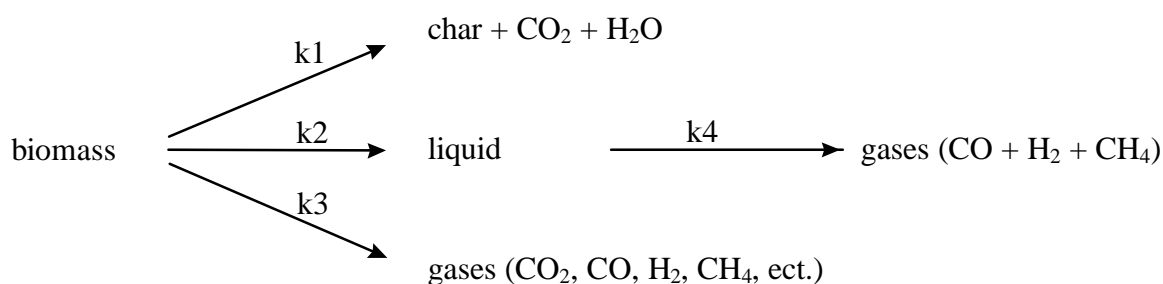


Figure 4: Simple kinetic model of the biomass pyrolysis by Radlein et al. [RPS91].

The simplified kinetic scheme shows the essential reaction paths of the pyrolysis of biomass. The different reaction paths proceed with different speed constants, k_1 , k_2 , and k_3 . Reaction 1 (k_1) predominates at a pyrolysis at low temperature (< 400 °C) and low heating rates (0.01 to 2 K/s). This corresponds to a conventional pyrolysis, which results in charcoal, CO_2 and water. The balance of these reaction paths is shifted to reaction 2 (k_2) with increasing temperature (400-800°C) and increasing heating rate (10-1000°K/s). Under these circumstances the products obtained are mainly liquids. Depending on the reaction conditions, the products can be cracked to CO , H_2 and CH_4 by secondary reactions (k_4 small at temperatures below 650°C). Biomass is converted predominantly to gasses at increasing temperatures and increasing heating rate (reaction 3 (k_3)).

Already in 1984 Scott and Piskorz [SP84] described maximal yields of 76 % for pyrolysis oil at temperatures of 500 °C. The composition of pyrolysis oil is also affected by coal produced in the reactor which can exert a catalytic influence on the reaction.

The mechanism of the decomposition of cellulose, hemicelluloses, and lignin has been previously discussed [Vor76, SFCSS79, Ant85, BPBA94, PDS94]. The experiments described in the literature utilize mostly pure cellulose. In spite of the complexity in the composition of biomass the results of the work on cellulose are often used in a first

approximation. The models published for degradation pathways of biomass include or ignore the possibility of the existence of an intermediate 'active' species. Until now a detailed mechanism is still under debate. L     et al. give a detailed account of possible degradation mechanism of biomass [LDPP99].

2.3.3 *Different pyrolysis processes*

2.3.3.1 Introduction

The following chapters summarize different processes of flash pyrolysis which is normally subdivided depending on the heat transfer to the biomass particle:

For all methods the very short residence time in the reaction zone, the high heating rates (except vacuum pyrolysis), and pyrolysis temperatures are characteristic. Secondary reactions can occur when the wood particle size is too large resulting in char or tar formation. Too small particles may not remain long enough in the reactor resulting in an uncompleted pyrolysis process [Lip85].

A wide range of differently configured reactors can be employed for the pyrolysis process. Among these fluidized bed reactors are the most popular because of their simple design. Moreover, fluidized bed reactors were already scaled-up successfully. A detailed review on different reactor designs for rapid pyrolysis is given by Meier and Faix [MF99].

2.3.3.2 Fluid bed flash pyrolysis processes

For pyrolysis processes fluidized bed reactors are the most popular configurations. A schematic diagram for a bubbling fluid bed pyrolysis reactor is presented in Figure 5. The Waterloo Fast Pyrolysis Process (WFPP) is based on this principle and was developed by a research group at the University of Waterloo, Canada. A fluidized bed of sand arises by blowing gas through nozzles at the bottom of the reactor. The required gas flow depends on the size and mass of the fluidizing material (for stationary fluidized beds at about 1-2 m/s, for circulated fluidized beds three to four times higher). A minimum size above the fluidized bed, the so-called freeboard, is required to prevent blowing out the whirl material from the reactor. The biomass is fed into the fluidized bed. The pyrolysis products exit the reactor at the top. To ensure very fast reactions biomass particle sizes have to be small.

Important features of flash pyrolysis are a reaction temperature of around 500   C, a short vapor residence time of typical less than 2 seconds, a very rapid cooling of the vapor to

give the liquid, and high heating and heat transfer rates. The main product of the flash pyrolysis processes is bio oil which is obtained in yields of up to 75 wt. % from dry feed.

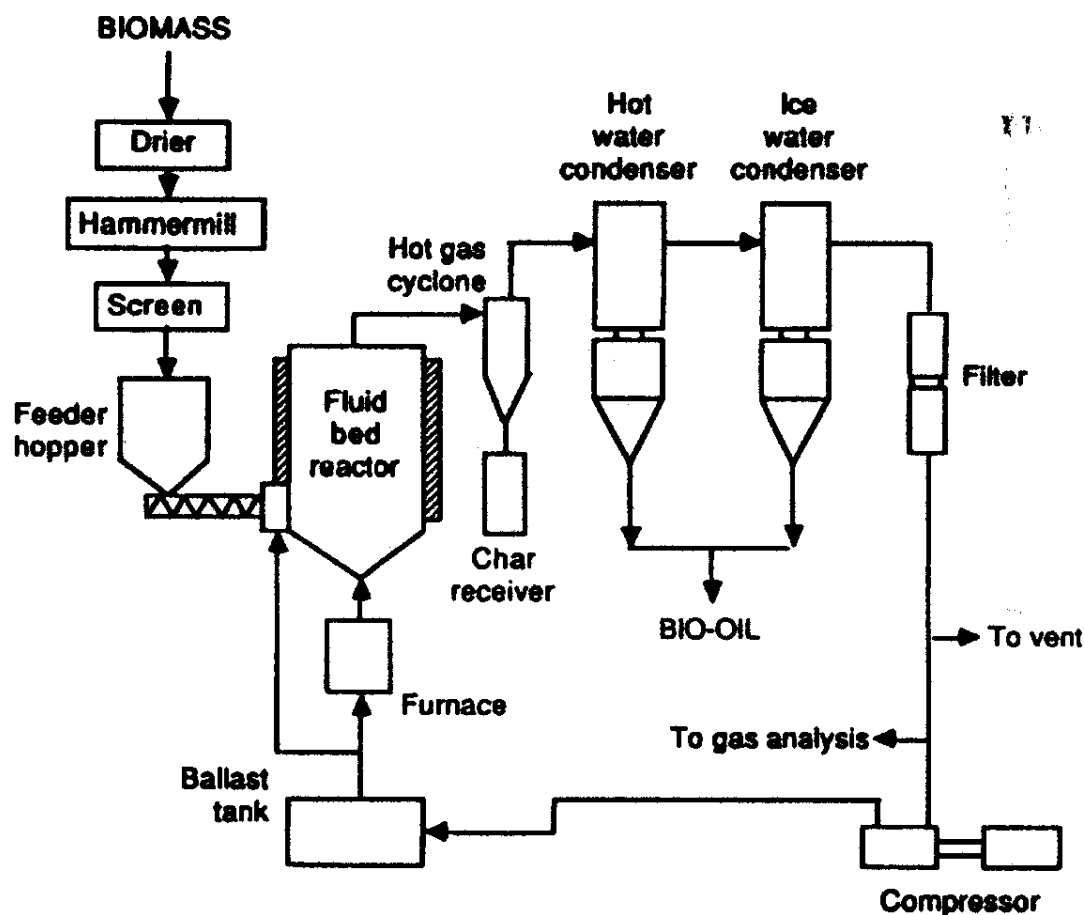


Figure 5: Fluidized bed flash pyrolysis process [SP82b].

At the Institute for Wood Chemistry (IWC) in Hamburg, Germany, this system has been further developed. A 5 kg/h operation unit was constructed within two years in cooperation with the University of Hamburg (Institute for Technical Chemistry, Prof. Dr. W. Kaminsky) [Sim96, Ger98]. Additionally, during this work a 100 g/h fluid flash pyrolysis reactor was in use at IWC. Today a 200-500 g/h fluidized bed reactor is in operation at IWC (see Figure 6).

The largest plant in Europe (capacity of 250 kg/h) working with a bubbling fluid bed reactor is situated in Meirama, Spain, and was operated by the Company Union Fenosa. Modification of the process for the use of catalysts for flash pyrolysis is straightforward. In addition to wood other substances such as waste wood and fast growing plants can be pyrolyzed. Currently, the plant is shut down and not operational. A second plant (250 kg/h) was built at Wellman near Birmingham (Great Britain). The construction has been finished

but the production was not started yet because of the missing permission from British authorities.

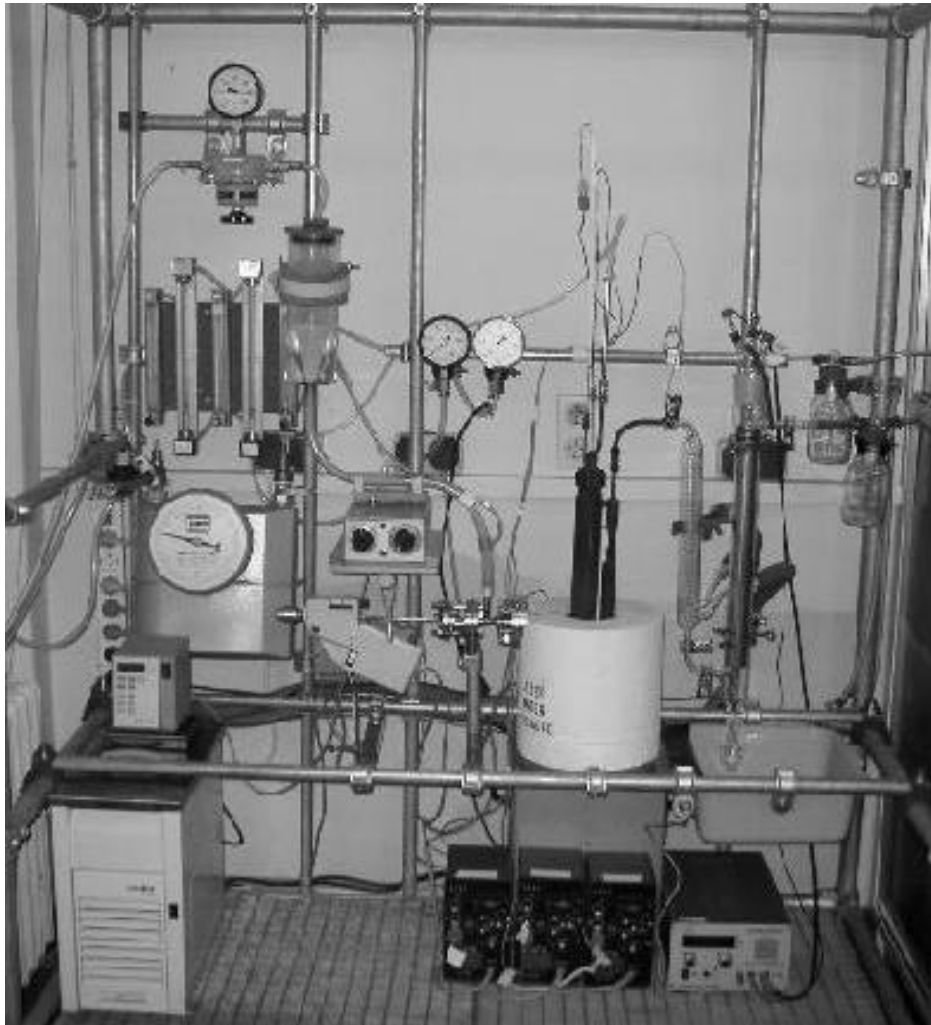


Figure 6: The 200-500 g/h fluidized bed reactor at IWC [Mei02].

A circulating fluidized bed reactor was developed by ENSYN, Canada. The fluidizing material is circulated during the entire operation time. The process is called Rapid Thermal Process (RTP™) [FGH96]. A small unit with 20 kg/h was installed at the Technical Research Center VTT, Finland. The unit with the highest capacity, 650 kg/h, was installed in Bastardo (Umbrien), Italy. This unit is partly funded by the European Union and currently used for research purposes.

2.3.3.3 Ablative pyrolysis

In 1994 Peacocke [Pea94] extended the ideas on ablative pyrolysis first reported by Diebold and Lédé [SER80, LPLV85]. Peacocke and Bridgwater [PB96] defined ablative pyrolysis as

the ‘melting’ or ‘thermal erosion’ of biomass in intimate contact with a hot solid or surface under such conditions that rapid thermal degradation of biomass occurs.

An example of an ablative pyrolysis reactor is the vortex reactor which was presented in 1988 by Diebold and Power [DP88]. A schematic representation of the vortex reactor is shown in Figure 7.

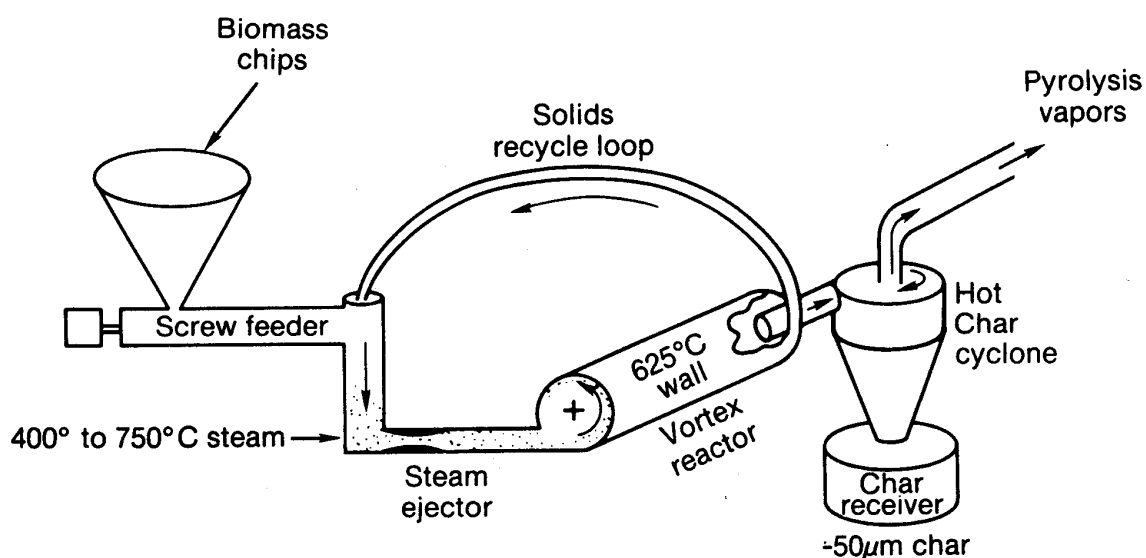


Figure 7: Schematic representation of the vortex reactor as presented by Diebold and Power [DP88].

The biomass feed is metered into the system, where the recycle stream to the super sonic jet of carrier gas entrains it. The solid particles are accelerated very rapidly in a long entrainment tube necessary to allow the biomass particles to gain the high velocities needed. The particles enter the vortex reactor tangentially, so that they are forced to the walls of the reactor by large centrifugal forces. Partially pyrolyzed biomass particles are recycled through the recycle loop at the end of the vortex reactor.

In the past 10 years another ablative pyrolysis reactor was developed at the University of Aston. The reactor (see Figure 8) has a circular plate that is heated. Dry biomass is fed into the reactor and ablated by rotating blades on the hot surface. The pyrolysis products exit through the reactor base near the center. A detailed description of the subsequent processing of the products is given by Peacock and Bridgwater [Pea94, PB96].

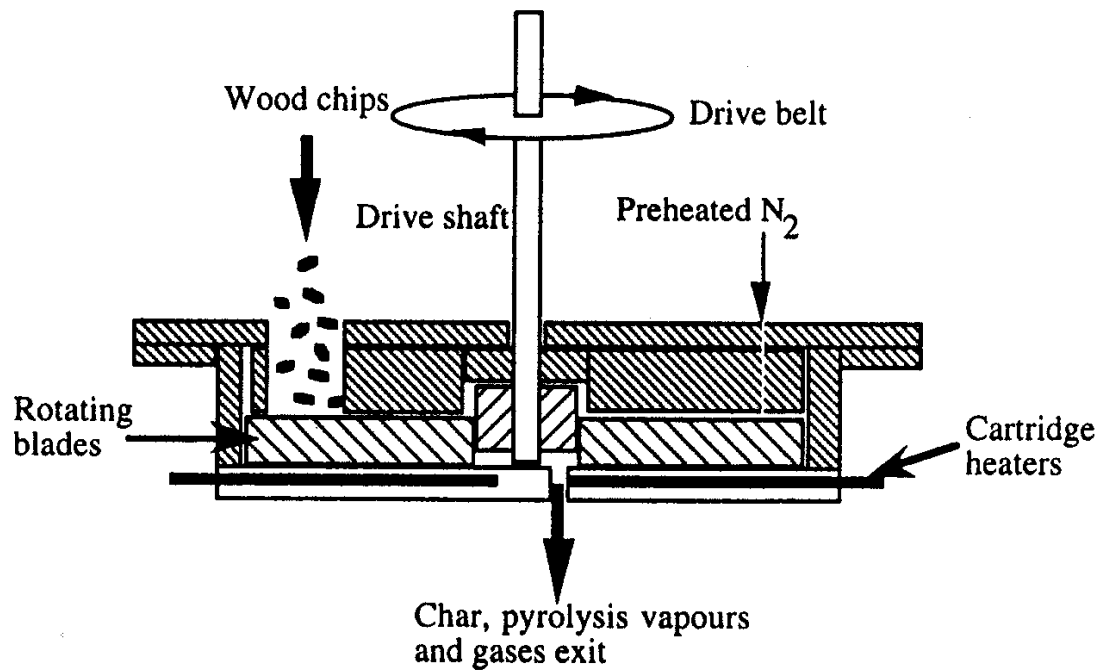


Figure 8: Schematic representation of the Aston ablative pyrolysis reactor [PB96].

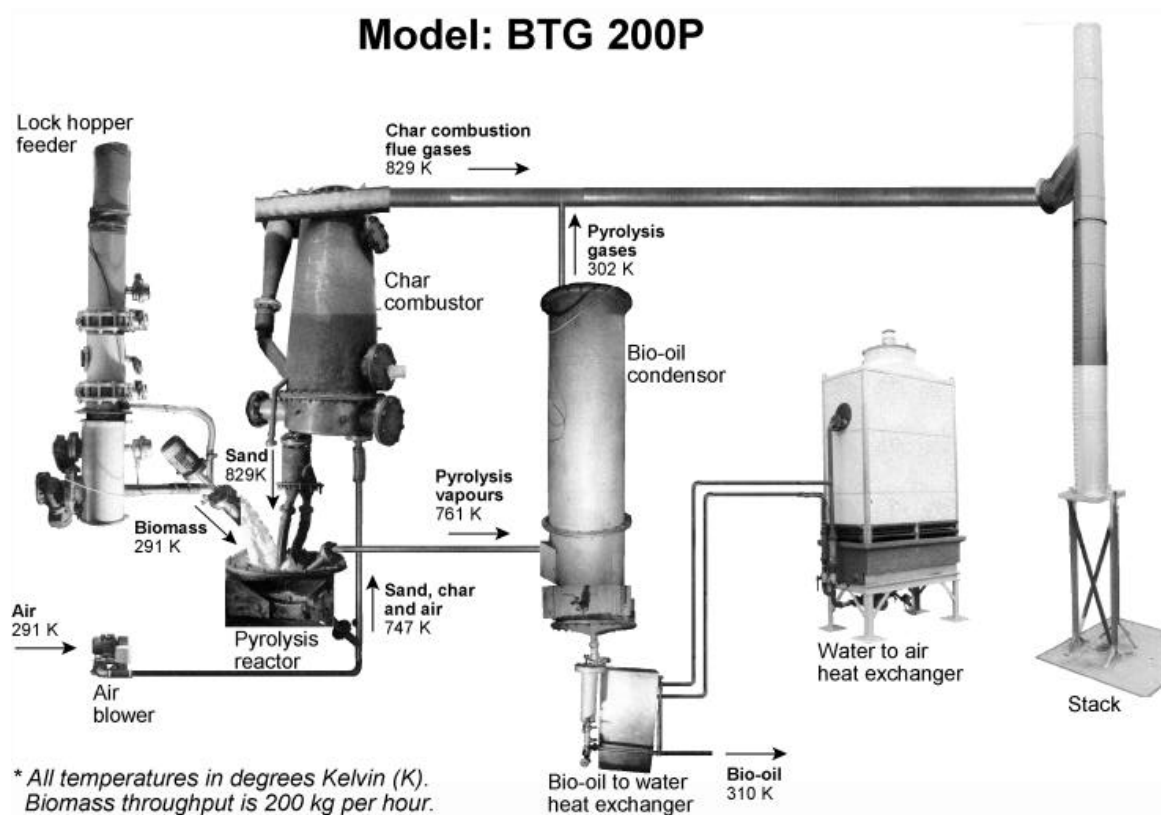


Figure 9: Model of the BTG rotating cone process [Mei02].

The rotating cone reactor, developed at the University of Twente and Biomass Technology Group (BTG), Enschede, The Netherlands, is another example for a pyrolysis reactor (the ablative character is still under debate, because the ratio of sand and biomass is 20:1). A schematic representation of this reactor is depicted in Figure 9. This reactor design consists of two cones. The stationary inner cone is heated while the outer cone is rotating. Biomass and sand is fed to the bottom of the cones and while transported by centrifugal forces to the top of the reactor the biomass particles are ablated. [PyN97]

2.3.3.4 Vacuum pyrolysis

The PyrocyclingTM Vacuum Process, as presented in Figure 10, was developed at the Institute Pyrovac Inc. in Sainte-Foy, Canada. A molten salt is used as heating medium. The molten salt flows through heating plates in the reactor to indirectly heat the feedstock conveyed over the heating plates [Roy97].

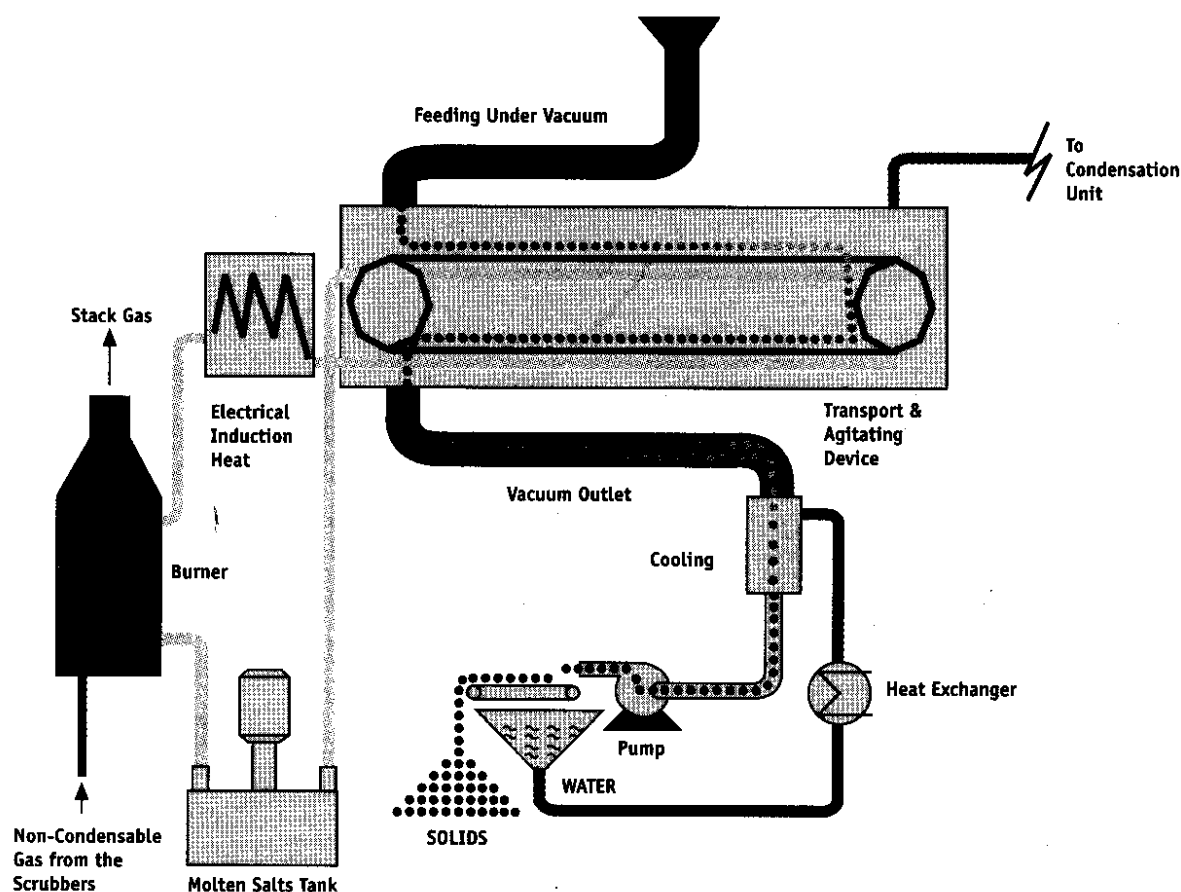


Figure 10: The ProcyclingTM process from PYROVAC [PyN97].

Compared to the other processes mentioned above, pyrolysis in vacuum employs a much lower heating rate. Here the vapors formed are removed rapidly under the low pressure conditions used. However, the plant is currently not in operation because of financial problems.

2.4 Physical and chemical properties of pyrolysis oils

2.4.1 Introduction

Physical and chemical properties of pyrolysis oils strongly depend on the raw materials and on the production conditions. In addition, all properties vary with time, temperature, and water content. The following chapters summarize properties of various pyrolysis oils. Homogeneity of pyrolysis liquids is the most critical factor for an accurate analysis. An extensive review on the chemical and physical properties of pyrolysis oils has recently been published [Fag95].

2.4.2 Physical data and external appearance of pyrolysis oils

Several physical properties of pyrolysis oils are given in Table 1.

Table 1: Physical data of pyrolysis oils.

Properties	Measured Data (Averages)
Higher heating value (HHV)	16-19 MJ/kg
Density	1.19 – 1.28 g/cm ³
pH value	2.5 – 3.5
Flash point	53 – 76 °C
Charcoal particles	Up to 3 wt. %
Ash content	Up to 0.2 wt. %
Viscosity	25 – 1000 cSt
Pour point	–12 to –33 °C

For technical applications it is customary and more practical to report the so-called higher heating value (HHV) of pyrolysis oils, instead of calculating the combustion enthalpy. The higher heating value can be calculated from elemental analysis data by Equation (1).

$$HHV [MJ / kg] = \left[338.2 \times \% C + 1442.8 \times \left(\% H - \frac{\% O}{8} \right) \right] \times 0.001 \quad (1)$$

The lower heating value (LHV) can be determined by using a Parr adiabatic bomb. The lower heating value can also be obtained from the higher heating value by Equation (2):

$$LHV (J/g) = HHV (J/g) - 218.13 * H \% (wt. \%) \quad (2)$$

Generally, the higher heating value is reported. The higher heating value of pyrolysis oil (~16-19 MJ/kg) is about half of that of conventional fuel oil. The heating value increases as the water and oxygen content of pyrolysis oil decreases.

Pyrolysis oil densities range from 1.19 g/cm³ to 1.28 g/cm³ [MD94]. The density of pyrolysis oil is high compared to that of light fuel oil (density about 0.85 kg/liter).

A pH value between 2.5 and 3.5 is obtained for pyrolysis oils [RPS87], mainly due to different water contents and organic acids.

The flash point, which indicates the lowest temperature at which vapors above the liquid ignite when exposed to a flame, was reported by Adjaye and Bakhshi [AB96] to be between 53 °C and 76 °C for ENSYN pyrolysis oil. Diesel fuel flash points are known to range from 45 °C to 70 °C. Generally flash points above 50 °C are considered to be safe.

Small charcoal particles are present in pyrolysis oils because the gas evolved transports these particles from the cyclone to the collected oil during the pyrolysis process. Maggi and Delmon [MD94b] presented charcoal particles up to 3 wt. % in pyrolysis oils. The char yield increases with alkali and ash content of the feedstock. The most effective reduction of the amount of small charcoal particles as well as the ash content in the oil is by hot gas filtration. A detailed description of this method was presented by Diebold et al. [DCSPF94]. The ash content of pyrolysis oils is correlated to the char content of the oil. Generally, ash contents of pyrolysis oils are reported to be between 0.03 - 0.2 wt. %. By using hot gas filtration the ash content was lowered to below 0.01 wt. % [DSCPF96].

More than any other of the physical data mentioned, the viscosity depends on the age and water content of the pyrolysis oil. Viscosity values between 25 cSt and more than 1000 cSt were observed.

The pour point, indicating the lowest temperature at which a fuel can be pumped [Dyr93], is an important parameter for fuel applications. Oasmaa et al. [OLKLT97] reported pour points of hardwood and softwood pyrolysis liquids in the range from -12 °C to -33 °C.

Already in 1985 Elliott [Ell85] emphasized the strong correlation between moisture content and pour point of pyrolysis oils. However, the author showed that the viscosity of the oils investigated remained constant as the water content was reduced from 14 wt. % to 3 wt. %.

The color of pyrolysis liquids depends on initial feedstock, mode of flash pyrolysis, presence of carbon, and water content. Colors have been observed from light red-brown to almost black. The more carbon is present in the oil, the darker appears the color. Therefore, the color of pyrolysis oils is more transparent when char has been removed by hot gas filtration. High nitrogen content can give a dark green color to the pyrolysis liquid [Bri99]. The smoky smell of pyrolysis oils reminds of campfire and barbecue.

2.4.3 *Chemical composition of pyrolysis oils*

The composition of the pyrolysis liquids obtained correlate to that of biomass. Pyrolysis oils consist of molecules of different size as a result of fragmentation reactions of cellulose, hemicellulose, and lignin polymers. Because fragmentation of these building blocks results in a large amount of different components, pyrolysis liquids are complex mixtures of low molecular and high molecular weight compounds and water [SM88].

Due to the complicated composition of the pyrolysis oils, a range of analytical tools is necessary for analysis including spectroscopic, chromatographic, and wet chemical techniques. Reviews were published on the application of standard methods for analysis of fuel and pyrolysis liquids [OLKLT97] and about chemical and physical characterization techniques [Fag95]. For the determination of the physical properties of pyrolysis oils, most of the standard methods can be applied directly or after minor modifications [MOP99].

The main elemental components of pyrolysis liquids are carbon, oxygen and hydrogen. Oasmaa et al. [OLKLT97] measured elemental analysis data and calculated for the oil on dry 'basis' (i.e. water free pyrolysis liquid) in the following ranges: C wt. % = 48.0 – 60.4; H wt. % = 5.9 – 7.2; N wt. % = 0 – 0.1; O wt. % = 33.6 – 44.9.

The authors showed that nitrogen and sulfur contents are quite low, below 0.1 wt. % and 500 ppm on dry basis, respectively. The oxygen content can be determined directly. However, calculation of the oxygen content from pyrolysis liquids after CHN elemental analysis by the following equation (3) is preferred:

$$\text{O wt. \%} = 100 - (\text{C wt. \%} + \text{H wt. \%} + \text{N wt. \%}) \quad (3)$$

Due to the formation of char and gases the raw pyrolysis liquids (wet basis) contain less carbon and more hydrogen and oxygen in comparison to wood (49 % C, 6 % H, 45 % O). However, on a dry basis the organic material is richer in carbon and hydrogen than wood.

The main compound of pyrolysis liquids is water. The water content can be determined by different methods such as Karl-Fischer-titration, toluol distillation, and by GC analysis. Normally, the Karl-Fischer-titration is preferred. The water content of pyrolysis liquids is reported to be in the range between 15 and 35 wt. %. To obtain pyrolysis liquids with water contents below 30 wt. % the feedstock has to contain less than 10 wt. % water.

The method used most frequently for pyrolysis oil analysis is gas chromatography. However, this technique is limited to volatile products. Because volatility depends on the boiling point of a compound and on its polarity, only a part of the oil (up to 40 wt. % based on wet oil) can be analyzed by this technique.

Already in 1985 Elliott [Eli85] identified and quantified by GC analysis more than 100 different compounds in pyrolysis oils. The relative amount of each compound depends on the water content of the feedstock and the process parameters.

In 1987 Evans and Milne [EM87] showed by molecular beam mass spectrometer (MBMS) that the initial vapor state contains very few molecules with a molecular weight over 200 Daltons. However, after condensing the vapor the liquid exhibits a much higher molecular weight average (over 500 Daltons) as determined by size excluding chromatography. Pyrolysis oil was reported to possess an average molecular size in the range of 400-900 Daltons with individual components of even higher molecular size [JC88].

Already in 1988 nuclear magnetic resonance (NMR) was employed to study pyrolysis oils [MBC88]. It was the intention of the authors to demonstrate how NMR can be used to give information on the content of pyrolysis oils.

Nicolaides [Nic84] was the first to quantify carbonyl groups in bio oils by using the method described by Bryant and Smith. Nicolaides reported carbonyl group data of pyrolysis liquids to be in the range of 3.8-6.3 mol carbonyl groups per kg oil sample.

Because the measurement of acid numbers is a standard method for fats and tars it is sometimes also used for pyrolysis liquids. Knight et al. reported acid number values for pyrolysis oils between 60 and 70 mg KOH/g [KHE77].

2.4.4 Behavior of pyrolysis oil with temperature and time

Pyrolysis liquids exhibit considerable changes in their chemical composition with time and temperature. Because pyrolysis oils contain a large amount of functional groups, polymerization and other reactions take place during storage. Hence, compared to fossil fuels pyrolysis liquids possess an inferior long-term stability. Because the time rate of chemical reaction increases with temperature, distillation of pyrolysis oils is not feasible, only to certain extent. Polymerization in pyrolysis liquids is strongly accelerated when they are heated to 80 °C or more. Only a small fraction of the volatile compounds could be removed from pyrolysis oil by distillation leaving behind a high viscose char residue [Wul95]. Thus, it has to be expected that the physical properties (e.g. viscosity) of pyrolysis oils may be significantly altered by any extended temperature treatment. Peacocke showed that the density of pyrolysis oil decreases from 1.205 g/cm³ at 20 °C to 1.150 g/cm³ at 80 °C [Pea94].

The change of physical properties of pyrolysis oils with time is denoted ‘aging’ in the following. Aging studies [Cze94] have shown that molecular weight and viscosity of pyrolysis oil increase with time. The properties and composition of pyrolysis oils are changed with time by the influence of heat, air, and light. To date polyaddition, polymerization, and condensation reactions during aging in pyrolysis oils have not been investigated in detail. Maggi et al. reported that mainly the C-C double bonds in aldehydes, ketons and carbon acids are responsible for the aging of pyrolysis oils [MD94]. As a result pyrolysis oils become more viscous with time and form an undesirable sludge. Therefore, storage of pyrolysis oils is restricted and use of the material for further processing is limited. Because aging of pyrolysis oils is unfavorable for many applications, long-term stability of pyrolysis oils is the subject of a large amount of ongoing research. Several authors studied the aging process of pyrolysis oils after hydrogenation [LPGD92, MD94, Bri94]. Since the early eighties, different authors investigated the possibility of changing the stability of pyrolysis oils by adding catalyst to the fuel during the pyrolysis process [Mar84, Die91]. In addition, stability of pyrolysis oils is influenced by the water content [Fag95]. Adjaye and Bakhshi [AB96] performed stability tests with ENSYN oil and monitored the changes in density, viscosity, pH, and distillation characteristics over a one year period. The pH and density values remained almost unchanged whereas the viscosity increased from 84.5 cSt (after 1 month) to 150.8 cSt (after 5 months) and to 162.3 cSt (after 12 months). These results show that the composition of the pyrolysis

oil changed rapidly after production but approached a stable composition after about 6 months.

2.4.5 Behavior of mixtures of pyrolysis oils with water

2.4.5.1 Introduction

Pyrolysis oils possess limited miscibility with water. Of course, the amount of water, which can be added to pyrolysis oil without resulting in phase separation, depends on the amount of water in the oil.

2.4.5.2 Two or more liquid phases

Typically, phase separations take place when the water content of pyrolysis oil is more than 35 – 40 wt. %. However, water contents below 35 wt. % do not guarantee a single phase pyrolysis oil. Increasing water content results in an increasing pH value and a decreasing heating value and decreasing viscosity [Fag95].

2.4.5.3 Liquid smoke

About two thirds of pyrolysis oil is water soluble. This solution of the water soluble molecules of pyrolysis oil is known as liquid smoke. Liquid smoke can be used as source of smoke flavors and browning agents [Rad99]. It reacts with proteins resulting in skin formation, brown color development, and flavor perception. Certain liquid smoke fractions have anti-microbial and anti-oxidant properties [Ram00]. Properties of liquid smoke were reviewed in 1984 by Toth and Potthast [TP84].

Piskorz et al. [PMR99] stated that water-soluble chemicals typically present in liquid smokes can only be determined by High Performance Liquid Chromatography (HPLC) if present in concentrations greater than 1 wt. %. Following the discovery of fire, the bacteriostatic and preservative properties of wood smoke were utilized. To date this knowledge is still used for the production of foodstuff like bacon and ham. By this process food obtain flavor, color, and aroma. Piskorz et al. emphasized, referring to a study by Scott [Sco86], that pyrolysis liquids are not carcinogenic or mutagenic. The results of Scott indicate that fast pyrolysis liquids do not contain hazardous levels of carcinogenic benzopyrans, although pyrolysis liquid is toxic to the organisms tested.

Kiln or plate type generation technology is commercially used for liquid smoke and smoke extract production. Tars are known to be troublesome in conventional smoke production [NB88]. The use of fast pyrolysis liquid produced in fluidized beds for food applications have been described by Underwood and Graham [UG89].

In 2000 Ramakrishnan [Ram00] reported that Hickory Specialities Incorporated (USA) was pyrolyzing hardwood sawdust in specially designed furnaces and produced liquid smoke by condensing the obtained vapors using water. The water insoluble tars and polynuclear aromatic hydrocarbons (PHA) were removed through a multi stage filtration process. The liquid smoke obtained had a pH value of 2-3.

2.4.5.4 Pyrolytic lignin

When biomass undergoes rapid pyrolysis, about 80 % of the lignin present is depolymerized, vaporized, and appears in solution in the liquid product [PMRS89]. Adding water to fast pyrolysis liquids results in separation into an aqueous and an organic phase. The latter is a adhesive brown tar containing the high molecular weight compounds derived from lignin. Radlein et al. were the first to record a ^{13}C -NMR spectrum from the 'tar' [RPS87; PSR88]. Because it looked similar to that of lignin, the material was named 'pyrolytic lignin'. The comparison of the spectra of milled wood lignin and the spectra of pyrolytic lignin show a clear progression in degree of degradation. Piskorz et al. [PMRS89] reported that yields of pyrolytic lignin may depend on the composition of the biomass. The authors found yields of pyrolytic lignin ranging from 16 % to 22 %.

In order to determine the content of pyrolysis lignin, two different methods exist: the addition of water to the oil [CP99] or the slow addition of pyrolysis liquid to water [MS97; OLKLT97; SKFO98]. Because the latter is more suitable for analytical investigations, it was employed in this work. However, to date there is no standardized procedure for the preparation of homogeneous pyrolytic lignin. Identifying the composition and the structure of pyrolytic lignin may be essential for investigations regarding aging of pyrolysis oils. Evidently, derivatisation of aromatic compounds with various functional groups can facilitate reactions to larger molecules. Lignin, for instance, condenses to larger molecules upon adding formaldehyde to its alkaline solution [Pan98]. In addition, the nature of aerosol, the generation of oligomers from biomass by pyrolysis and whether these compounds are formed by

recombination of low molecular weight compound or directly ‘ejected’ during pyrolysis is still under debate [LDPP99; PMR99, SHM01].

2.5 Practical applications

2.5.1 Introduction

Direct combustion of wood can be used for heating and for steam production to generate electricity. Fuel gas obtained from biomass gasification can be applied in engines and turbines for generation of electricity or for direct heating. Liquid fuels obtained from pyrolysis of biomass can replace fossil fuel oil in heating or generation of electricity. Additionally, pyrolysis liquids are a pool for various chemical compounds.

However, if bio fuels became economically competitive, they would open up an enormous market window for several bioenergy products. Therefore, the improvement of pyrolysis oil is an important subject for research and development (R&D) in academia and industry. An overview of application for pyrolysis oils is given in Figure 11.

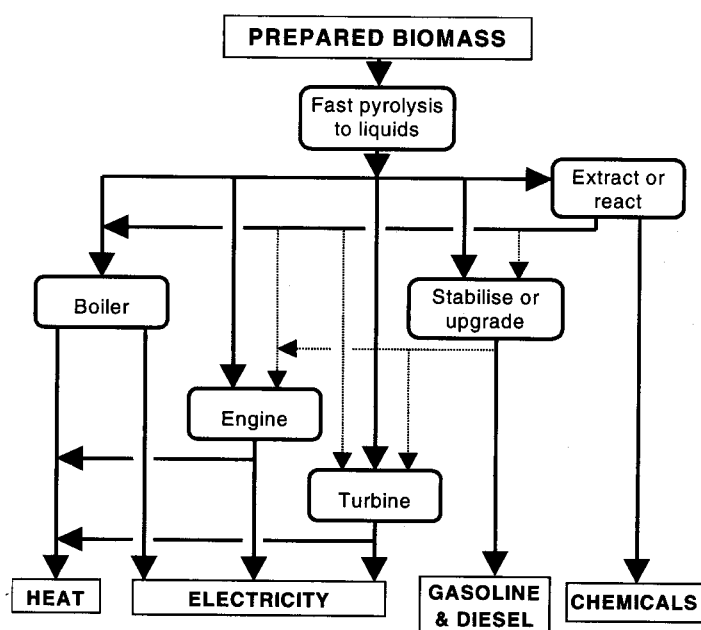


Figure 11: Applications for bio oil (thicker lines have been demonstrated; thinner lines are possible) [Bri99].

Pyrolysis oil may replace conventional fuel oil in boilers or can be upgraded by hydrogenation to hydrocarbon fuels or to extract various fine chemicals. To date the long-term stability of pyrolysis oils does not warrant their application as liquid fuels. This is partially due to the fact

that production, handling, and storage of bio oils are not standardized in any way. In addition to the production and potential application of pyrolysis liquids, gasification of biomass has been studied extensively. However, because gasification was not in the focus of this work, no detailed account of the wealth of information available on this subject is presented here.

2.5.2 *Liquid fuels from biomass*

Flash pyrolysis oil is a potential fuel to be used in boilers, gas turbines or diesel engines. Based on the present knowledge of the properties of primary flash pyrolysis oil, it can be roughly classified somewhere between light fuel oil (LFO) and low sulfur heavy fuel oil (LSHFO). In general, flash pyrolysis oil contains less sulfur, is less viscous, and has a lower pour point than heavy fuel oil. Moreover, under appropriate conditions it can be combusted with simple mechanical vaporization equipment. However, compared to light fuel oil it possesses the following disadvantages:

- Difficult to ignite
- High viscosity
- Low energy content
- Poor stability when exposed to air or elevated temperatures
- Low pH, corrosive, and poor lubricity
- Higher emission using simple mechanical vaporization

While choosing the appropriate equipment and materials can control some of these problems, it is unlikely, that untreated, primary flash pyrolysis oil can meet the requirements of a residential heating fuel oil. Replacement of heavy fuel oil is possible but this would be economically more difficult and would require the use of feedstock with zero or negative costs i.e. waste utilization [Gus96].

The costs of bio oils have been analyzed over a range of plant sizes and feed costs. The calculated costs include all processing steps from receiving wet tree chips through preparation and pyrolysis, and the storage of cold oil. The collected data were reduced to a simple equation (4) and presented by Bridgwater [Bri99]:

$$\text{Bio Oil Cost} = 8.87 * (\text{Wood Capacity, dry [t/d]})^{-0.3407} + \frac{(\text{Feed Cost [ECU/dry t]})}{0.625 * \text{Wood LHV [GJ/t]}} \quad (4)$$

[ECU/GJ (LHV)]

Equation 4 expresses the bio oil cost in lower heating value terms and in ECU 1998 costs. For the calculation a higher heating value of 19 GJ/t and a bio oil energy yield of 62.5 % was expected. The exchange rate to US dollars is US\$ 1.15/ECU.

Up to now, bio diesel and bio alcohols have been used commercially in Brazil, the United States, and Central Europe. Bio alcohol is mainly produced from corn and wheat. Wood-based alcohol is still under investigation [SOSAN99].

Certain limitations in particular regarding viscosity and solid content must not be exceeded if pyrolysis oils are to be burned in boilers and burners, and blocking of nozzles is to be prevented. Because of the aging of pyrolysis oil during storage the main problem is to keep nozzles operational after shut down. Additionally, small scale boilers normally contain no equipment to preheat the oil. In contrast, diesel engines and heavy fuel oil boilers have preheating up to 150 °C. Sipilä et al. showed for heavy fuel and light fuel nozzles that the viscosity should be below 20 cSt and 10 cSt, respectively [SOSAN99]. Although adding alcohol can reduce the viscosity, safety reasons (i.e. the increasing flash point) limit the addition of alcohol to pyrolysis oils for commercial application.

Since the early nineties combustion tests were performed in special scale burners [Gus97, KS91, WPY94, SH97]. Different groups were able to show that pyrolysis liquids can be burnt either in standard or in slightly modified equipment [SNG94, SOAWSAGNG96]. Nevertheless, modified boilers or burners are more expensive than commercial ones. With slight modifications of the burners, carbon monoxide and nitrogen oxides in exhaust gases were reduced to acceptable levels: CO < 50 ppm and NO_x < 140 ppm [Gus99]. The results of Gust show that particle emission was more than two times higher than from light fuel oil but still notably less than from small wood scale combustion. For reduction of particle emission to the light fuel oil level, combustion system need to be improved and the pyrolysis liquid need to be upgraded. Ormrod Diesel in the United Kingdom possess a long standing experience in long term test of burning pyrolysis oils in diesel engines [Lee97]. Irrespective of the economic situation up-to-date bio oils exhibit problems in storage, handling, and combustion that limit their practical applications. Moreover, quality description and standards for pyrolysis liquids for commercial applications, as required by the end users, are still lacking [RV91, DMCBCGHP97].

Two-phase pyrolysis oils results in considerable problems for commercial utilization. Two-phase oils consist of a high water content phase and, a more viscous low water content

phase. Both phases cause several problems in boilers and burners. The upper phase exhibits a small heating value and particular methods for flame stabilization are required. The lower phase, which possesses a higher density, generates pumping problems because of the higher viscosity.

To date there is minor industrial interest in new biomass power plant investments because of the low-price power available. However, this situation may be changed in the future by a common CO₂ tax in Europe. Because nowadays, heavy fuel oil is priced lower than light fuel oil (because of the lower tax than for light fuel oil) the intention is to replace the latter. However, the company FORTUM (Finland) is building up a 500 kg/h pyrolysis plant.

2.5.3 Chemicals from pyrolysis oil

Isolating special chemicals from bio oils requires that they are provided in sufficiently large quantities. Otherwise the recovery process is not economically useful. The majority of compounds in pyrolysis oil are hydroxyacetaldehyde, acetic acid, formic acid, and levoglucosan (1,6-Anhydro- α -D-glucopyranose). The chemical formula of the latter is shown in Figure 12. Other highly valued specially products that can be produced from bio oil are food flavors, adhesives, and fertilizers [HGG00, CRWRLC00, ARCLPA99, Bri99].

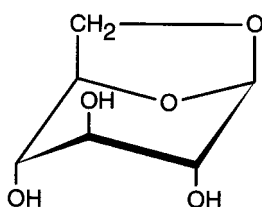


Figure 12: Chemical formula of levoglucosan.

Several research groups [Moe95, RPS91, Rad99] described the recovery of levoglucosan from pyrolysis oils. The yield of levoglucosan from wood can be improved by traces of acid catalysts. Levoglucosan is known in carbohydrate chemistry as a chiral synthon. Radlein gives further information on the application of levoglucosan [Rad99].

Liquid smokes for food flavoring and browning applications are traditionally produced by pyrolysis and partial combustion systems. In 1953 Hodge [Hod53] presented the most effective browning agents: glucoaldehyde, glyceraldehydes, pruvalldehyde, dihydroxyacetone, acetoin, and diacetyl. Because these compounds are also present in bio oils these oils can be

used as a source of smoke flavors and browning agents. Underwood and Graham were the first to patent this process in 1989 and 1991 [UG89, UG91]. Scott [Sco86] had reported earlier that fast pyrolysis liquids do not contain dangerous levels of carcinogenic benzopyrans.

2.5.4 Char from biomass

The particle size of the char formed during pyrolysis of biomass depends on the particle size of the feed used, the mechanism of char formation, and the attrition of the char by the pyrolysis reactor system. After the char is removed from the process gases and vapors that exit the reactor, it is collected in a cyclone. Char produced by pyrolysis of biomass and possessing a small particle size is highly flammable, similar to powdered coal. In fast pyrolysis processes, char is mainly used as an energy source for heating the reactor. The auto ignition temperature of biomass charcoal is typically between 200°C and 250°C [DB99]. Therefore, hot char received from the pyrolysis process should be handled with care to avoid self-ignition. Before it can be shipped commercial charcoal must be stored for several days exposed to air to prevent accidental ignition from exothermic oxygen adsorption during transit [Bro86].

2.6 Upgrading of pyrolysis oils

2.6.1 Introduction

Various methods exist to modify the properties of pyrolysis oil, for example, to reduce its viscosity and, therefore, to make the oil more suitable for combustion applications. Physical methods include hot-gas filtration, char removal in the gas phase, liquid filtration, and solvent addition. Chemical methods are, for example, reactive solvent addition and catalytic upgrading of pyrolysis vapors as well as of the crude pyrolysis oil by hydrogenation.

2.6.2 Hot-gas filtration

During the pyrolysis process, the char formed is generally separated from vapors and gases by using cyclones. However, for small particle sizes, cyclones are not effective enough in removing solids from vapors. Therefore, hot-gas filtration has been proposed as a more effective method. Char and ash removal from the hot gases during pyrolysis affords a pyrolysis oil with a very low content of solids which minimizes catalytic side-effects during oil storage such as condensation and polymerization reactions [ABE94 and DCSPF94]. The

filters used for hot gas filtration are made of sintered metal and flexible ceramic, and are operated at 400°C - 420°C [CMP99]. As a drawback, hot-gas filtration results in a yield of pyrolysis oil that is about 10 % less than that obtained by the same reactor system using a cyclone. Nevertheless, the advantage of hot-gas filtration lies in a lowering of both the viscosity of the pyrolysis oil and the rate of viscosity increase during storage. However, hot-gas filtration has not yet been demonstrated in long-term operation. Therefore, new developments are needed to make this technology suitable for commercial processes.

2.6.3 Vapor phase catalytic reactions

Since the end of the nineteen eighties, catalytic reactions in the vapor phase during the pyrolysis processes have been discussed [SPBGO88, SCPR90, SPR93, BC92, BC93, SGV92, SV94, MLGD92]. However, only few studies exist, where upgrading of the vapor phase after the pyrolysis process was investigated using mostly zeolite materials as catalysts.

Employing catalysts in a fluidized bed reactor during pyrolysis of biomass was described in some detail by Katikaneri et al. [KAIB97]. In their experiments, the authors used the solid catalyst (for example HZSM-5) as fluidizing material in the pyrolysis reactor, while the biomass was introduced into the reactor from the top. The liquid pyrolysis product and the gas were separated and collected. In addition, in 1997 Katikaneri et al. presented results on the catalytic upgrading of pyrolysis oil produced from maple wood by the RTP™ process from ENSYN Technologies Inc. [KIB97]. Zeolites and silica-alumina catalysts were used for these investigations. On the one hand, the zeolite HZSM-5 afforded the highest selectivity for aromatic hydrocarbons and the highest yield of 'organic liquid product'. On the other hand, the silica-alumina catalyst exhibited the highest selectivity for aliphatic hydrocarbons. Williams and Horne and Williams et al. presented investigations on the vapor phase upgrading of pyrolysis oils in the presence of zeolites [WH95, WNH97]. The aim of this study was to reveal whether upgrading in the presence of zeolites increased or decreased the formation of hazardous polycyclic aromatic hydrocarbons (PHA). Apparently, using zeolites for vapor phase upgrading, in particular in the presence of steam, resulted in an increased formation of PHAs. In addition, the yield of pyrolysis oil decreased, while an increased char and gas formation was observed. In 1999 Wulzinger confirmed these results [Wul99].

Radlein et al. presented a study on the pyrolysis of biomass and celluloses in a fluidized bed reactor in the presence of catalysts and hydrogen [RMPS91]. Various oxides or

reduced metal catalysts (such as Fe, Ni, Co, Zn, Cr, Mo, W, Si, Ti, Al, and Mg) were used and afforded a sufficiently high yield of hydrocarbons even under 'nonoptimized' conditions. Leppämäki et al. described a rapid technique to pre-screen catalysts for the vapor phase upgrading of pyrolysis oils [LKKN97]. For the pyrolysis experiments, a Pyroprobe 1000 pyrolyser was directly connected to a gas chromatograph. The injection port of the GC was used as a fixed bed reactor and the catalyst was placed into the liner tube of the GC injector. Wulzinger [Wul99] employed this technique to investigate the effect of a number of different catalysts on the pyrolysis process.

Vapor phase upgrading experiments in a fluidized bed reactor using various catalysts (zeolite, slate, char, magnesium acetate on pumice stone) were described by Salter et al. [SWBM99]. During the pyrolysis process, the catalysts were introduced by co-feeding with the feedstock, replacing the fluidizing sand, or by adding a close-coupled reactor to the fluidized bed reactor. The authors concluded that the most stable pyrolysis oil was produced using a thermally expanded slate fluidized bed. In 1999 Wulzinger was able to confirm these results on a larger scale [Wul99].

In total, the studies described above are difficult to compare with each other because of the complex composition of the pyrolysis oils used and the insufficient structural characterization thereof. Furthermore, many of the investigations mentioned focused on different characteristic properties of the pyrolysis oil. However, in order to improve the suitability of pyrolysis oil for technical applications it is of paramount importance to gain a deep understanding of the structure and the characteristic chemical reactions of pyrolysis oils. Only based on this knowledge, it will be possible to tailor the properties of pyrolysis oils to become more stable during the necessary transportation and storage.

2.6.4 Hydrogenation of pyrolysis oils

Hydrogenation of pyrolysis oils may be a promising way to obtain high quality bio oils. A brief overview on different methods for mild hydrogenation of pyrolysis oils has been recently presented by Meier et al. [MBDP97]. Already in 1988 Gagnon and Kaliaguine described mild hydrogenation tests of vacuum pyrolysis oil in the presence of a commercial ruthenium on γ - Al_2O_3 catalyst and a copper chromite catalyst [GK88]. The authors showed that for hydrodeoxygenation the optimum temperature is as low as 80 °C. Boocock et al. presented a study on removing and/or modifying the phenolic and methoxy groups in pyrolysis oils

[BACF88]. Molybdenum oxide / cobalt oxide on α -alumina and molybdenum oxide / nickel oxide on α -alumina were used as catalyst both in their sulfided and in their unsulfided forms. It was found that using the sulfided cobalt oxide catalyst resulted in the greatest loss of methoxy groups in the pyrolysis oils obtained. In 1988 Baker and Elliott presented investigations on catalytic hydrogenation of biomass-derived oils [BE88]. By using a batch reactor and a sulfided cobalt molybdenum oxide catalyst for the deoxygenation of pyrolysis liquids, it was possible to deoxygenate pyrolysis liquids by catalytic hydrogenation. However, it turned out that a low temperature catalytic pre-treatment step is required. In 1997 Baldauf and Balfanz from the VEBA OEL AG presented hydrogenation test of pyrolysis liquids [BB97]. The authors concluded that hydrogenation could not be recommended for the upgrading of pyrolysis oil because hydrogenation in a fixed bed reactor is not feasible and the upgrading costs are extremely high compared to fossil fuel available. However, at the point when fossil fuel resources begin to dry out, higher upgrading costs may actually become economically competitive and, hence, acceptable. Until then, maybe new catalysts can be developed that are less expensive and afford good results in the hydrogenation of pyrolysis oils.

To err is human but to really foul things up
requires a computer.

Anonymous

Farmers' Almanac for 1978

"Capsules of Wisdom"

3 Experimental

3.1 Pyrolysis laboratory plant and material

The beech bio oil, which was used for stability tests (see chapter 4.1.2), was produced in a 100 g/h pyrolyser in the Institute for Wood Chemistry and Chemical Technology of Wood, Hamburg.

Table 2: Organization, feedstock and production process of different pyrolysis oils.

Organization	Feedstock	Process
Federal Research Center for Forestry and Forest Products, Institute for Wood Chemistry (IWC), FRG	beech	fluidized bed
ENSYN Technologies Inc. (ENSYN), Can	mixed hardwood	fluidized bed
Union Electrica FENOSA (FENOSA I), E	eucalyptus	fluidized bed
Union Electrica FENOSA (FENOSA II), E	wheat/straw	fluidized bed
Aston University (ASTON), UK	poplar	ablative pyrolysis
National Renewable Energy Laboratory (NREL) ^a , US	poplar	ablative pyrolysis
Twente University (BTG), NL	mixed softwood	ablative pyrolysis
Technical Research Center of Finland (VTT), Fin	pine	fluidized bed

^a hot filtered oil

S. Wehlte [Weh97] determined the parameters for optimal operation of the plant used and produced the pyrolysis oil. Beech wood with a particle size of 350 μm to 500 μm was pyrolyzed at 475 $^{\circ}\text{C}$. The pyrolysis liquid was collected in two containers during the process and afterwards the laboratory plant was washed with methanol. The pyrolysis liquid from the methanol solution was retrieved by distillation.

The beech pyrolysis oil fractions used for the stability tests described in chapter 4.1.4, were produced in a 5 kg/h pyrolyser in the Institute for Wood Chemistry and Chemical Technology of Wood, Hamburg by T. Ollesch.

The other pyrolysis oils used for the investigations presented in chapter 4.1, 4.3 and 4.4, were obtained from different organizations. The origin of these pyrolysis oils, the feedstock, and the processes are shown in Table 2.

The upgrading tests of the catalytic vapor phase were performed in a 100 g/h pyrolyser in the Institute for Wood Chemistry and Chemical Technology of Wood. The schematic representation of the laboratory plant is depicted in Figure 13. Beech wood with a particle size of 150 μm to 500 μm was pyrolyzed at 475 $^{\circ}\text{C}$ over half an hour. The pyrolysis liquid was collected in one container and the pyrolysis oil was collected for 1 hour after the end of the run. To increase the yield the oil obtained was investigated without adding any solvents like methanol.

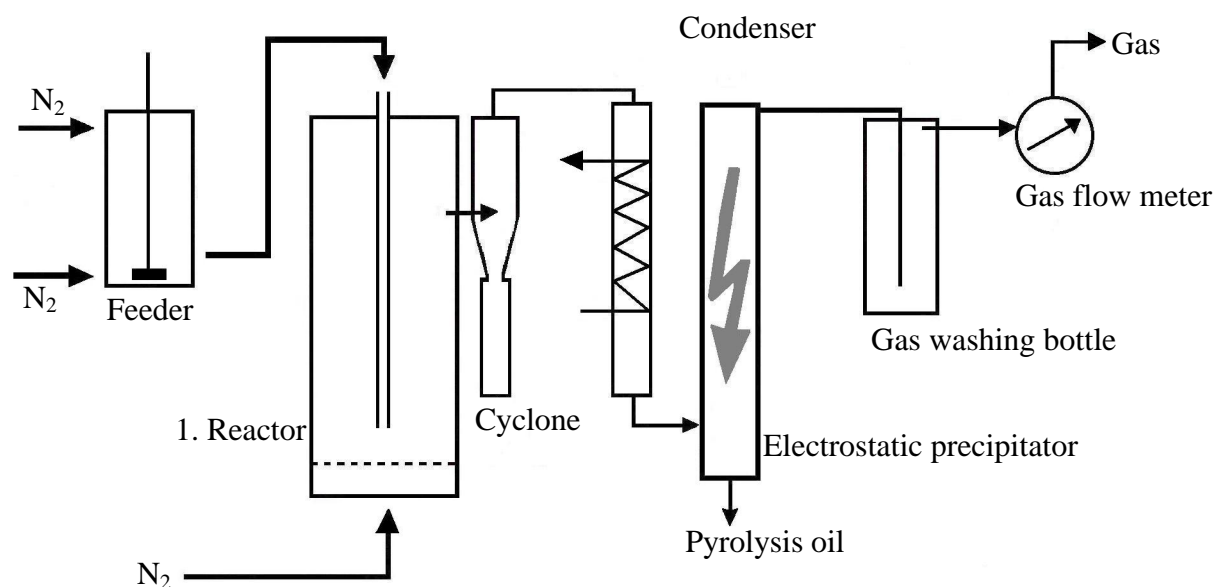


Figure 13: Schematic representation of 100 g/h laboratory plant at IWC.

3.2 Preparation of catalysts

The catalysts employed were prepared according to the incipient wetness technique. Therefore, the corresponding metal chloride was dissolved in water and, subsequently, the slate was treated with the solution obtained. After incipient wetness and drying, the slate was calcined in a wet air stream at 500 °C in order to obtain the corresponding metal oxides supported on the slate.

3.3 Preparation of pyrolytic lignin

Pyrolytic lignin was obtained from pyrolysis oil by dropwise adding 60 ml of the oil to 1000 ml of ice-cooled water in a rate of ca. 1.0 ml/min while stirring the liquid with an ultra turrax (oil to water ratio must be at least 1:10, turrax speed 6000 r.p.m). A schematic diagram of the experimental setup is depicted in Figure 14.

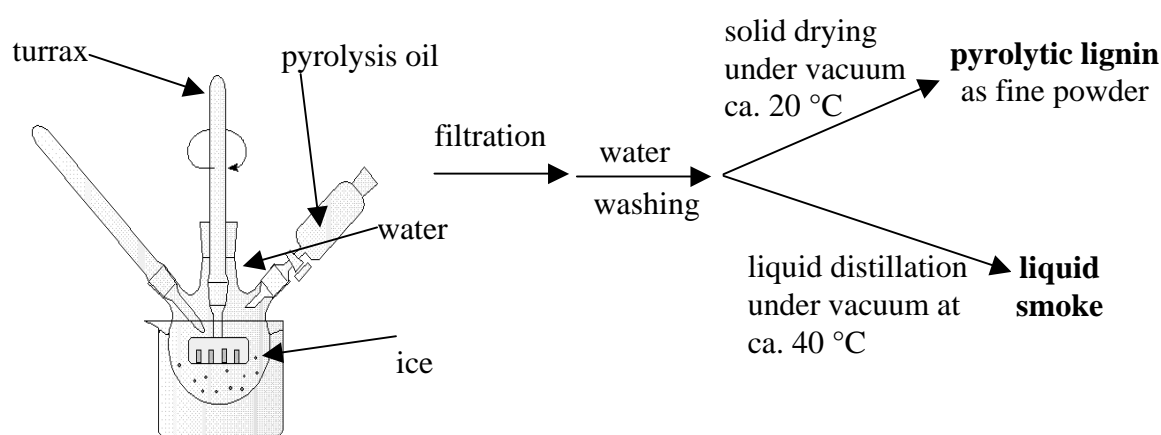


Figure 14: Schematic diagram of the setup used for the production of liquid smoke and pyrolytic lignin.

After slowly adding the pyrolysis oil to water, pyrolytic lignin precipitated. After precipitation the liquid smoke (water soluble part of pyrolysis oil) is dissolved in a large amount of water. The water insoluble fraction was filtered with a Büchner funnel. Subsequently, the pyrolytic lignin was resuspended in water under stirring for about four hours. The solution was filtered and the wet pyrolytic lignin was dried under vacuum at 298 K. Because reproducibility of pyrolysis oils is still under investigation, all pyrolytic lignins in this study were produced only once. The origin of the eight pyrolysis oils used for the preparation of pyrolytic lignin is shown in Table 3. Additionally, several properties of the pyrolysis oils used are presented.

Table 3: Origin, feedstock, water content, elemental analysis and higher heating value (HHV) of pyrolysis liquids used for preparation of pyrolytic lignin.

Organization	Feedstock	Water content [wt.%]	Elemental analysis ^a				HHV [MJ/kg]
			C [wt.%]	H [wt.%]	N [wt.%]	O [wt.%] ^b	
Federal Research Center for Forestry and Forest Products, Institute for Wood Chemistry (IWC), FRG	beech	31.9	54.35	6.80	0.22	38.63	21.2
ENSYN Technologies Inc. (ENSYN), Can	mixed hardwood	26.4	59.89	5.98	0.34	33.79	22.8
Union Electrica FENOSA (FENOSA) I, E	eucalyptus	25.6	54.44	6.10	0.39	39.07	20.2
Union Electrica FENOSA (FENOSA) II, E	wheat/ straw	36.0	53.53	6.42	0.64	39.41	20.3
Aston University (ASTON), UK	poplar	16.1	53.55	6.50	0.35	39.60	20.3
National Renewable Energy Laboratory (NREL) ^c , US	poplar	16.3	56.20	6.64	0.30	36.86	21.9
Twente University (BTG), NL	mixed softwood	18.6	54.84	6.51	0.39	38.26	21.0
Technical Research Center of Finland (VTT), Fin	pine	17.4	55.23	6.60	0.11	38.06	21.3

^a based on water free oil; ^b calculated by difference; ^c hot filtered oil

3.4 Analytical methods

3.4.1 Gas chromatography (GC)

The GC-FID measurements were performed with a CHROMPACK system CP9000. Helium was used as a carrier gas at a pressure of 2 bar and the products were separated by a DB 1701 (from J&W) 60 mm × 0.25 mm capillary column with 0.25 µm film thickness. The oven temperature was kept isothermal for four minutes at 45 °C, then increased to 280 °C at

3 K/min, and finally kept at 280 °C for 15 min. The injector temperature and the detector temperature were 250 °C and 280 °C, respectively.

3.4.2 Gas chromatography - mass spectroscopy (GC/MS)

The GC/MS measurements were performed on a MSD 6890 system from HEWLETT PACKARD. Helium was used as a carrier gas with a constant flow of 1 ml/min. The measurements were performed using a 60 m * 0.25 mm capillary column (Chrompack DB 1701) with 0.25 µm film thickness. The oven temperature was kept isothermal for four minutes at 45 °C, then increased to 280 °C at 3 K/min, and finally kept at 280 °C for 15 min. The injector temperature and detector temperature were 250 °C and 280 °C, respectively. The compounds were identified by their retention time and/or by comparison to mass spectra of well known compounds. For this particular purpose the Institute of Wood Chemistry has assembled a mass spectra library containing a large number of spectra of various organic compounds probably present in pyrolysis oils.

3.4.3 Analytical pyrolysis - gas chromatography - mass spectroscopy

Already in 1988 Faix et al. [FMF88] presented analytical pyrolysis. The analytical pyrolysis experiments with pyrolytic lignin described in this work were performed using a Pyroprobe 100 (CDS) directly coupled to a HP GC/MSD series 6890. The schematic representation is depicted in Figure 15. Helium was used as carrier gas. Approximately 60 µg of the sample to be pyrolyzed were placed in a quartz tube (2.5 cm * 2 mm).

In order to avoid undesirable secondary reactions a short pyrolysis time was chosen. For transferring pyrolysis products as quickly as possible from the hot zone of the pyrolysis chamber to the GC column, the chamber was purged with helium. A pyrolysis temperature of 450 °C was employed at a heating rate of 1000 K/s. The analytical pyrolysis was performed using a 60 m * 0.25 mm capillary column (Chrompack DB 1701) with 0.25 µm film thickness. This column was chosen for its good separation properties of pyrolysis products from wood. The oven temperature was kept isothermal for four minutes at 45 °C, then increased to 280 °C at 3 K/min, and finally kept at 280 °C for 15 min. The injector temperature and detector temperature were 250 °C and 280 °C, respectively. Pyrolysis products were identified by their retention time and/or by comparison to mass spectra of well known compounds.

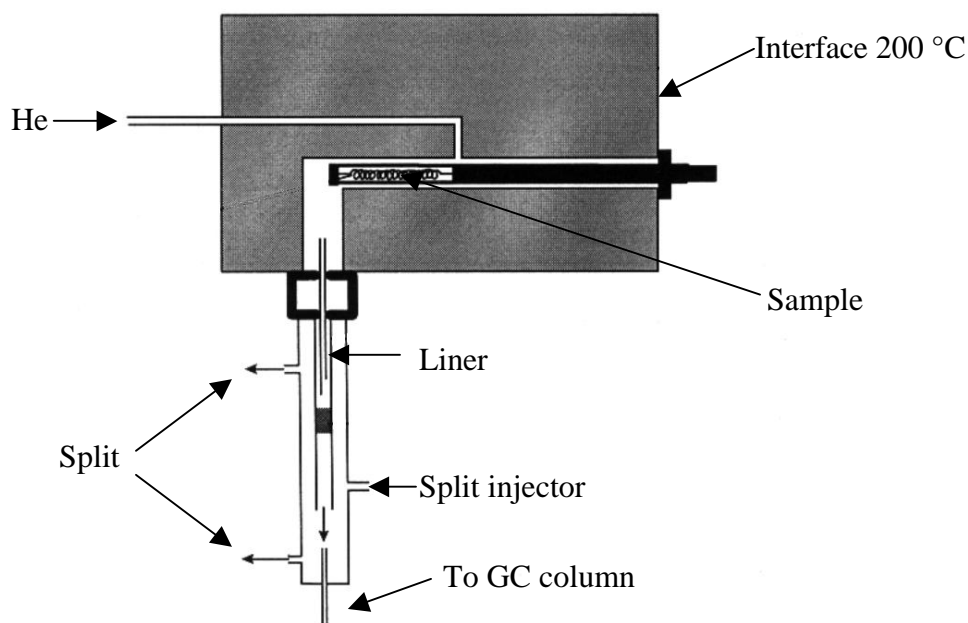


Figure 15: Schematic representation of a Pyroprobe for analytical pyrolysis of pyrolytic lignin [Wul99].

3.4.4 Fourier transform infrared spectroscopy (FTIR)

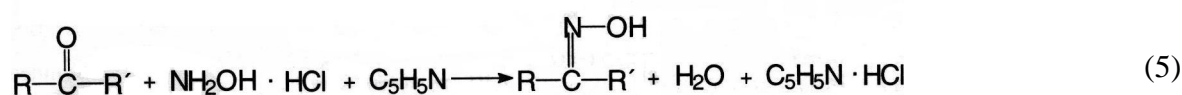
Pyrolysis oils and pyrolytic lignins were investigated by FTIR spectroscopy using a BIORAD FTIR model FTS-40. For each sample 32 spectra accumulated between 4000 cm^{-1} and 400 cm^{-1} were averaged. The resulting spectra were normalized to the highest peak in the 'fingerprint region' between 2000 cm^{-1} and 700 cm^{-1} . ZnSe windows from PERKIN ELMAR were used for liquid samples. For the fine pyrolytic lignin powders about 2 mg of the dried sample were carefully mixed with 300 mg of dry KBr and pressed into a self-supporting pellet.

3.4.5 Elemental analysis

Elemental analysis of carbon, hydrogen and nitrogen contained in the pyrolysis oils was performed using equipment from HERAEUS (Model: CHN-O-RAPID). Because of the pyrolysis mechanism and the feedstock used, the oxygen content of the pyrolysis oils was very high. The oxygen content was calculated by a difference equation. Because the oils have different water contents, the elemental analysis was additionally calculated on a water free basis.

3.4.6 Carbonyl groups

Nicolaides [Nic84] determined the amount of carbonyl groups in bio oils by using the method described by Bryant and Smith. In this work a slightly modified version of the method used by Nicolaides was employed to determine the amount of carbonyl groups in pyrolysis oil, pyrolytic lignin, and liquid smoke. Depending on the estimated amount of carbonyl groups in the pyrolysis oil (2.5 g - 4.5 g) and the pyrolytic lignin (1 – 3 g), the sample was weighted, with an accuracy of 0.1 mg into an erlenmeyer flask. The samples were mixed with solution of 50 ml hydroxylamin hydrochloride in ethanol (35 g hydroxylamin hydrochloride in 1 liter ethanol) and 100 ml pyridine in ethanol (20 ml pyridine in 1 liter ethanol). Subsequently, these mixtures were stirred for about 18 hours at room temperature. Afterwards, the liberated hydrochloric acid in the mixture was titrated with standard 0.1 N sodium hydroxide solution in an automatic Schott® titrator (Titroline alpha). Hydroxylamine hydrochloride reacts with carbonyl groups by forming an oxime and releasing hydrochloric acid. As shown in equation 5 one carbonyl group yields 1 molecule of hydrochloric acid in the form of pyridine hydrochloride. In this reaction the complete formation of the oxime is aided by pyridine which binds to the hydrochloric acid and, hence, prevents hydrolysis of the formed oxime.



Subsequently, the total carbonyl content can be obtained by titration of the formed hydrochloric acid. In order to define the pH of the end point of the titration of the carbonyl groups, the quantification was additionally performed with 3-Hydroxy-benzaldehyde as a calibration standard. Knowing the number of carbonyl groups in 3-Hydroxy-benzaldehyde the pH value at the titration end point was calculated. This pH-value was then taken as endpoint for the titration of the different samples.

On the one hand, a large number of different aromatic and aliphatic aldehydes and ketones can be successfully analyzed by the method described. On the other hand, carboxylic acids and esters do not react because the oximation reaction is specific to the carbonyl group of aldehydes and ketones. Thus, by the procedure employed the titration afforded only a relative measure for the purpose of comparison of the amount of carbonyl groups in the oil samples, the pyrolytic lignins, and the liquid smokes investigated in this work.

3.4.7 Hydroxyl groups

The amount of hydroxyl groups in the pyrolytic lignin was determined according to a method described by Verley and Bölsing [VB01]. 50 mg pyrolytic lignin were acetylated with a solution of 0.5 ml pyridine and 0.5 ml acetic anhydride at a temperature of 50 °C. The liquid obtained was mixed with 15 ml acetone and 1 ml water, and the solution was titrated with sodium hydroxide.

3.4.8 Methoxyl groups

Methoxyl groups were determined according to the method described by Vieböck and Schwappach [VS53]. When heated with hydroiodic acid, methoxyl groups react to form methyl iodide. The latter is distilled into a solution of sodium acetate and bromine in acetic acid. The resulting iodine acid is then reacted with potassium iodide, and subsequently the iodine formed is titrated. For each methoxyl group three Iodine molecules, I_2 , which are determined by titration with thiosulfate, are formed, which make this method very accurate and suitable for the work described here.

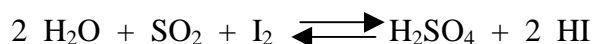
3.4.9 Gel permeation chromatography (GPC)

The molecular weight distribution of pyrolytic lignin was measured by GPC using Chrompack Microgel[®] columns (pore size 50, 100, 10^3 , 10^6 Å, length 250 mm each, I.D.: 7.7 mm). A pyrolytic lignin sample was dissolved in tetrahydrofuran (THF) (4 ml/mg and 6 ml/mg). Afterwards the sample was filtered (pore size: 0.45 µm, material: regenerated cellulose) to avoid damage of the GPC columns from impurities with larger particle sizes. The temperature of the GPC oven was set to 40 °C and a volume of 100 µl of each sample was injected. THF was used as eluent with a flow rate of 1 ml/min (Pump: Waters 510). A differential refractometer (RI) (detector: Shodex RI 71) and a photometer in the ultraviolet range (UV-photometer) (280 nm) were used as detectors. For calibration polystyrene samples with various molecular weights were used. The molecular weight distribution was calculated from the experimental data using the software PSS WinGPC scientific ver. 4.01.

3.4.10 Water content

Because pyrolysis oils contain several volatile compounds the water content cannot be measured by any drying methods which uses elevated temperatures. Therefore, the water

content in the oil samples was determined by Karl-Fischer titration [JJ86, FW84]. The Karl-Fischer solution contains iodine, pyridine, sulfur dioxide, and methanol. In the presence of water, sulfur dioxide and iodine react according to the following equation:



Upon quantitative reaction of water iodine appears in the solution which can be determined. The pyrolysis liquids were dissolved in methanol and titrated using a SCHOTT titrator (TitroLine alpha) and Hydranal Composite 2 titrant from RIEDEL-DE-HÄEN. The water content determination was repeated 4-5 times and the average values are reported.

3.4.11 Viscosity

The viscosity was measured with various UBBELOHDE capillary viscometers from SCHOTT. During the measurement a fixed volume of the samples flow under the force of gravity through a calibrated capillary. The kinematic viscosity is calculated from the flow time multiplied by the calibration constant of the viscometer. Temperatures of 20 °C, 40 °C, or 50 °C were used and the temperature was controlled with a water bath.

3.4.12 Heating value

The heating value of bio oils depends on the elemental composition. Because a high water content reduces the heating value, heating values are reported as higher and lower heating value, LHV and HHV, respectively. The difference between HHV and LHV is equal to the heat of vaporization of water formed by combustion of the fuel. These higher and lower heating values can be measured by calorimetry. In this work the heating values were calculated from elemental analysis data (Heraeus) using Doulong's formula [Röm95] as already shown in part 2.4.2:

$$HHV [MJ / kg] = \left[338.2 \times \% C + 1442.8 \times \left(\% H - \frac{\% O}{8} \right) \right] \times 0.001 \quad (1)$$

3.4.13 Density

The density was measured at 20 °C using a 5 ml pycnometer. Before the measurement, the volume of the pycnometer was determined with water. Because blocking of the glass capillaries of the pycnometers by fine char particles can produce erroneous results, the measurements for each pyrolysis oil were repeated for at least three times.

3.4.14 Acid number

Acid numbers were determined according to the industrial norm DIN 53 402. Methanol was used as a solvent and a KOH solution in ethanol with a concentration of 0.5 mol/L was used for titration. About 3 g of pyrolysis oil were employed for each measurement.

3.4.15 pH value

The pH was determined using a particular electrode for ion-poor media from INGOLD, type 405-88-TE. The electrode was directly immersed into the liquids. However, the unknown influence of both the pyrolysis oil and the water of the electrode on the individual effective $[\text{H}_3\text{O}^+]$ concentration, may lead to uncertainties in the galvanic potential determination. Therefore, seemingly different results of the pH determination may actually correspond to pyrolysis oils, which possess the same pH value. Nevertheless, this fact does not influence the determination of the acid number because here only the inflection point of the titration curve is being used.

3.4.16 ^{13}C -NMR spectroscopy (^{13}C -NMR)

^{13}C -NMR spectra of beech milled wood lignin and pyrolytic lignins were recorded from Dimethylsulfoxid- d_6 solutions (15-20 %) at 100.6 MHz and at a temperature of 60 °C using a VARIAN Mercury 400 MHz spectrometer. For each sample about 10^5 scans were accumulated, using 90° pulse widths with broadband proton decoupling.

3.4.17 Scanning electron microscopy (SEM)

For scanning electron microscopy measurements a fine beam of electrons, focused by electromagnets, is scanned across the sample [Web98] while the scattered intensity is recorded. The slate samples investigated in this work were first fixed with a carbon adhesive on the sample holder and, thereafter, the samples were sputtered with gold. For the measurements an accelerating voltage of 25 keV and a spot size of 50 nm were used.

The distinction between past, present and future is only an illusion, however persistent.

Albert Einstein 1879-1955

Letter to Michelangelo Besso,

21 March 1955

4 Results and Discussion

4.1 Stability and storage of pyrolysis oils

4.1.1 Introduction

Storability of pyrolysis oils is a considerable advantage compared to other sources of renewable energy. However, pyrolysis oil is not as stable as conventional petroleum fuels. Several authors have reported that the physico-chemical properties of pyrolysis oils change as a function of time under regular storage conditions [SPR88, ASB92, BA94, CJB94, Cze94, OLKLT97]. In order to improve the usability of bio oils in technical applications it is important to obtain further information on how the storage conditions can affect pyrolysis oil properties. In this work pyrolysis oils were systematically stored and changes in their properties were monitored with time.

Bio oils contain a large number of components that can react with each other during storage. Many of these components contain oxygen and are volatile. Apparently, aging of pyrolysis oil can have at least two reasons. First, polymerization reactions can influence the stability of the oil. If components of the oil react with each other, chemical and physical properties will change. Second, components possessing a high volatility also affect bio oil aging. Samples stored open or even samples stored in not well sealed bottles are prone to loose volatile components rapidly resulting in a change in physical properties such as the viscosity.

One possibility to define the quality of pyrolysis oils is to determine the concentration of certain components in stored pyrolysis oils as a function of time. Because pyrolysis oil is a chemically complex system, this work focused on concentration changes of the most

important components in pyrolysis oil. In addition, certain physical properties were monitored as a function of time.

The investigation of the aging behavior of pyrolysis oils in this work is divided into chapters which review the storage tests for the different pyrolysis oils employed.

- (I) Physico-chemical properties of four different pyrolysis oils from pilot plants (FENOSA, ENSYN, and IWC) are monitored during storage under well-defined conditions. Unfortunately, it was not possible to get bio oils that were less than 3 months old.
- (II) VTT pine pyrolysis oil was treated with hydrogen, then stored for a certain time, and then compared to untreated VTT pine oil stored under the same conditions.
- (III) During the pyrolysis process several fractions of IWC beech pyrolysis oil were collected, stored, and properties were monitored with storage time.

4.1.2 Storage of FENOSA, ENSYN, and IWC pyrolysis oils

4.1.2.1 Materials and storage conditions

The origin, feedstock, and some properties of the four pyrolysis oils investigated in this chapter are presented in Table 4 and Table 5. The beech pyrolysis oil was produced in a 100 g/h pyrolyser in the Institute for Wood Chemistry in Hamburg. Beech wood with a particle size of 150 μm to 500 μm was pyrolysed at 475 $^{\circ}\text{C}$. The pyrolysis liquid was collected in two containers and the laboratory plant was washed with methanol. To retrieve the pyrolysis liquid from the methanol solution, the liquid was distilled.

Table 4: Organization, feedstock, water content, and higher heating value (HHV) of FENOSA, ENSYN and IWC pyrolysis oils.

Organization	Feedstock	Water content [wt. %]	HHV [MJ/kg]
Federal Research Center for Forestry and Forest Products, Institute for Wood Chemistry, FRG, (IWC)	beech	10.0	18.9
ENSYN Technologies Inc., Can, (ENSYN)	mixed hardwood	22.9	13.1
Union Electrica FENOSA, E, (FENOSA I)	eucalyptus	25.6	15.0
Union Electrica FENOSA, E, (FENOSA II)	pine	20.9	16.2

Because the oils had different water contents, the elemental analysis was calculated on a water free basis. The results obtained are presented in Table 5.

Table 5: Organization and elemental analysis of FENOSA, ENSYN and IWC pyrolysis oils.

Organization	Elemental analysis ^a			
	C [wt.%]	H [wt.%]	N [wt.%]	O ^b [wt.%]
IWC (beech)	51.68	7.5	0.37	40.45
ENSYN (mixed hardwood)	57.2	6.21	0.32	36.26
FENOSA I (eucalyptus)	54.44	6.10	0.39	39.07
FENOSA II (pine)	54.73	6.22	0.47	38.58

^a ater free basis, ^bcalculated by difference

The pyrolysis oils were stored continuously under different conditions:

- Room temperature, closed
- 50 °C, closed
- Minus 20 °C, closed
- Room temperature, open
- Room temperature, under nitrogen
- Room temperature, additional amount of methanol (20 wt. %)

Every month each sample was investigated by gas chromatography. All the other methods used in this work were applied in longer time periods.

4.1.2.2 Gas chromatography data

Gas chromatography is an analytical separation technique that offers rapid, high resolution separations over a wide range of compounds. Using conventional gas chromatography, about 40 wt. % of the compounds in pyrolysis oil can be detected. In the Institute for Wood Chemistry pyrolysis oils are analyzed by comparison to known compounds. During the last 10 years a large library of retention times and mass spectrometry data of different organic compounds was assembled. With the aid of this library most of the detected peaks in the pyrolysis oils can be identified. In addition, by using an internal standard, identified components can be quantified. In the four pyrolysis oils studied here, about 60 different components were identified and quantified. However, in the following only the main

components are discussed. Because the composition of the oil depends among other things on the raw material, the GC analysis of the four oil samples afforded very different results. The gas chromatograms in the retention time window between 5 and 75 minutes are depicted in Figure 16. Quantification of the main compounds is presented in Table 6.

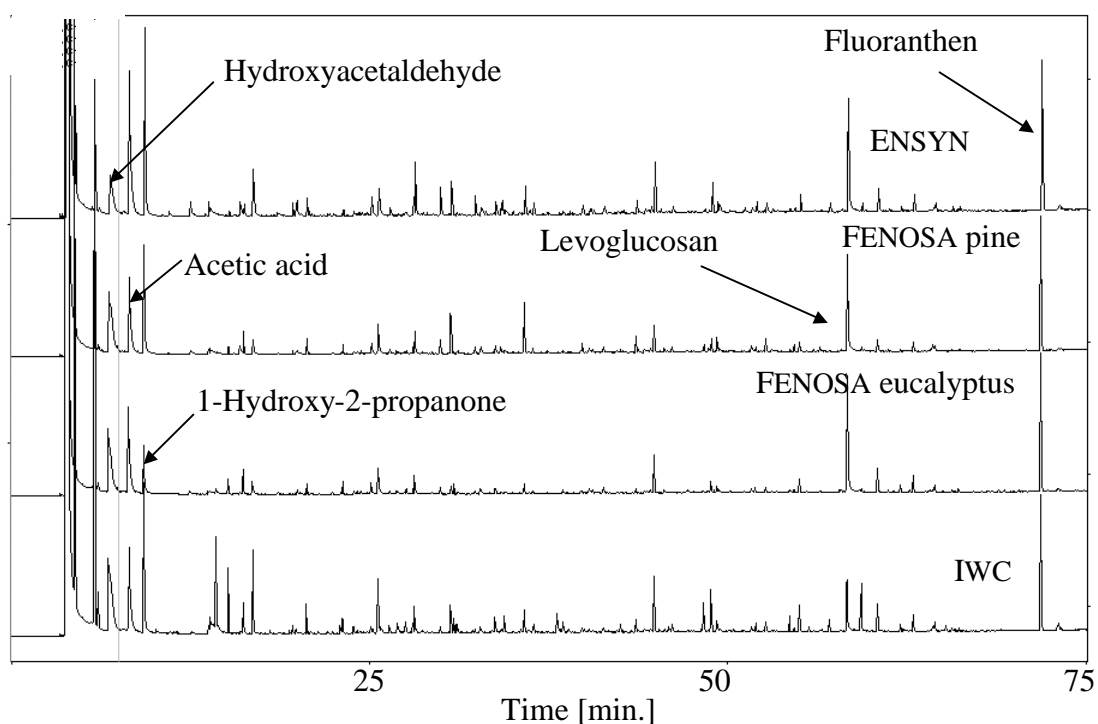


Figure 16: Gas chromatograms of different pyrolysis oils. From bottom to top: gas chromatograms of IWC beech bio oil, FENOSA eucalyptus bio oil, FENOSA pine bio oil, and ENSYN mixed hardwood bio oil.

Figure 17 shows the evolution of the concentration of hydroxyacetaldehyde in IWC (beech) pyrolysis oil stored under different conditions. It can be seen that samples stored at $-20\text{ }^{\circ}\text{C}$ exhibit the smallest decrease of the concentration of hydroxyacetaldehyde with time.

Table 6: GC analysis data of IWC beech pyrolysis oil, ENSYN mixed hardwood pyrolysis oil, FENOSA eucalyptus pyrolysis oil, and FENOSA pine pyrolysis oil.

Compound	Content [wt.%]			
	IWC	ENSYN	FENOSA I (eucalyptus)	FENOSA II (pine)
Hydroxyacetaldehyde	10.90	4.57	7.45	8.40
Acetic acid	4.28	5.67	3.68	3.28
1-Hydroxy-2-propanone	3.42	3.08	1.18	2.22
1-Hydroxy-2-butanone	0.08	0.12	n.a.	0.05
2-Furaldehyde	0.85	0.57	0.15	0.22
(5H)-Furan-2-one	0.73	0.35	0.33	0.37
4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one	0.13	0.02	0.02	0.02
2-Hydroxy-1-methyl-1-cyclopentene-3-one	0.23	0.33	0.12	0.13
Phenol	0.07	0.12	0.07	0.07
Guaiacol	0.17	0.17	0.05	0.22
4-Methylguaiacol	0.13	0.17	0.07	0.30
trans-Isoeugenol	0.18	0.02	0.02	0.05
Vanillin	0.10	0.10	0.07	0.15
Levoglucosan	1.80	3.98	4.80	3.92

n.a. = not analyzed

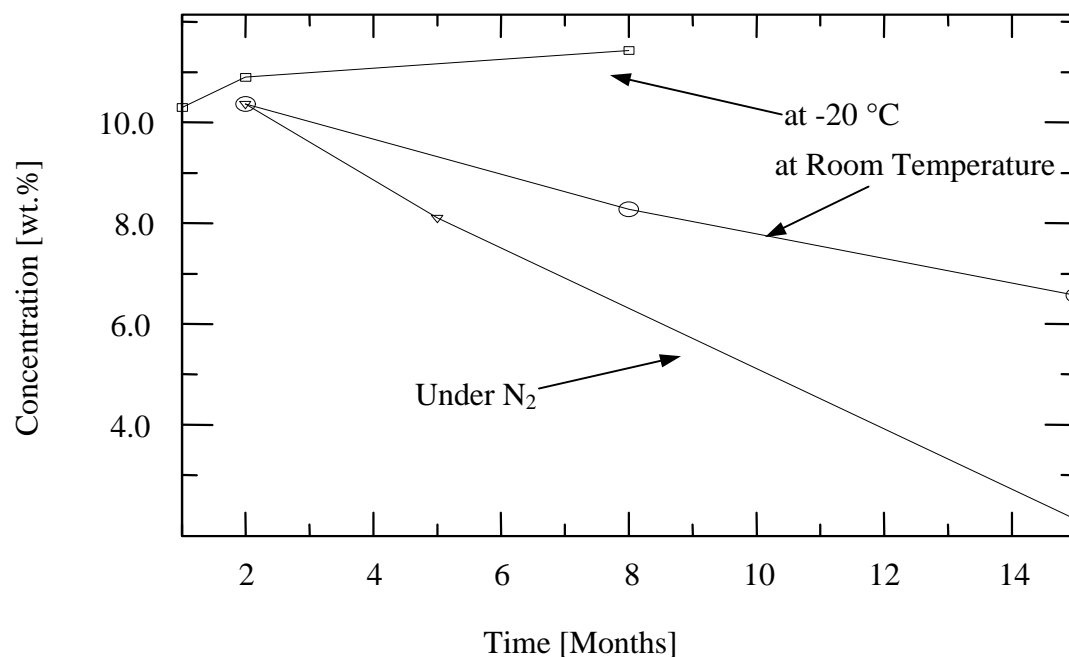


Figure 17: Evolution of the concentration of hydroxyacetaldehyde in IWC beech pyrolysis oils stored under different conditions.

4.1.2.3 Fourier transform infrared spectroscopy data

Fourier transform infrared spectroscopy (FTIR) is a suitable technique to investigate compositional and structural changes of pyrolysis oils as a function of time and storage conditions. A proceeding polymerization can be easily monitored by a weakening and eventual disappearance of certain frequencies. In addition, several structural alterations or the formation of new entities can also be recognized from their corresponding effect on the FTIR spectrum.

Because of the chemical complexity of pyrolysis oil samples, it is difficult to obtain quantitative results from FTIR spectra. Placed in a commercially available IR sample holder with a fixed thickness, the dark-brown colored pyrolysis oils absorb too much of the primary beam intensity and, hence, cannot be measured as is. Consequently, pyrolysis oils have to be mixed with a diluent to obtain suitable and less colored samples. In order to be suitable as an internal standard, the diluent should have at least one IR peak that does not interfere with the spectrum of the pyrolysis oils. However, because pyrolysis oils have a large amount of different functional groups, finding a solvent that does not react with one of the many compounds present is rather difficult. IR spectra of pyrolysis oils exhibit adsorption peaks in the region between 700 cm^{-1} and 1750 cm^{-1} that appear to be influenced by aging processes. Additionally, absorption bands can be observed above 2000 cm^{-1} . Often only one peak is visible in this region because the large amount of water in pyrolysis oils results in major background originating from O-H vibrations. Hence, only qualitative FTIR measurements were performed and are described in the following.

With respect to the aromatic core frequency, it was suggested [Wul99] that the integrated intensity under the corresponding peak should remain constant with storage time and serve as internal standard. Apparently, this method is not suitable, because this absorption will be influenced not only by the amount of aromatic cores but also by the different ligands. Therefore, FTIR spectra were normalized to the highest peak to compare them to each other.

Fourier transform infrared spectroscopy was performed only for selected bio oil samples. Figure 18 shows three spectra of IWC oil samples stored under different conditions. It can be noticed, that the spectra corresponding to samples stored for one month at RT or 11 months at $50\text{ }^{\circ}\text{C}$ exhibit only minor differences in the region between 2000 and 1250 cm^{-1} . On the contrary, the spectrum of the sample stored at RT over 14 months exhibit significant differences in the carbonyl peak and in the frequency region from 1500 to 700 cm^{-1} . These

modifications indicate a further degraded and polymerized sample also corroborated by a decreased carbonyl frequency (1720 cm^{-1}). It seems that the samples stored for a short time at RT or a longer time at higher temperature are only slightly different. These results cannot be explained by the general idea that higher temperatures should result in an increased degree of polymerization.

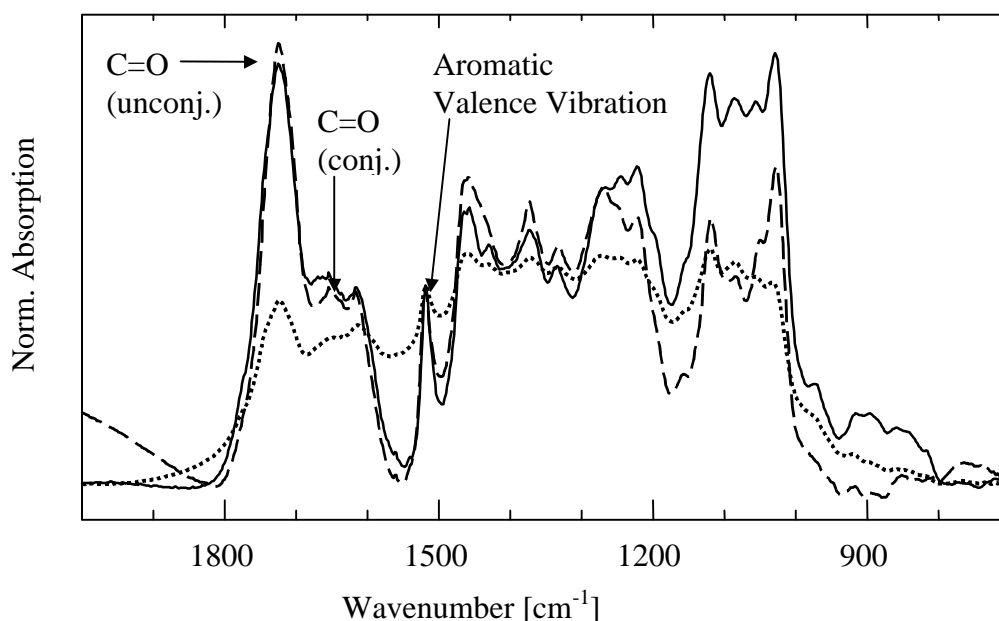


Figure 18: *solid*: IWC pyrolysis oil after one month at RT; *dash*: IWC pyrolysis oil after 11 months at $50\text{ }^{\circ}\text{C}$; *dot*: IWC after 14 months at RT.

In contrast to the spectrum of IWC pyrolysis oil, the FTIR spectra of the oil sample from ENSYN and the two oil samples from FENOSA exhibited a strong carbonyl peak. Figure 19 shows the FTIR spectra of four different pyrolysis oils obtained from different kinds of wood and stored for 11 months at $50\text{ }^{\circ}\text{C}$. The IWC pyrolysis oil that was found to possess the smallest degree of polymerization, exhibits the smallest carbonyl peak. The fact that the pyrolysis oils were obtained from different woods may be a reason for the different intensities of the carbonyl peaks. Apparently, it is not possible to compare the carbonyl peak of the FTIR spectrum of one pyrolysis oil with the carbonyl peak of the FTIR of another pyrolysis oil and, thus, conclusions on the various degrees of polymerization cannot easily be obtained.

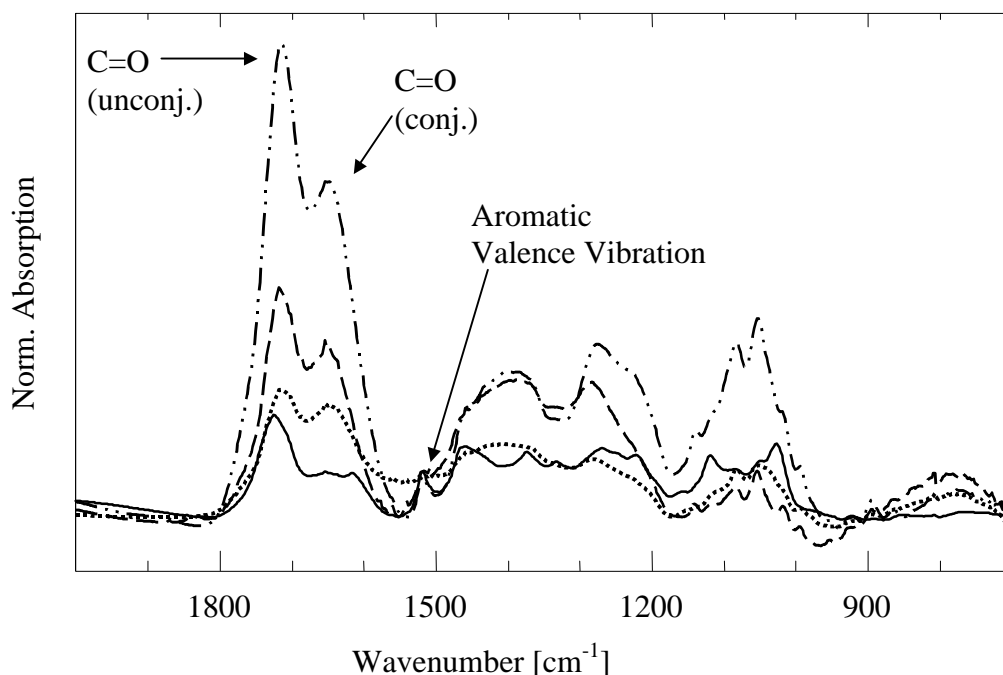


Figure 19: *solid*: IWC after 11 months at 50 °C; *dash*: ENSYN after 11 months at 50 °C; *dot*: FENOSA eucalyptus after 11 months at 50 °C; *dash-dot*: FENOSA pine after 11 months at 50 °C.

4.1.2.4 Gel permeation chromatography data

Pyrolysis oils from IWC, ENSYN, and FENOSA were investigated by gel permeation chromatography (see part 3.4.9) in order to estimate the molecular weight distribution (MWD). The retention times as determined by GPC depend not only on the molecular size but also on the functional groups of the chemical compounds included. In general, suitable standards that are used for obtaining calibration curves for GPC measurements need to possess the same functional groups as the compounds to be analyzed. However, because pyrolysis oils consist of a complex mixture of various compounds with a large number of different functional groups, finding suitable standards for GPC of pyrolysis oils is not readily possible. Hence, the absolute value of the molecular weight determined by GPC for the pyrolysis oils investigated may possess a certain systematic error. However, because this error should be similar in the data collected, the average molecular weight obtained remains a valuable tool for comparing different pyrolysis oils with each other.

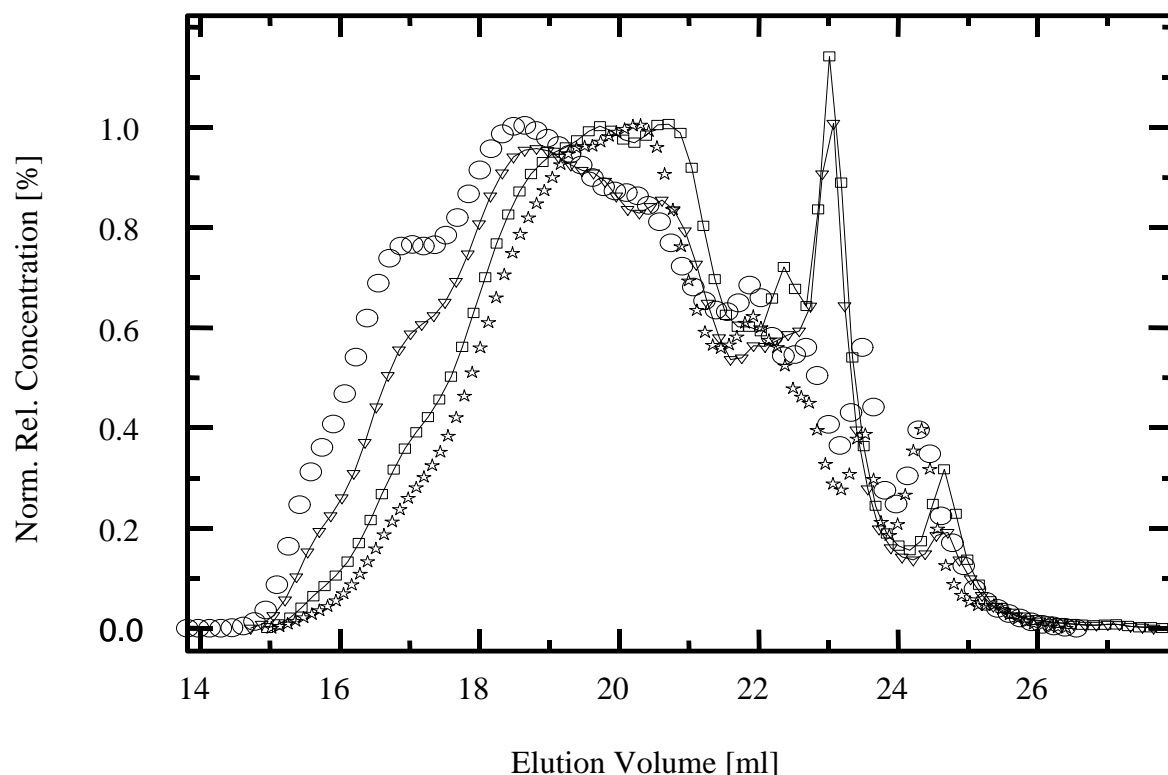


Figure 20: Gel permeation chromatograms. *Stars*: IWC pyrolysis oil; *circles*: ENSYN pyrolysis oil; *triangles*: FENOSA (eucalyptus) pyrolysis oil; *squares*: FENOSA (pine) pyrolysis oil (all samples stored closed in the dark for 4 months).

The molecular weight distributions of the pyrolysis oil samples stored are presented in Figure 20 and Figure 21. In order to facilitate the comparison of the different pyrolysis oil samples, the mass average (M_w) and the number average (M_n) of the molecular weight as well as the dispersity (D) of the pyrolysis samples stored are given in Table 7.

Figure 20 and Table 7 show the differences in the molecular weights of the four oils obtained from different processes. The IWC sample possesses the smallest average of molecular weight. This may be because of the treatment of the oil and/or the age of the oil. Fresh pyrolysis oils normally exhibit a small average of molecular weight. However, because the IWC pyrolysis oil was diluted with methanol after production there may be still some methanol left in the oil, in spite of the subsequent distillation. Because methanol has a small molecular weight, the molecular weight average of the oil may be smaller than it should be without that treatment.

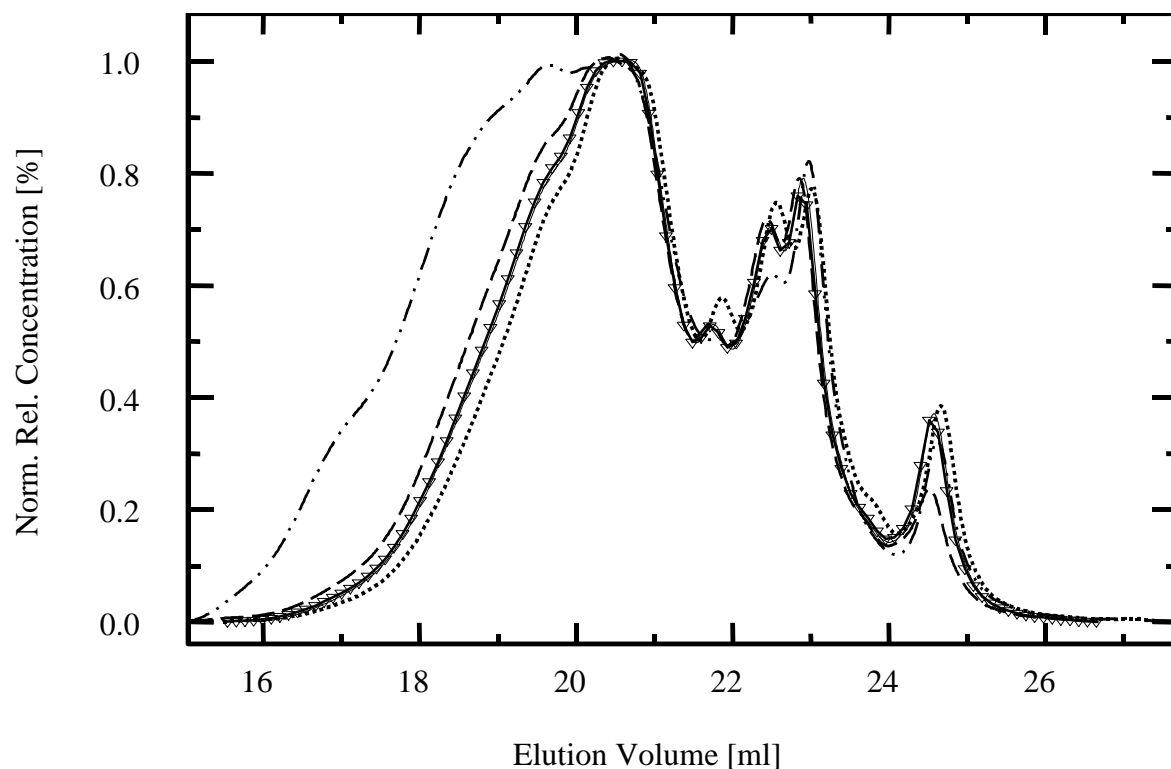


Figure 21: Gel permeations chromatograms of IWC bio oils stored for 4 months. *Solid*: closed in the dark; *dash*: open in the dark; *triangles*: under nitrogen; *dash-dot*: closed at 50 °C; *dot*: deep frozen.

Table 7: Different molecular weight numbers and dispersity (D) for different pyrolysis oil samples.

Pyrolysis oil sample	M _w [g/mol]	M _n [g/mol]	D (M _w /M _n)
ENSYN ¹	592.2	164.6	3.6
FENOSA eucalyptus ¹	765.1	210.6	3.6
FENOSA pine ¹	607.8	187.4	3.2
IWC ¹	385.4	145.5	2.6
IWC stored open in the dark	424.0	167.6	2.5
IWC stored under nitrogen	392.5	147.8	2.7
IWC stored closed at 50 °C	581.5	182.2	3.2
IWC stored at - 20 °C	355.2	131.2	2.7

¹ stored closed in the dark

As shown in Figure 21, GPC data measured for samples stored closed in the dark, under nitrogen, and deep frozen do not exhibit significant differences. In Figure 21 a small elution volume corresponds to a large molecular weight. The curves of the sample stored open and of that stored at 50 °C appear to be shifted towards smaller elution volumes indicating a shift towards increased molecular weights. The corresponding values can be seen in Table 7. The oil sample stored at 50 °C possesses the largest molecular weight. Interestingly, the oil sample stored at -20 °C exhibits the samples molecular weight. This effect may explain why higher storage temperatures afforded pyrolysis oils with a high degree of polymerization of several compounds.

4.1.2.5 Acid numbers

Acid numbers are standard data in tar and fat investigations. Therefore, the evolution of acid numbers was investigated for pyrolysis oils. The acid numbers of the oils kept closed at room temperature were measured every second month. Therefore, a small amount of bio oil was dissolved in 150 ml methanol and titrated with 0.5 mol/l potassium hydroxide. The consumption of KOH was monitored by simultaneously measuring the pH-value of the solution. The acid number was then determined with respect to the bio oil amount and the molarity of the KOH solution. The acid numbers of the above-mentioned four pyrolysis oils (from IWC, ENSYN and FENOSA) were determined. Table 8 contains the evolution of the acid numbers of the four different bio oils over one year. Only for the IWC sample, a decreasing acid number with time was obtained. Measurements of the FENOSA and ENSYN samples yielded increasing acid numbers with time. The increase itself indicates that the number of functional acidic groups increase with storage time.

Table 8: Acid numbers of the bio oils from FENOSA, ENSYN and IWC after storage for several months (m).

Sample	Acid number [mg KOH/g]							
	1 m	2 m	3 m	5 m	6 m	9 m	11 m	14 m
IWC (beech)	56.2	53.6	n.a.	n.a.	47.9	44.4	43.7	40.8
FENOSA (eucalyptus)	89.9	89.9	n.a.	91.4	n.a.	91.4	92.2	92.2
FENOSA (pine)	n.a.	87.3	n.a.	89.4	n.a.	91.1	n.a.	93.7
ENSYN (hardwood)	n.a.	n.a.	91.2	91.4	n.a.	92	93.6	93.7

n.a. = not analyzed

4.1.2.6 Water contents

In the first year the water content of oils stored closed at room temperatures was also determined periodically. The water content of the pyrolysis oils was measured on a monthly basis. Subsequently, the interval was changed to every second month. Owing to the inevitable polymerization of the pyrolysis oils, a continuously increasing water content is to be expected, if this reaction would be a polycondensation.

Table 9: Water content of pyrolysis oils stored at different times and conditions.

Sample	Water content after 3 months [wt. %]	Water content after 4 months [wt. %]	Water content after 5 months [wt. %]
IWC (close and in the dark)	10.5	9.8	10.3
ENSYN(close and in the dark)	22.9	22.5	22.4
FENOSA (eucalyptus) (close and in the dark)	25.2	24.4	25.6
FENOSA (pine) (close and in the dark)	20.9	19.8	20.8
IWC (open and in the dark)	7.1	5.4	4.8
ENSYN (open and in the dark)	n.a.	5.1	4.9
FENOSA (eucalyptus) (open and in the dark)	7.0	5.2	5.4
FENOSA (pine) (open and in the dark)	7.5	5.3	5.4
IWC (at 50 °C)	12.5	12.6	13.1
ENSYN (at 50 °C)	n.a.	22.9	33.4
FENOSA (eucalyptus) (at 50°C)	25.7	31.1	30.9
FENOSA (pine) (at 50 °C)	23.0	20.3	29.9

n.a. = not analyzed

Naturally, this increase should approach a certain limit with time. The evaluation of the water content of the four different oils is given in Table 9. Interestingly there is no significant effect of storage on the water content of the oils within the experimental error. Because bio oils

polymerize with time, the constant water content may indicate that polymerization in bio oils does not proceed predominantly by polycondensation reactions.

Measuring the water content and acid number at the time of delivering revealed significant differences between the two FENOSA and the ENSYN oil, and the IWC oil. Whereas FENOSA pine, FENOSA eucalyptus, and ENSYN hardwood exhibit water contents between 22 wt. % and 26 wt. % and acid numbers at about 90 mg KOH/g, IWC has a water content of 10 wt. % and an acid number of 56 mg KOH/g. In subsequent long time studies these two subsets (in the following referred to as 'high water/acid' and 'low water/acid' oils) exhibited an intriguingly different behavior. Stored closed at 50 °C, for instance, the 'high water/acid' oils developed a phase separation into a thick sludge at the bottom of the container and a less viscous phase. In contrast, the 'low water/acid' oil does not show any phase separation after more than 3 years. A similar behavior was observed for samples stored closed and in the dark. Whereas the 'high water/acid' oils underwent extensive polymerization and showed increased viscosity, the 'low water/acid' oil remained liquid with only a minor increase in viscosity after several weeks.

4.1.2.7 Summary

Pyrolysis oil samples stored at -20 °C were still homogeneous after 6 months (or even longer) whereas samples stored at 50 °C developed varying amounts of sludge at the bottom of the container. Less sludge formation was observed in the IWC oil samples compared to ENSYN and FENOSA pyrolysis oil samples stored at similar conditions. After more than two years of storage time the thick, gummy sludge at the bottom of the storage vessels of the FENOSA and the ENSYN samples was estimated to be about 90 % by weight of the samples.

The investigations described here comprised four typical pyrolysis oils. All samples stored at -20 °C showed a small increase in the amount of the main components, i.e. hydroxyacetaldehyde, acetic acid, and 1-hydroxy-2-propanone, with storage time. Only for FENOSA eucalyptus oil stored at - 20 °C the concentration of acetic acid decreased. A very different evolution of the concentration of hydroxyacetaldehyde, acetic acid, and 1-hydroxy-2-propanone was observed for samples stored at room temperature. Here, for most samples the concentration of the main components decreased.

Apparently, the FTIR data of pyrolysis oils studied are difficult to be interpreted. Most prominently aging of pyrolysis oils can be seen from the ratio of the maximum of the carbonyl bands at 1715 cm⁻¹ and 1650 cm⁻¹, and the maximum in the region from 1500 to 700 cm⁻¹.

This ratio ranges from 0.6 to 1 and it approaches one with increasing age of the oils. This method is suitable to monitor changes within an oil sample, however it may not be useful to compare different bio oils.

The GPC data showed an increase of the elution volume determined for each bio oil with storage time. Because a smaller elution volume corresponds to a larger molecular weight these data indicate polymerization processes in the oils with storage time.

Remarkably, the acid number of FENOSA and ENSYN oil samples increased with storage time. In contrast the acid number of IWC oil decreased with storage time. No effect of storage on the water content of closed stored oils was observed within the experimental error.

The most important result of this study is the high stability of IWC beech pyrolysis oil. Even samples stored at 50 °C were considerably stable. After more than two years only a thin film but no sludge had developed at the bottom of containers. For the IWC oil the handling after the productions may account for the differences observed. After production the oil was diluted with methanol and afterwards distilled. Apparently, light reactive components were removed together with methanol, resulting in a more stable oil. Moreover, reactions of methanol with aldehydes may take place in the bio oils leading to the formation of acetals.

4.1.3 Untreated and hydrogenated VTT pine pyrolysis oil

4.1.3.1 Materials and storage conditions and physico-chemical analyses

Because hydrogenation is one possibility to improve the quality of pyrolysis oil, the following hydrogenation study was performed on both hydrogenated and untreated VTT pine oil. The VTT bio oil manufactured from pine wood was supplied by the Technical Research Center of Finland, VTT, situated in Espoo, Finland. The oil production took place on March 10th to 14th 1997. This pyrolysis oils is denoted in the following as VTT pyrolysis oil number 1. The Institute of Wood Chemistry received the pyrolysis oil at the beginning of June 1997. Table 10 contains some results of physico-chemical analyses performed by IWC and VTT. The VTT oil was first stored as-is. In a second series two different hydrogenated oils were studied to evaluate the effectiveness of mild hydrogenation.

The hydrogenation tests were performed without catalysts, and therefore they are denoted as reference hydrogenation test in the following, at the following conditions:

(A) 3 hours at 30 °C, stir velocity: 1000 r.p.m. and H₂ pressure: 3 bar (hydrogenated VTT pyrolysis oil reference A).

(B) 24 hours at 60 °C, stir velocity: 1000 r.p.m. and H₂ pressure: 6 bar (hydrogenated VTT pyrolysis oil reference B).

These reference hydrogenation tests serve as references for further hydrogenation tests performed in the presence of various catalysts. The results described in this chapter refer to hydrogenation of pyrolysis oils without addition of a catalyst. Utilization of catalysts for the upgrading of pyrolysis oils and investigations of the pyrolysis oils obtained is described in detail in chapter 4.2.

Table 10: Physico-chemical analysis of IWC pyrolysis oil and VTT pine bio oil number 1.

Analysis methods	Analysis results by IWC	Analysis results by VTT
pH	2.4	2.4
Moisture [%]	17.4	17.0
Density [g/cm ³]	1.24 (at 20 °C)	1.24 (at 15 °C)
Viscosity at 50 °C [cSt]	35.0	28.0
Heating value [MJ/kg]	HHV: 17.62 (calculated)	LHV: 17.2
Elemental analysis		
C [wt.%]	45.62	45.7
H [wt.%]	7.38	7.0
N [wt.%]	0.09	< 0.1
O [wt.%] (by difference)	46.91	47.2

After hydrogenation the pyrolysis oils were analyzed. Results of the analysis of the oils before and after the two reference hydrogenation tests are shown in Table 11. The corresponding gas chromatograms are depicted in Figure 22 and Figure 23. Evidently, there are only small changes in the concentration of the compounds detected.

Table 11: Analysis results before and after reference hydrogenation tests.

Analysis methods	Analysis results before hydrogenation	Analysis results after reference hydrogenation A	Analysis results after reference hydrogenation B
Moisture [%]	17.44	n.a.	12.8
pH value	2.05	2.41	2.44
Viscosity at 20 °C[cSt]	n.a.	525.3	606.4
Elemental analysis			
C [wt.%]	45.62	45.81	46.00
H [wt.%]	7.38	7.46	7.28
N [wt.%]	0.09	0.20	0.32
O [wt.%] (by difference)	46.91	46.53	46.34

n.a. = not analyzed

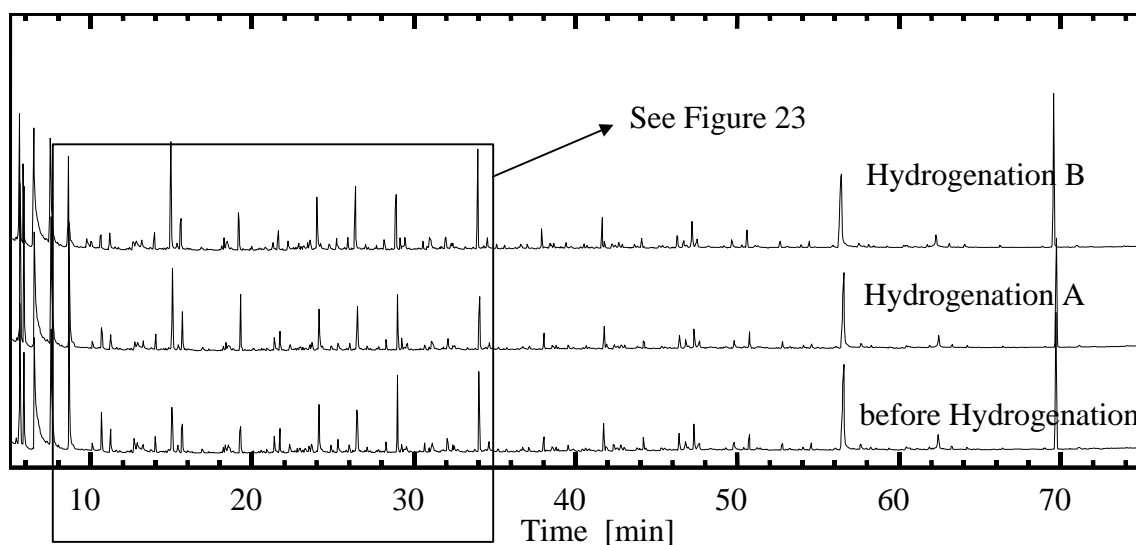


Figure 22: Gas chromatograms of reference hydrogenation tests. From bottom to top: before hydrogenation; after hydrogenation reference A; after hydrogenation reference B.

The crude VTT pine pyrolysis oil number 1 and the two oils obtained by a hydrogenation treatment and without catalyst were stored at three different temperatures. Loss of volatile compounds during storage was avoided by carefully closing the containers. The oil samples were stored at room temperature, at 80 °C, and at -20 °C 3 days. Certain properties such as number of carbonyl groups and acid number were measured for the various samples stored. A systematic rheological study of samples stored under different conditions was performed to

monitor the evolution of viscosity as a function of time. Additionally, GC-FID, GC-MS, and FTIR measurements were performed for the samples stored, and are reported in detail in the following paragraphs.

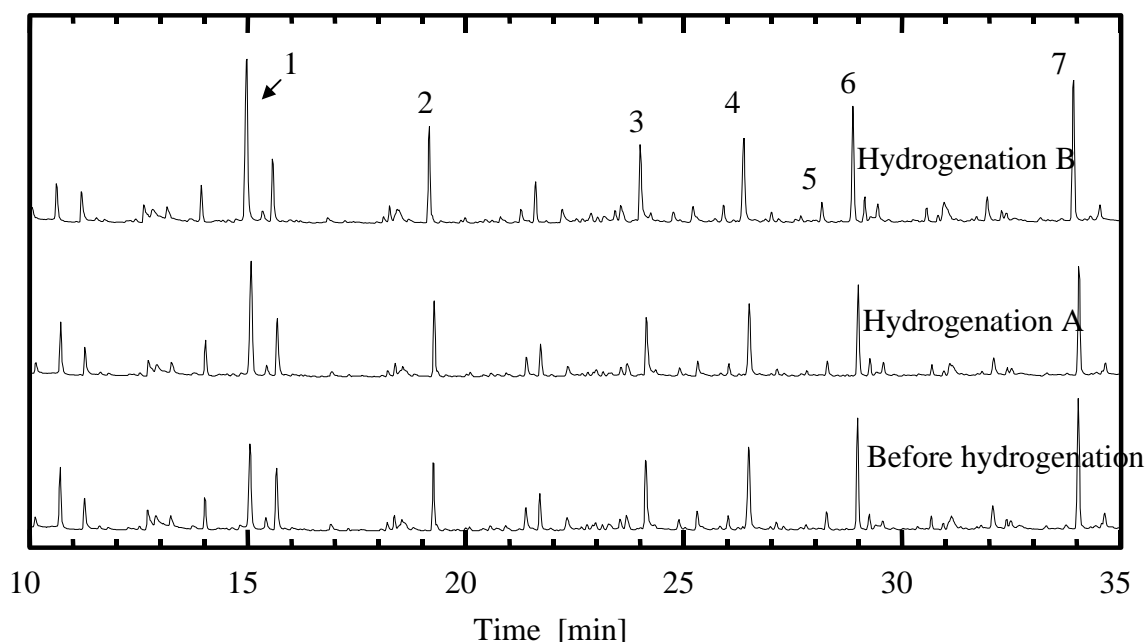


Figure 23: Gas chromatograms of reference hydrogenation tests. From bottom to top: before hydrogenation; after hydrogenation reference A; after hydrogenation reference B. [Identified peaks: (1) unknown; (2) trans-2, 5-Dimethoxytetrahydrofuran and 2-Furfural; (3) (5H)-Furan-2-one; (4) 2-Hydroxy-3-methyl-2-cyclopentene-1-one; (5) Phenol; (6) Guaiacol; (7) 4-Methylguaiacol].

4.1.3.2 Gas chromatography data

After storage for certain intervals the two pyrolysis oils, which were obtained by hydrogenation, were investigated by gas chromatography. The results for the hydrogenated reference oil A stored at -20 °C and at 80 °C are summarized in Table 12. It can be seen that for samples stored at -20 °C the concentrations of hydroxyacetaldehyde and 1-hydroxy-2-propanone are higher than for samples stored at 80 °C.

Analysis of oil samples by GC-MS took about 2 hours each. Since pyrolysis oils have high viscosities and solid contents, injection ports are occasionally blocked and, hence, gas chromatography is rendered difficult for these samples.

Table 12: GC analysis of hydrogenated (A) VTT oil stored at different times and temperatures.

Compound	Hydrogenated reference pyrolysis oil A			
	content [wt.%]			
	48 hours at -20 °C	72 hours at -20 °C	48 hours at 80 °C	72 hours at 80 °C
Hydroxyacetaldehyde	5.33	5.41	2.78	2.04
1-Hydroxy-2-propanone	3.56	3.84	2.59	2.48
1-Hydroxy-2-butanone	0.09	0.11	0.07	0.07
isomer of dihydro-methyl- furanone	0.10	0.11	0.04	0.05
isomer of Dihydro-methyl- furanone	0.07	0.08	0.04	0.03
Dihydro-2(3H)-furanone	0.06	0.06	0.10	0.10
(5H)-Furan-2-one	0.25	0.26	0.23	0.23
4-Hydroxy-5,6-dihydro-(2H)- pyran-2-one	0.06	0.06	0.05	0.06
2-Hydroxy-3-methyl-2- cyclopentene-1-one	0.17	0.18	0.16	0.17
Phenol	0.04	0.04	0.03	0.03
Guaiacol	0.18	0.19	0.17	0.17
4-Methylguaiacol	0.19	0.20	0.18	0.17
4-Ethylguaiacol	0.04	0.05	0.04	0.04
cis-Isoeugenol	0.04	0.04	0.02	n.a.
trans-Isoeugenol	0.07	0.07	0.05	0.04
4-Methylsyringol	0.05	0.04	0.03	0.04
Vanillin	0.13	0.13	0.11	0.12
Levogluconan	1.62	1.60	1.60	1.50

4.1.3.3 Fourier transform infrared spectroscopy data

The FTIR spectra of VTT pine pyrolysis oil, stored for 3, 6 and 72 hours at 80 °C, are shown in Figure 24. It can be noticed that the spectra exhibit differences in the carbonyl region and

are very similar in the region between 1600 and 900 cm^{-1} . The longer the oil is stored at 80 °C the higher the carbonyl peak compared to the aromatic peak at about 1500 cm^{-1} .

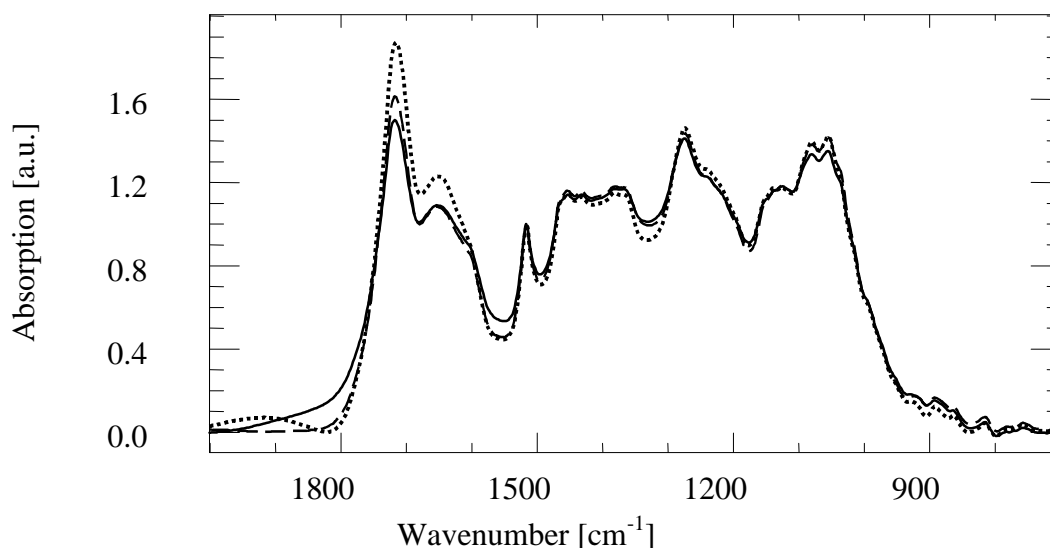


Figure 24: FTIR spectra of VTT pine pyrolysis oil stored at different times at 80 °C. *Solid*: 3 hours at 80 °C; *dash*: 6 hours at 80 °C; *dot*: 72 hours at 80 °C.

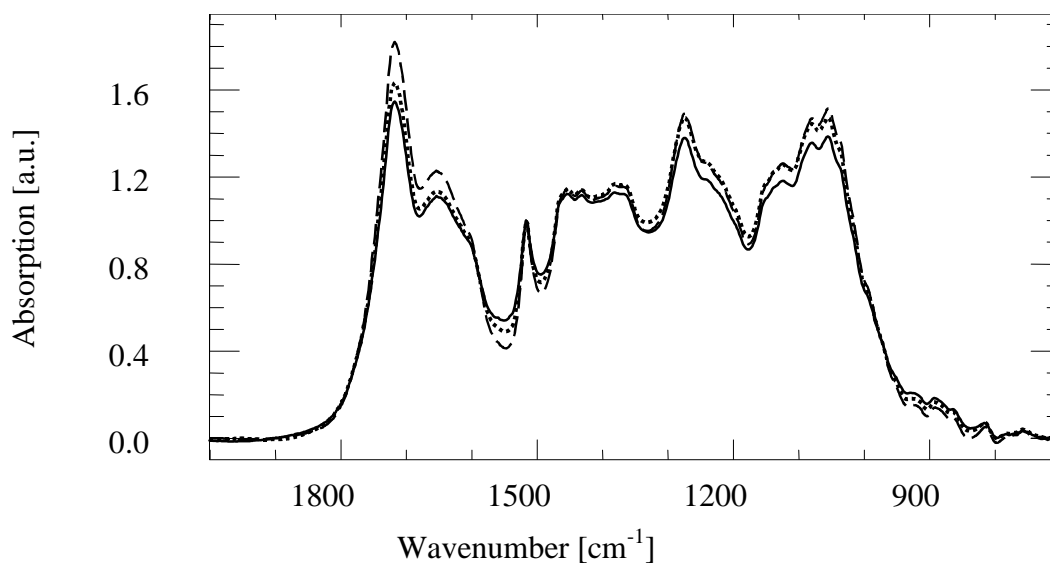


Figure 25: FTIR spectra of VTT pine pyrolysis oil stored different times at -20 °C. *Solid*: 3 hours at -20 °C; *dash*: 6 hours at -20 °C; *dot*: 72 hours at -20 °C.

In order to compare the effect of different storage conditions Figure 25 presents FTIR spectra of VTT pine oil stored for 3, 6 and 72 hours at -20 °C. Slight differences between three spectra are evident in the region corresponding to carbonyl groups as well as in the region between

1300 and 900 cm^{-1} . However, it can be noticed that the peak ratios in the FTIR spectra of the oil stored are similar, independent of the storage time at -20 °C. These results confirm that, as expected, the aging of pyrolysis oils is accelerated at higher temperatures.

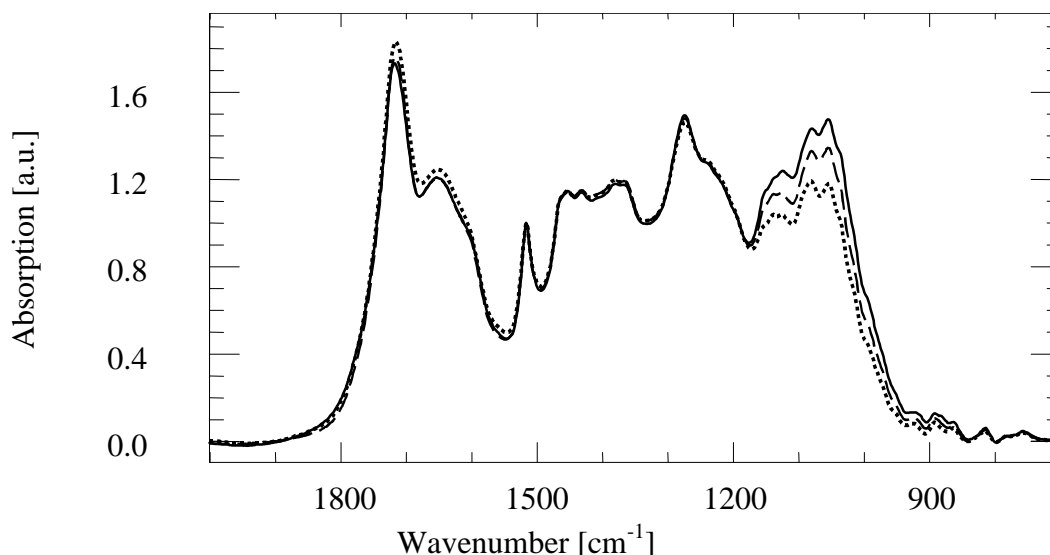


Figure 26: FTIR spectra of VTT hydrogenated pyrolysis oil. *Solid*: stored at room temperature; *dash*: stored 1 day at 80 °C; *dot*: stored 3 days at 80 °C.

In addition to FTIR measurements of the original VTT pyrolysis oil, FTIR measurements were performed of the hydrogenated VTT pyrolysis oil. The spectra are depicted in Figure 26. The spectra of the untreated oil show variations in the carbonyl region. In contrast, the spectra of various samples of the hydrogenated pyrolysis oil are quite similar in the carbonyl region. However, significant differences in the region between 1200 and 900 cm^{-1} can be seen.

4.1.3.4 Carbonyl groups measurements

A detailed study of the changes of the amount of carbonyl groups in stored oil samples was performed for both hydrogenation A and B. The results obtained for stored samples from hydrogenation A and hydrogenation B are depicted in Figure 27 and Figure 28, respectively. It seems that the polymerization of several compounds in the oil is accelerated at higher temperatures. The evolution of the amount of carbonyl groups stored at 80 °C for the two hydrogenated pyrolysis oils and the crude oil are presented in Figure 29. Evidently, the decrease in the amount of carbonyl groups is smaller for the two hydrogenated oils than for the crude VTT bio oil.

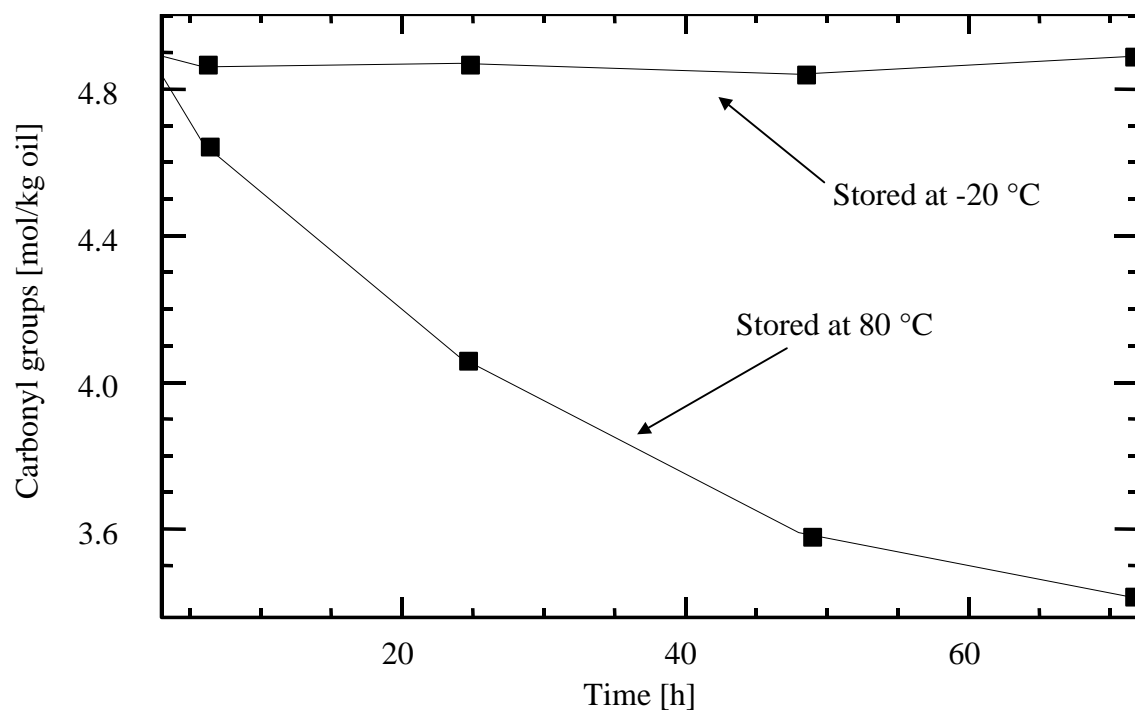


Figure 27: Amount of carbonyl groups of stored samples obtained from hydrogenation A at 80 °C and -20 °C.

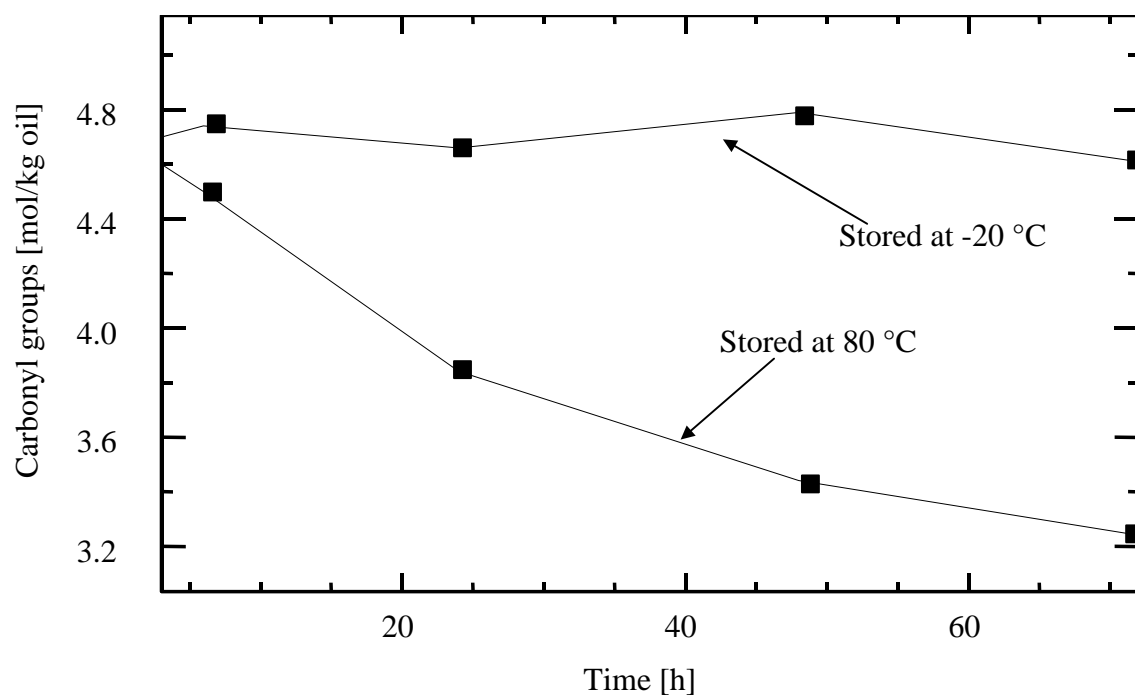


Figure 28: Amount of carbonyl groups of stored samples obtained from hydrogenation B at 80 °C and -20 °C.

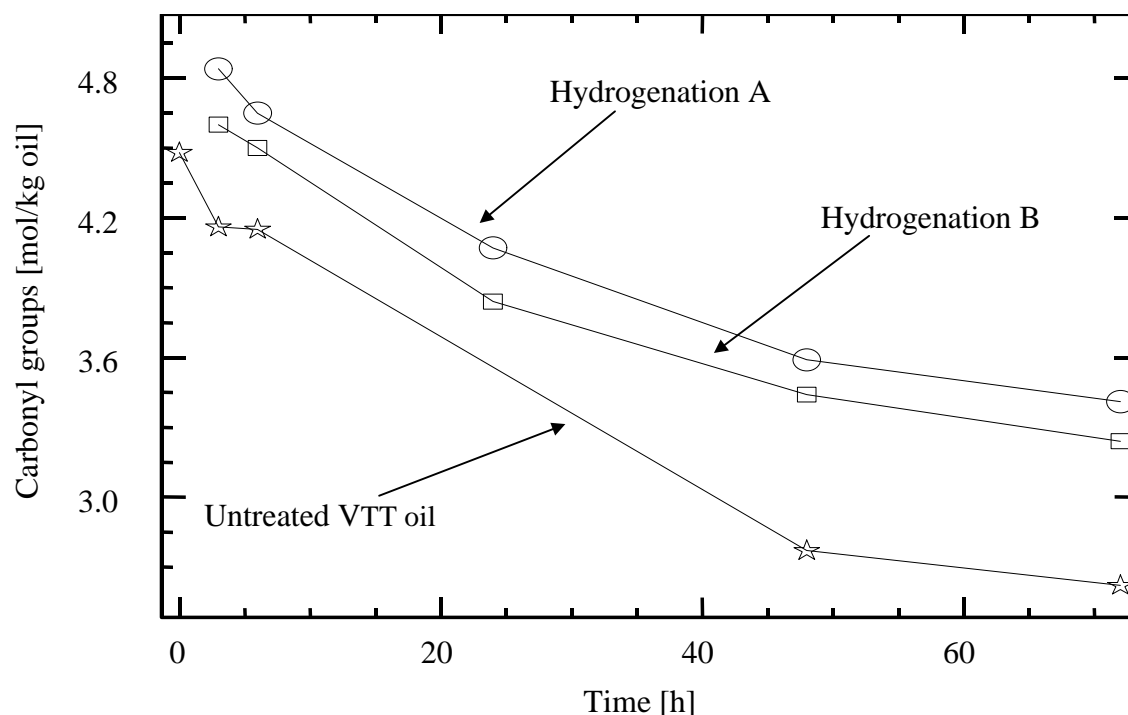


Figure 29: Amount of carbonyl groups of samples obtained from hydrogenation A, B, and untreated VTT pine pyrolysis oil stored at 80 °C.

4.1.3.5 Viscosity data

A systematic rheological study was performed with oil samples obtained from hydrogenation A and B. The results of the viscosity measurements at 20 °C and at 50 °C for hydrogenation A and B are summarized in Figure 30 and Figure 31, respectively. The samples stored at 80 °C exhibited a significant increase of viscosity after storage time. Because viscosity is related to the average molecular weight of the material, the increase in viscosity indicates the occurrence of polymerization reactions in the oil. Because the aging, and, hence, the polymerization of the bio oils is accelerated at higher temperatures, the increase in viscosity is more pronounced for samples stored at 80 °C.

As expected viscosity values for samples measured at 50 °C are significant smaller than the viscosity values for the same samples measured at 20 °C.

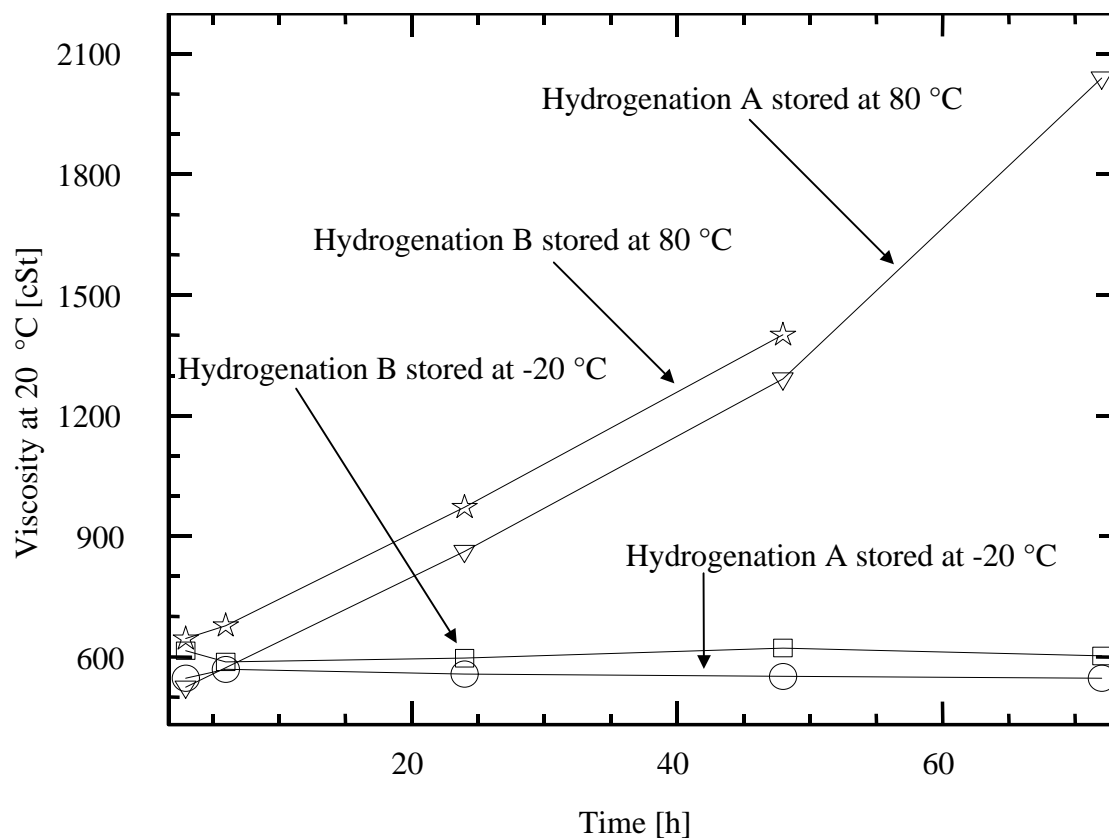


Figure 30: Evolution of the viscosity measured at 20 °C for samples obtained from hydrogenation A and hydrogenation B and stored at -20 °C and 80 °C.

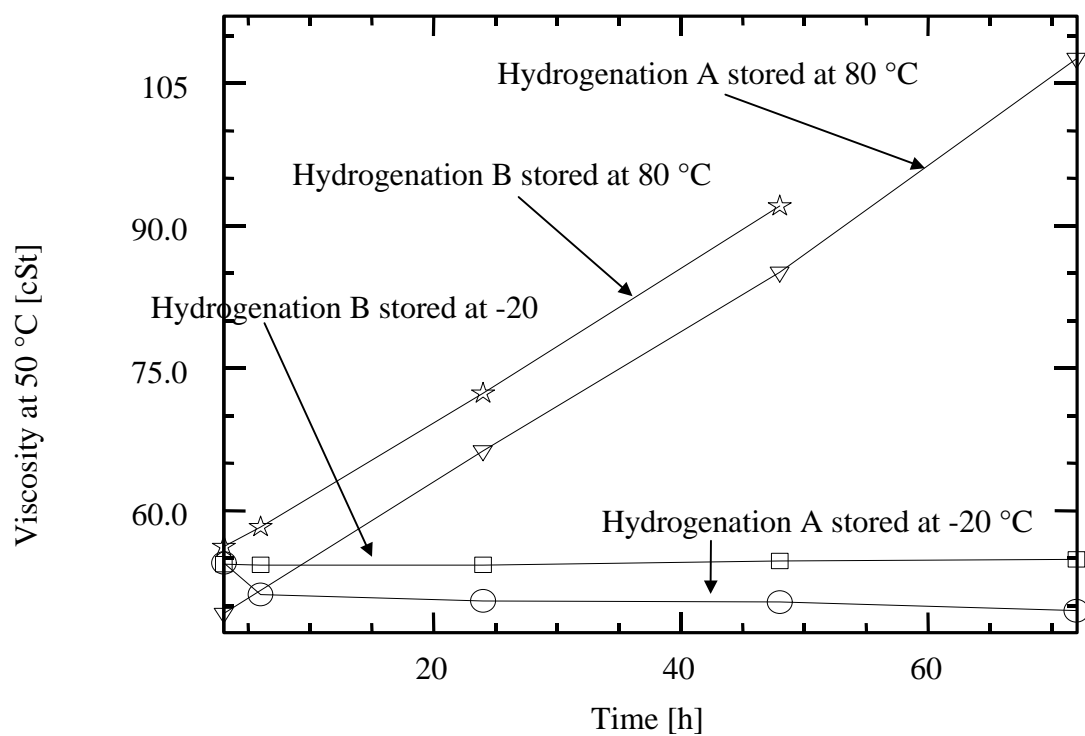


Figure 31: Evolution of the viscosity measured at 50 °C for samples obtained from hydrogenation A and hydrogenation B and stored at -20 °C and 80 °C.

4.1.3.6 Acid numbers

Acid numbers obtained for the hydrogenated VTT oil B are given in Table 13. It can be seen, that the acid numbers of the VTT pyrolysis oil after hydrogenation B and stored at 80 °C and -20 °C increased with time. This increase indicates that the number of functional acidic groups increase with storage time.

Table 13: Acid number of VTT oil after hydrogenation B and stored at 80 °C and - 20 °C.

Storage conditions	Acid number [mg KOH/g]
3 hours at 80 °C	68.6
3 hours at -20 °C	68.9
6 hours at 80 °C	69.4
6 hours at -20 °C	69.5
72 hours at 80 °C	78.8

4.1.3.7 Concluding remarks

All samples showed a considerable decrease in the number of carbonyl groups with storage time, and the decrease in number of carbonyl groups was smaller for samples stored at -20 °C than for samples stored at 80 °C. Hydrogenated oils showed a smaller decrease of the number of carbonyl groups than the crude VTT pyrolysis oil. This decrease in the amount of carbonyl groups observed substantiates the assumption that polymerization is a key reaction in the aging of bio oils.

The viscosity is another parameter, which indicates polymerization in pyrolysis oils. The systematic rheological study performed with hydrogenated and crude oil showed an increase of viscosity after storage time. The increase in viscosity is more pronounced for samples stored at higher temperatures.

4.1.4 Different fractions of IWC pyrolysis oil

4.1.4.1 Materials and storage conditions

The oil used for the following storage tests was produced from beech wood at the Institute of Wood Chemistry on January 10th 1997. Four pyrolysis oil fractions were obtained: three different cooling fractions and a forth from the electrostatic precipitator. Pyrolysis was performed at 475 °C with 3.33 kg wood per hour and beech wood as raw material with a moisture content of about 8.5 %. Nitrogen gas was circulated with a flow rate of 4.9 m³ per hour.

Table 14: Analysis results of IWC pyrolysis oil fractions.

Analysis method	Condenser 1	Condenser 2	Condenser 3	Electrostatic precipitator
Water content [wt. %]	12.1	40.7	46.4	10.1
pH	3.15	2.10	2.07	2.57
Elemental analysis				
C [wt.%]	48.05	30.57	24.20	51.83
H [wt.%]	6.97	8.33	9.11	6.98
N [wt.%]	0.28	0.14	0.17	0.23
O [wt.%] ¹	44.7	60.96	66.52	40.96

¹ calculated by difference

The yield of the different fractions was as follows: condenser 1: 9.7 %, condenser 2: 23.3 %, condenser 3: 12.8 %, electrostatic precipitator: 24.6 %. GC analysis was employed to monitor changes of the pyrolysis oil after the first month. Additionally, other analysis methods such as FTIR and viscosity measurements were performed. The analysis results obtained for the four different oil fractions are summarized in Table 14. Pyrolysis oil from the first condenser was stored in the dark at room temperature. Oils obtained from condenser 2, condenser 3, and the electrostatic precipitator were stored at room temperature, at 3 °C in a refrigerator, 50 °C, and -20 °C and in the dark as well as exposed to light.

4.1.4.2 Gas chromatography data

The four fractions stored under different conditions were analyzed by gas chromatography. All fractions exhibited a fast sludge formation. Because a very viscous oil was originally obtained

from the electrostatic precipitator, sludge formation was not observable. Only little sludge was found in samples stored at -20 °C.

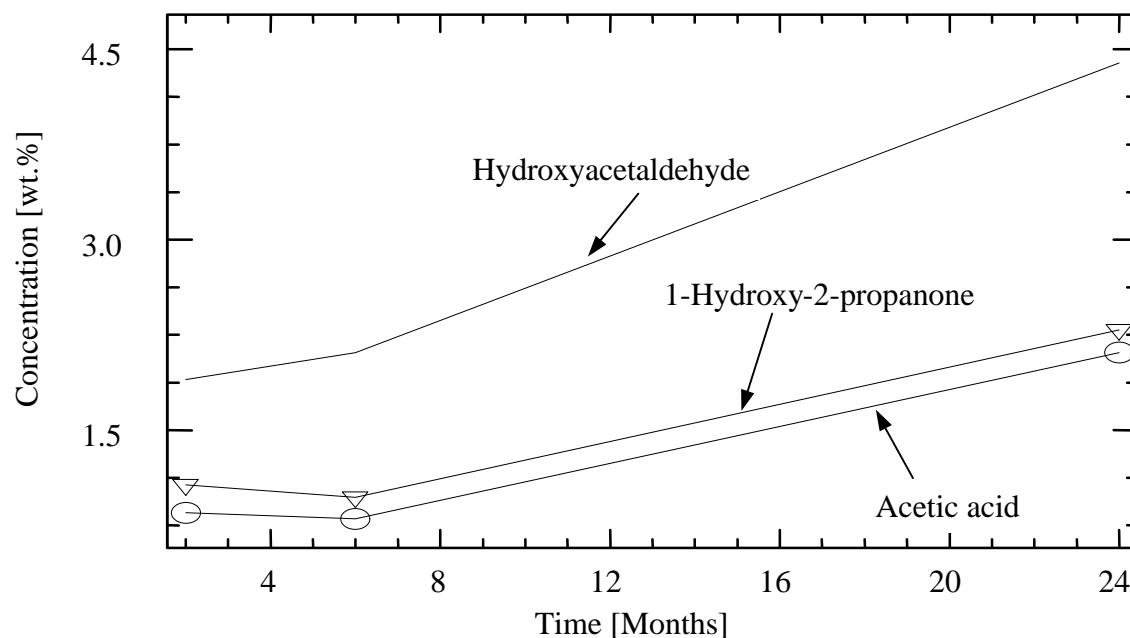


Figure 32: GC analysis data of IWC beech pyrolysis oil from condenser 1 stored closed at room temperature.

Compared to the IWC oils discussed above the oil fractions in this study showed a higher sludge formation. Especially, samples of condenser 2, condenser 3, and the electrostatic precipitator stored at 50 °C exhibited very high sludge formation. After 2 years at 50 °C the bottle of condenser 2 oil contained about 50 vol. % sludge and 50 vol. % liquid phase. At the same conditions the oil obtained from condenser 3 separated in about 30 vol. % sludge and 70 vol. % liquid phase. The oil sample obtained from the electrostatic precipitator consisted of about 98 vol. % sludge and 2 vol. % liquid phase. The sludge was formed in one piece and not attached to the container walls for condenser 2 and 3. In contrast, the sludge formed in the oil obtained from the electrostatic precipitator was attached to the bottle. In total, all samples stored of the described oil fractions showed either a high viscosity or phase separation. Figure 32 displays the evolution of the concentration of hydroxyacetaldehyde, acetic acid, and 1-hydroxy-2-propanone in the oil obtained from condenser 1. The concentrations for these components increased with storage time.

Interestingly, for the IWC pyrolysis oil obtained from condenser 2 and stored in the dark and under nitrogen, the concentrations of the main components are smaller than those for

samples exposed to light during storage. The assumption that the concentrations of all GC detectable components decrease with storage time could be confirmed.

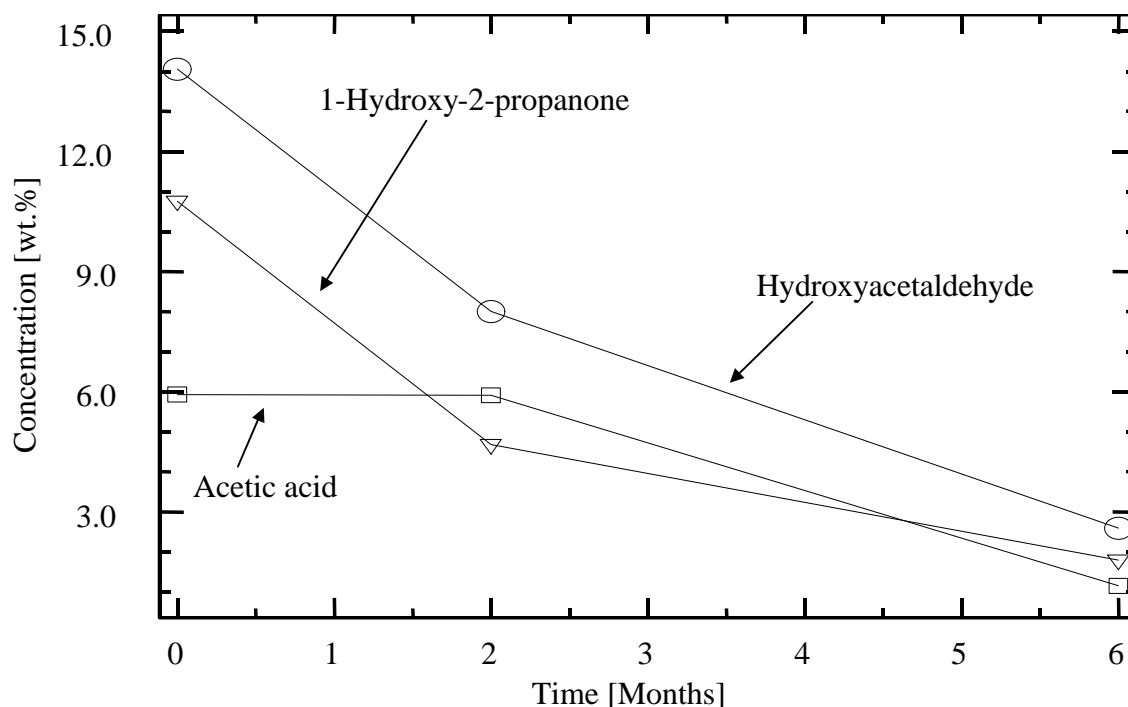


Figure 33: GC analysis data of IWC pyrolysis oil obtained from condenser 3 stored at RT in the dark.

The concentrations for hydroxyacetaldehyde, acetic acid and 1-hydroxy-2-propanone increased with storage time, possibly because of phase separation. Because at 50 °C the IWC pyrolysis oil separated into two phases, comparing quantitative results is rendered difficult. Nevertheless, it can be noticed that the liquid phase contains higher concentrations of hydroxyacetaldehyde, acetic acid, and 1-hydroxy-2-propanone.

As depicted in Figure 33, the concentrations of hydroxyacetaldehyde, acetic acid, and 1-hydroxy-2-propanone in the IWC pyrolysis oil obtained from condenser 3 decrease with storage time. Evidently, the concentrations of detectable components in the samples stored 24 months were higher than those in samples stored 2 or 6 months. During the first month the concentrations for compounds in the IWC pyrolysis oil obtained from the electrostatic precipitator and stored at room temperature decreased. After 24 months the concentrations of hydroxyacetaldehyde, acetic acid, and 1-hydroxy-2-propanone increased, possibly because of phase separation. The concentrations of the main components for the sample stored under nitrogen were smaller than those in the sample, which was exposed to light during storage.

4.1.4.3 Summary

Comparing this study with former investigations is rather difficult. In this work tests were performed using different oil fractions, whereas earlier studies considered the entire pyrolysis oil. Nevertheless, it was confirmed that the oil fractions exhibited a rapid sludge formation. The amount of sludge formed at the bottom of the containers increased with temperature. Interestingly, aging of samples stored at 50 °C exhibited differences to foregoing studies. Earlier studies had shown an extremely high viscose sludge attached to the bottom of containers. In this study the sludge was obtained in one piece and not attached to the container walls. However, all samples showed either a high viscosity or phase separation. The assumption that one of the fractions may contain less reactive compounds and, therefore, may be more stable was not confirmed.

Everything should be made as simple as possible
but not simpler.

Albert Einstein, 1879-1955

4.2 Catalytic upgrading of pyrolysis oils

4.2.1 *Introduction*

Both, catalytic treatment of pyrolysis oil in the vapor phase during production and hydrogenation of the pyrolysis oil after production in the presence of catalyst are possible procedures for chemical upgrading of bio oils. For upgrading of pyrolysis oil in the vapor phase in a fluidized bed reactor, four different methods for catalytic treatment can be envisaged. First, a mixture of wood and the catalyst can be continuously fed into the pyrolyser. Second, the catalyst can be mixed with the fluidizing material in the fluidized bed reactor. Third, the catalyst can be used as fluidizing material. Forth, the catalyst can be fixed in a second reactor coupled to the pyrolyser. In this work, the forth procedure for vapor phase upgrading of pyrolysis oil was performed and its effect on the pyrolysis oil obtained was investigated.

Hydrogenation of pyrolysis oil after production was performed in a batch reactor. Because the physical and chemical properties of pyrolysis oil change with temperature, mild hydrogenation conditions are necessary. Here mild conditions refer to lower hydrogen pressure and lower temperatures than for industrial hydrogenation of conventional petroleum oil (200-300 °C and > 50 bar).

The aim of the investigations described here was to obtain a pyrolysis oil which can be stored without significant changes in its physico-chemical properties. It is desirable to obtain pyrolysis oils with low viscosity and a high heating value because these properties are important regarding the use of pyrolysis oils for diesel engines and boiler combustion. Because aging of bio oils results in polymerization of carbonyl groups, a low amount of carbonyl groups is desirable with priority.

4.2.2 Vapor phase upgrading

4.2.2.1 Introduction

The small fluidized bed reactor used for the experiments described here is of the ‘Waterloo Fast Pyrolysis Process’ type. Beech wood meal with a particle size of 150 μm to 500 μm (moisture below 10 %) is transported pneumatically from the feeder into the fluidized bed reactor. The moisture content of the wood was measured for each experiment. At larger pyrolysis plants air-dry wood is regularly employed, because previous drying of the feed is not economic. Additionally, the moisture of the feed does not appear to have any negative influence on the pyrolysis process. For each pyrolysis run 85 g of sand or slate were employed as fluidizing material and nitrogen was used as fluidization gas. The residence time of the vapors in the original fluidized bed reactor was 1 second. The second reactor that was used for the vapor phase upgrading experiments employed a modified fluidized bed. The modified fluidized bed in the second reactor resulted in different residence times of the vapor phase. For the setup including the second reactor, Wulzinger [Wul99] calculated residence time between 0.67 seconds and 1.3 seconds.

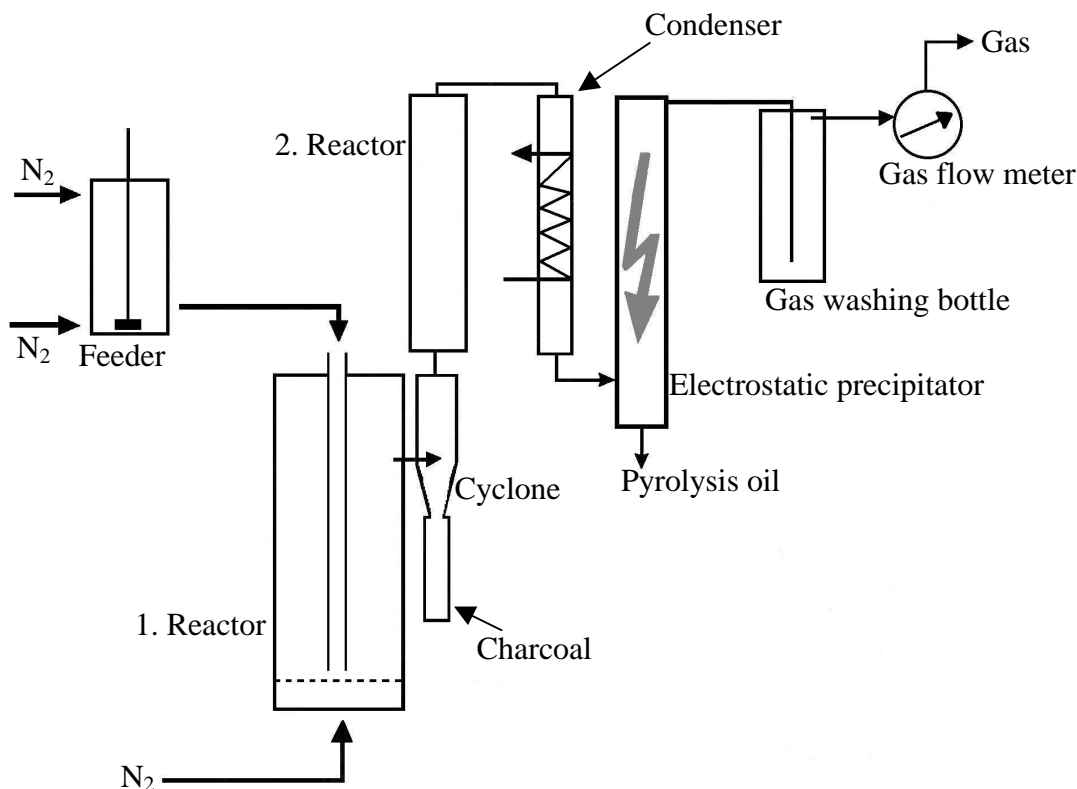


Figure 34: Schematic representation of the modified fluidized bed reactor.

The schematic representation of the experimental setup used is depicted in Figure 34. The fluidized bed is heated and the nitrogen enters the first reactor at the bottom of the bed. The first reactor, the cyclone, and the char pot are located in the same furnace and kept at a temperature of 475 °C.

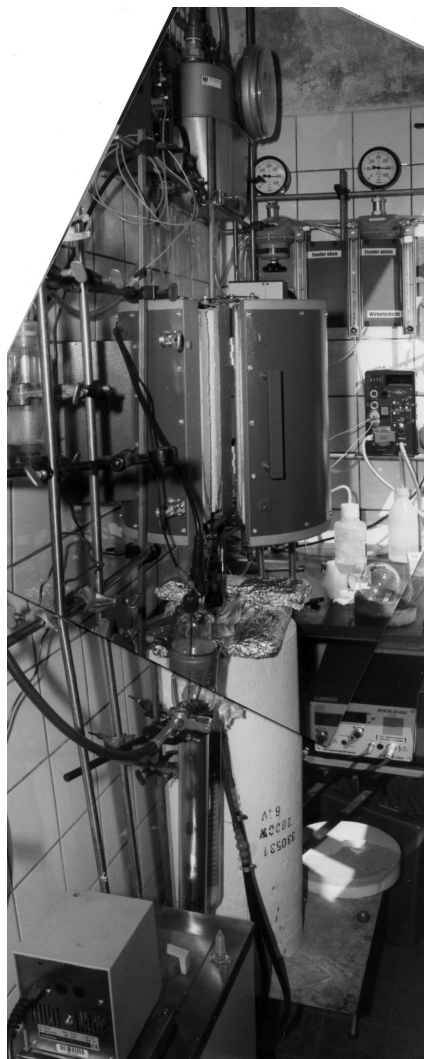


Figure 35: Photograph of the fluidized bed experiment at the IWC labor.

In previous investigations [Weh97, Wul99] it was noticed that at this temperature the maximum yield of pyrolysis oil is obtained. After leaving the first reactor, gases and aerosols pass the cyclone to the second reactor. A second furnace is used to regulate the temperature for the second reactor to 475 °C. For the investigations in this work, the second reactor contained the metal oxide catalysts supported on slate. Gases and aerosols had to pass the catalyst and, after leaving the second reactor, they were accumulated in the collection

assembly. In the set-up used, a single experimental run took half an hour. The transfer sections between the first and the second reactor as well as between the second reactor and the beginning of the condenser were thermally insulated. The condenser was operated with ethanol at $-5\text{ }^{\circ}\text{C}$ to $-15\text{ }^{\circ}\text{C}$ and the incondensable vapors were captured in the electrostatic precipitator. The latter consists of a glass housing with a metal tube, acting as the positive electrode and a thin metal wire hanging in the center of the tube acting as a negative electrode. Pyrolysis oils from the condenser and the electrostatic precipitator were collected together in one flask. A photograph of the experimental setup is presented in Figure 35. Because the pyrolysis oil produced was attached to the walls of the condenser and electrostatic precipitator, one hour was needed to collect the main part of the oil in the flask. Therefore, in all experiments the pyrolysis oil was collected for one hour after terminating the production procedure. The pyrolysis oil obtained was thoroughly analyzed with respect to water content, viscosity, carbonyl groups, acid number, and chemical and elemental composition (GC, FTIR, etc.).

4.2.2.2 Different catalysts for vapor phase upgrading experiments

Employing catalytically active materials during the pyrolysis of bio oils may be a possible way to modify the distribution of products obtained. For the investigations described here, slate was selected as a support material for various metal oxides. Slate is a very suitable support material for heterogeneous catalysts because it possesses a large surface area (large pore size) (see Figure 36 and Figure 37), it is inert to acid, and it is thermally stable. The catalysts employed were prepared according to the incipient wetness technique using solutions of various metal chlorides. After incipient wetness and drying, the slate was calcined at $500\text{ }^{\circ}\text{C}$ (as already explained in chapter 3) in order to obtain the corresponding metal oxides supported on the slate. At the high temperature and the calcination time used, a complete reaction of the metal chlorides to the corresponding oxides can be assumed. Therefore, the quantitative calculations and considerations presented in the following were made for metal oxide catalysts supported on slate. However, a detailed phase analysis by the techniques available (e.g. XRD) was prevented by the low metal oxide loading on the slate ($< 5\%$). After calcination, the metal oxides on slate were used as catalysts during the pyrolysis procedure.

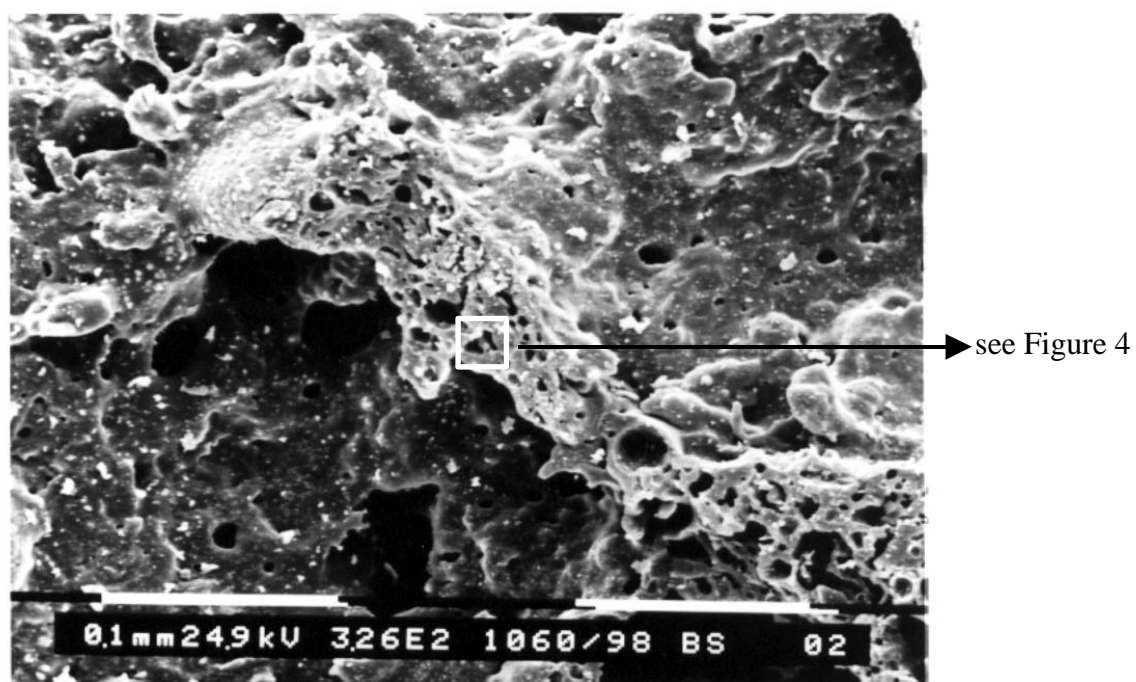


Figure 36: Scanning electron microscopy image of untreated slate (white bar on left side corresponds to 0.1 mm).

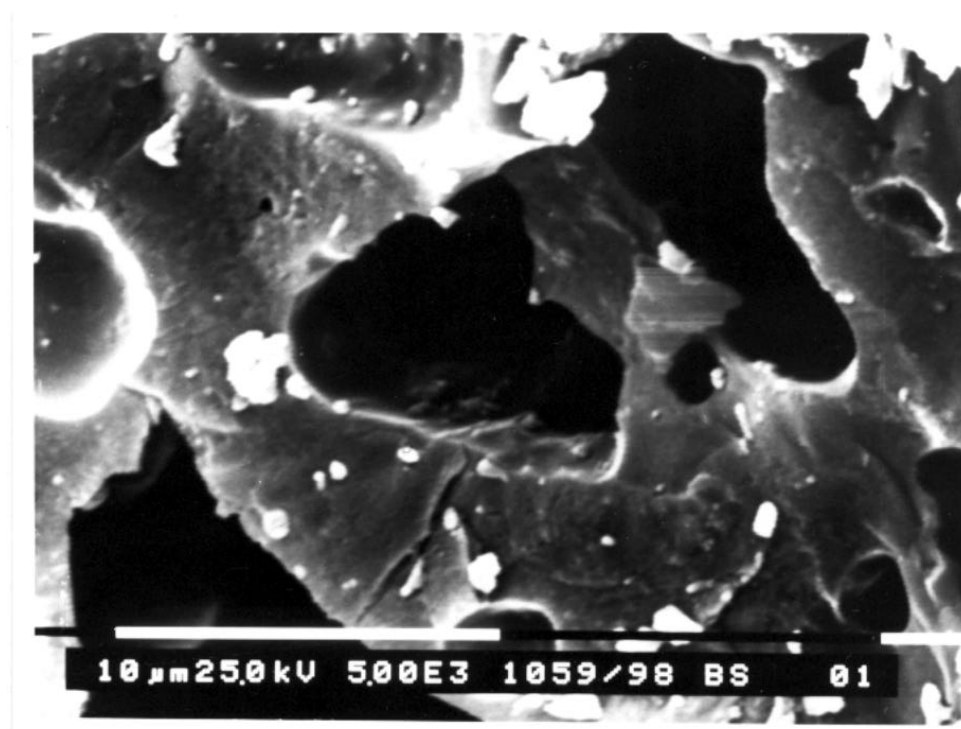


Figure 37: Scanning electron microscopy image of untreated slate (white bar on left side corresponds to 10 μm).

To date, only few experiments of vapor phase upgrading of pyrolysis oil with slate or metal oxides on slate have been described [Wul99]. Therefore, the experiments performed in this work constitute a first systematic step towards the use of heterogeneous catalysts during pyrolysis of bio oils. Successful leads identified in the studies described in the following, may be further exploited in the future to improve the physico-chemical properties of pyrolysis oils.

The following metal chlorides were used for the preparation of metal oxides on slate:

- a) Cerium chloride
- b) Manganese chloride
- c) Iron chloride
- d) Zinc chloride
- e) Cobalt chloride

Transition metal oxides are extensively employed in heterogeneous catalysis because of their ability to be stable in different oxidation states and to accommodate various coordination geometries. Both properties are assumed to be key characteristics of the “active site” of heterogeneous catalysts in e.g. isomerization reactions, hydrogenation, and partial oxidation. Furthermore, many of the transition metal oxides are so-called non-stoichiometric compounds that possess ample semi-conducting properties. In spite of insufficient structure-activity correlations in heterogeneous catalysis to date, both a particular defect structure and electronic structure should be essential ingredients of active and selective heterogeneous catalysts. Therefore, supported transition metal oxides could be suitable candidates for catalytic upgrading of pyrolysis oils.

For the pyrolysis experiments performed in this work, the transition metals selected have already been successfully used in heterogeneous catalysis mostly because of the chemical properties of the metals. Manganese, iron, and cerium form various oxides in formal oxidation states of +2 (MnO , FeO), 2.67 (Mn_3O_4 , Fe_3O_4), +3 (Mn_2O_3 , Fe_2O_3 , Ce_2O_3), and +4 (MnO_2 , CeO_2), and have been employed as catalyst in, for instance, partial oxidations or photocatalytic reactions. Zinc oxide is a defect-rich semi-conducting oxide with applications in, for instance, hydrogenation or dehydration reactions, and was therefore selected for the experiments described here. Cobalt was also chosen because of its ability to form stable species in multiple oxidation states and the ease of electron transfer between these states via

unstable intermediates or free radicals. In commercial applications cobalt is often used in combination with molybdenum for the gas and oil industry [CHSW00]. The transition metals selected are supposed to yield first leads to identify potential active catalyst for upgrading of pyrolysis oils. Based on the results described in the following, binary oxides or even more complex compositions may be selected and tested in future upgrading experiments.

4.2.2.3 Results

Because sand and slate have a different influence on the composition of pyrolysis oil, both sand and slate were used as fluidizing material. The pyrolysis runs employed the second reactor (see Figure 34) containing the metal oxide catalyst. For comparison several reference runs were performed without the second reactor in place or with the second reactor empty. The conditions for the various experiments are presented in Table 15.

For comparing the properties of heterogeneous catalysts, the number of active sites on the surface and the number of conversions per active site and time (the so-called ‘turn over frequency’, TOF) can be calculated. However, to determine the TOF of a particular catalyst not only the surface area of the catalyst but also the nature of the active site for a certain reaction need to be known. This is feasible neither for the catalysts used in this work nor for the chemical reactions occurring during pyrolysis. In order to calculate the surface area of the metal oxides on slate, the particle sizes of metal oxides supported on the slate need to be known. Because of the low metal oxide loading, no particle sizes could be obtained by XRD measurements. The SEM images shown in Figure 38 and Figure 39 indicate that for the various catalyst used, the particle size of the metal oxides is reasonably similar. Therefore, to avoid crude approximations but still enable a comparison of the catalysts used, the concentration of the metal oxide catalyst on slate (Γ) is given as the ratio of the amount of substance of metal oxide n and the mass m of the slate.

$$\Gamma = n_{\text{oxide}} / m_{\text{support}}$$

It is assumed that the catalysts produced consist of those metal oxides that are most stable at 500 °C in air. The resulting oxides and concentrations for the various catalysts employed are presented in Table 16.

Table 15: Content of the first and the second reactor during vapor phase upgrading experiments.

Sample	1. Reactor	2. Reactor
	85 g of fluidizing material	
BRIKAT A	sand	without 2nd reactor
BRIKAT B	sand	without 2nd reactor
BRIKAT C	slate	without 2nd reactor
BRIKAT D	sand	without 2nd reactor
BRIKAT E	sand	empty
BRIKAT F	sand	empty
BRIKAT G	slate	empty
BRIKAT H	slate	slate (15 g)
BRIKAT I	slate	slate (15.2 g)
BRIKAT J	slate	slate (15 g)
BRIKAT K	sand	slate (15 g)
BRIKAT L	sand	slate (15.4 g)
BRIKAT M	slate	cerium oxide on slate (14.5 g)
BRIKAT N	slate	cerium oxide on slate (14.8 g)
BRIKAT O	slate	manganese oxide on slate (15 g)
BRIKAT P	sand	manganese oxide on slate (15 g)
BRIKAT R	slate	manganese oxide on slate (15 g)
BRIKAT S	sand	iron oxide on slate (15.0 g)
BRIKAT T	sand	zinc oxide on slate (16.1 g)
BRIKAT U	sand	iron oxide on slate (15.5 g)
BRIKAT V	slate	cobalt oxide on slate (15.2 g)



Figure 38: Scanning electron microscopy image of manganese oxide on slate (white bar corresponds to 0.1 mm).

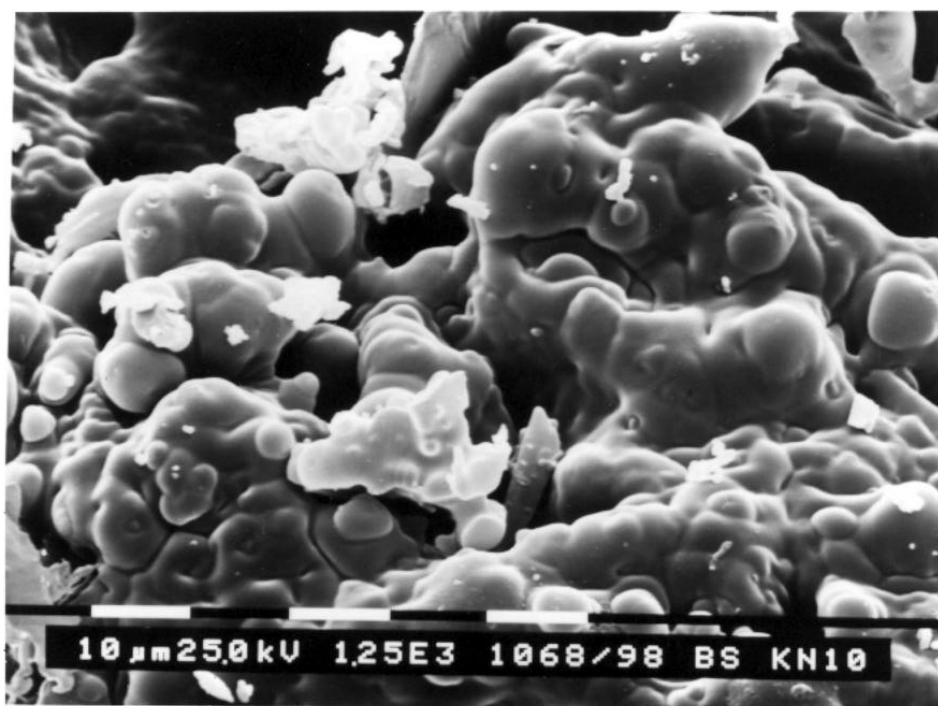


Figure 39: Scanning electron microscopy image of iron oxide on slate after the experiment (white bar on left side corresponds to 10 µm).

Table 16: Oxides, amount of oxides, mass of slates, and concentration of the metal oxides on slate for the various experiments performed.

Experiment	Oxide	Amount of substance [mmol]	Mass _{support} [g]	Γ [mmol/g]
BRIKAT M	CeO ₂	2.240	14.8153	0.151
BRIKAT N	CeO ₂	2.480	16.0510	0.155
BRIKAT O	MnO ₂	8.135	15.0111	0.542
BRIKAT P	MnO ₂	1.676	20.2278	0.083
BRIKAT R	MnO ₂	1.529	18.4747	0.083
BRIKAT S	Fe ₂ O ₃	1.135	19.9918	0.057
BRIKAT T	ZnO	1.310	18.2713	0.072
BRIKAT U	Fe ₂ O ₃	0.076	19.8773	0.004
BRIKAT V	Co ₃ O ₄	2.320	20.7673	0.112

The sample BRIKAT O exhibited the largest concentration of metal oxide on slate while sample BRIKAT U exhibited the smallest concentration. For all other catalysts employed the concentration Γ varied between 0.155 mmol/g and 0.057 mmol/g.

The amount of material in the feed, moisture of the feed, and the yield of the products obtained for the various pyrolysis runs are presented in Table 17. Obviously, small differences exist in the amount of feed used for the experiments without catalyst. Apparently, these differences did not depend on the fluidizing or catalytic material in the reactor but seem to be caused by variations in the amount of the feed. For small plants these variations in the feed and the resulting variations in the yield of pyrolysis oil have been previously reported [Weh96, Wul98]. Variations in the feed may be caused by short time blocking of the feeder system because of large wood particles or by an early blocking of the pipe in the first reactor. Interestingly, a higher feed resulted in a higher yield of pyrolysis oil rather than char and gas.

In the pyrolysis experiment performed with catalysts no similar dependence of the yield of oil on the amount of material in the feed was observed. In the experiment denoted as BRIKAT N and BRIKAT P the same amount of feed was used resulting, however, in yields of pyrolysis oil of 73.8 % and 80.3 %, respectively. This difference of 6.5 % in the yield of pyrolysis oil is outside the experimental error. Similarly, the yields of pyrolysis oil in the

experiment denoted as BRIKAT R and BRIKAT T differ only by 0.9 %, while the amount of feed of BRIKAT T is twice as high as that of BRIKAT R.

Table 17: Feed, yields, moisture of feed, and concentrations of the metal oxides on slate.

Experiment	Feed (wet) [g/h]	Yield pyrolysis oil [wt.%]	Yield char [wt.%]	Yield gas [wt.%] ¹	Moisture of feed [wt.%]	Γ [mmol/g]
BRIKAT A	108.8	69.4	19.2	11.4	9.3	-
BRIKAT B	217.4	72.9	16.1	11.0	8.9	-
BRIKAT C	91.2	64.4	18.7	16.9	8.7	-
BRIKAT D	225.9	72.3	15.5	12.2	8.5	-
BRIKAT E	210	72.7	17.5	9.8	8.5	-
BRIKAT F	227	72.6	19.8	7.6	8.4	-
BRIKAT G	133.2	71.0	22.3	6.7	8.6	-
BRIKAT H	132	72.0	17.8	10.2	8.5	-
BRIKAT I	130.2	69.6	11.5	19.0	8.2	-
BRIKAT J	130.4	70.3	13.7	16.0	8.1	-
BRIKAT K	137	70.8	12.2	17.0	8.5	-
BRIKAT L	227.4	72.2	10.8	17.0	7.0	-
BRIKAT M	109.8	73.0	10.0	17.0	8.1	0.079
BRIKAT N	200.2	73.8	11.8	14.4	8.1	0.081
BRIKAT O	49.6	66.1	8.9	25.0	8.2	0.542
BRIKAT P	200.8	80.3	10.6	9.1	8.0	0.083
BRIKAT R	62.6	69.0	5.8	25.2	8.2	0.083
BRIKAT S	114.8	70.2	14.8	15.0	8.2	0.057
BRIKAT T	227.1	69.9	11.8	18.3	7.4	0.072
BRIKAT U	219.8	70.9	10.6	18.5	7.4	0.004
BRIKAT V	104.8	77.5	10.7	11.8	7.9	0.112

¹ calculated by difference

In the experiment denoted as BRIKAT O and BRIKAT R small amount of feed values resulted in small yields of pyrolysis oil. In addition, these experiments afforded a rather large yield of gas (about 25 %). Conversely, experiment BRIKAT P exhibited the largest yield of pyrolysis oil (80.3 %) and the third smallest yield of gas (9.1 %) of all experiments performed.

Apparently, these variations do not depend on the different concentrations of the catalyst on slate (catalyst used in experiment BRIKAT P and BRIKAT R possess the same Γ value). However, experiment BRIKAT P, BRIKAT O, and BRIKAT R were performed with a different fluidizing material in the first reactor. The experiment BRIKAT P was performed with sand and the other two experiments used slate in the first reactor. Evidently, a combination of slate in the first reactor and manganese oxide on slate in the second reactor afforded a small yield of pyrolysis oil and a considerable increase in the gas production.

The experiments denoted as BRIKAT M and BRIKAT N, were both performed with slate in the first reactor and with cerium oxide on slate in the second reactor, and a difference of 50 % in the amount of the feed. Nevertheless, both experiments resulted in the same yield of pyrolysis oil and almost the same yield of char and gas. In these experiments apparently the same concentration of catalyst on slate resulted in similar yields.

Interestingly, experiments BRIKAT S and BRIKAT U afforded similar yields comparable to the yields obtained in the experiments BRIKAT M and BRIKAT N between each other. Both experiments BRIKAT S and BRIKAT U were performed with sand in the first reactor and with iron oxide on slate in the second reactor. Although, the catalyst of experiment BRIKAT U exhibited a significant smaller Γ value (0.004 mmol/g) than the catalyst of experiment BRIKAT S (0.057 mmol/g). The experiments resulted in a similar yield of pyrolysis oil and almost in the same yields of char and gas. The experiments denoted as BRIKAT T and BRIKAT V were the only pyrolysis runs that employed zinc oxide on slate and cobalt oxide on slate, respectively.

The elemental analysis, the heating values, and acid numbers of the pyrolysis oils produced are shown in Table 18. Elemental analysis of the pyrolysis oils yielded carbon contents between 36.50 wt.% and 40.62 wt.% and hydrogen contents between 7.52 wt.% and 7.86 wt.%. Only the pyrolysis oil obtained from experiment BRIKAT O showed a significant deviation in carbon and hydrogen content (30.78 wt.% and 8.28 wt.%, respectively).

The higher heating values (HHV) of the pyrolysis oils obtained from experiments BRIKAT A - BRIKAT V were calculated from the elemental analysis (see part 3.4.12 for detailed procedure). Pyrolysis oil with a high heating value is generally more suitable for the combustion in boilers or engines. The pyrolysis oils obtained from experiments denoted as BRIKAT T and BRIKAT U exhibited the highest HHV of all pyrolysis oil samples

(15.14 MJ/kg and 15.41 MJ/kg, respectively). Oils obtained from BRIKAT O and BRIKAT R exhibited the lowest heating value of all oils produced.

Table 18: Elemental analysis and calculated heating values of pyrolysis oils produced.

Experiment	Elemental analysis				Higher heating value ² [MJ/kg]
	C [wt.%]	H [wt.%]	N [wt.%]	O [wt.%] ¹	
BRIKAT A	38.96	7.58	0.34	53.12	14.53
BRIKAT B	39.70	7.52	0.39	52.39	14.83
BRIKAT C	36.69	7.80	0.30	55.21	13.71
BRIKAT D	40.05	7.57	0.31	52.07	15.08
BRIKAT E	39.50	7.69	0.25	52.56	14.97
BRIKAT F	39.44	7.65	0.28	52.63	14.88
BRIKAT G	37.38	7.83	0.24	54.55	14.10
BRIKAT H	37.22	7.80	0.29	54.69	13.98
BRIKAT I	38.31	7.71	0.32	53.66	14.40
BRIKAT J	39.17	7.58	0.41	52.84	14.65
BRIKAT K	37.48	7.72	0.30	54.50	13.99
BRIKAT L	40.14	7.61	0.28	51.97	15.18
BRIKAT M	36.78	7.85	0.25	55.12	13.82
BRIKAT N	39.40	7.61	0.29	52.70	14.80
BRIKAT O	30.78	8.28	0.20	60.74	11.40
BRIKAT P	38.19	7.79	0.28	53.74	14.46
BRIKAT R	36.50	7.80	0.33	55.37	13.61
BRIKAT S	37.23	7.86	0.37	54.54	14.10
BRIKAT T	39.88	7.67	0.28	52.17	15.14
BRIKAT U	40.62	7.60	0.27	51.51	15.41
BRIKAT V	39.54	7.60	0.29	52.57	14.86

¹ Calculated by difference, ² calculated from elemental analysis, n.a. = not analyzed

The water contents of the pyrolysis oils produced, the viscosities of these oils stored at 3 °C, and stored for 24 hours at 80 °C as well as the number of carbonyl groups of some pyrolysis oils are shown in Table 19.

Provided that the moisture of the feed is completely contained in the water content of the pyrolysis oil produced, the experiment denoted as BRIKAT O and BRIKAT R exhibited the largest content of water (36.7 wt.% and 30.1 wt.%, respectively) of all pyrolysis oils produced. The pyrolysis oils obtained from experiments BRIKAT M, BRIKAT O, BRIKAT R, and BRIKAT S, performed with catalysts, exhibited larger water content than the average water content of oils from experiments performed without catalysts. Pyrolysis oils obtained from experiments BRIKAT P and BRIKAT U exhibited smaller water contents than the average water content of oils from experiments performed without a catalyst.

After storage at 3 °C the pyrolysis oils obtained from experiments BRIKAT H - BRIKAT L possess a low viscosity (between 17.0 cSt and 24.4 cSt) while oils stored for 24 hours at 80 °C exhibited viscosity values between 22.5 cSt and 51.8 cSt. The experiments denoted as BRIKAT H - BRIKAT L were performed with slate in the second reactor, while the experiments BRIKAT A - BRIKAT G were performed without the second reactor or using an empty second reactor. The pyrolysis oils obtained from these experiments exhibited higher viscosity values for samples stored at 3 °C (between 21.8 cSt and 55.6 cSt) and 80 °C (between 29.9 cSt and 88.2 cSt) compared to those of oils obtained from experiments performed with slate in the second reactor.

The viscosity values of pyrolysis oils obtained from experiments performed with catalysts were lower than the average in viscosities of oils obtained from experiments performed without the second reactor or using an empty second reactor. The experiment BRIKAT O afforded a pyrolysis oil with a rather low viscosity for the sample stored at 3 °C. However, this value may be due to the high water content of the pyrolysis oil. The pyrolysis oil obtained from experiment BRIKAT S possesses a low viscosity for the sample stored at 3 °C and for the sample stored at 80 °C.

Because determining the number of carbonyl groups in bio oils is a time-consuming method, only some oil samples were investigated. The values obtained were in the range from 5.40 mol/kg to 6.43 mol/kg.

Table 19: Water content, viscosity for samples stored at 3 °C and at 80 °C, and number of carbonyl groups of pyrolysis oils.

Experiment	Water content [wt.%]	Viscosity ¹ for sample stored for 24-48 hours at 3 °C [cSt]	Viscosity ¹ for sample stored for 24 hours at 80 °C [cSt]	Number of carbonyl groups [mol/kg]
BRIKAT A	24.8	36.7	51.2	n.a.
BRIKAT B	28.1	40.2	48.9	5.78
BRIKAT C	28.5	21.8	n.a.	6.10
BRIKAT D	23.8	43.6	88.2	5.91
BRIKAT E	25.0	34.6	66.7	n.a.
BRIKAT F	25.6	55.6	66.3	5.40
BRIKAT G	27.6	26.9	29.9	5.70
BRIKAT H	28.4	17.0	39.2	n.a.
BRIKAT I	26.5	19.8	39.0	n.a.
BRIKAT J	25.4	23.5	47.1	6.34
BRIKAT K	27.4	19.5	22.5	5.86
BRIKAT L	24.8	24.4	51.8	n.a.
BRIKAT M	29.4	19.1	34.6	n.a.
BRIKAT N	25.9	23.0	40.2	n.a.
BRIKAT O	36.7	8.1	n.a.	n.a.
BRIKAT P	24.9	28.4	49.7	5.69
BRIKAT R	30.1	n.a.	n.a.	6.43
BRIKAT S	29.1	20.1	30.7	5.80
BRIKAT T	25.0	22.4	46.5	n.a.
BRIKAT U	24.3	29.5	69.5	n.a.
BRIKAT V	n.a.	25.3	55.9	n.a.

¹ measured at 20 °C, n.a. = not analyzed

4.2.2.4 Concluding remarks

For the catalytic upgrading experiments described in this work, slate was chosen as a support material for various metal oxides. Slate exhibits a large pore size, a large surface area, and sufficient thermal stability. Because of the low metal oxide loading, the particle size and, hence, the surface area of the metal oxide could not be determined. In order to compare the catalysts used with respect to their metal loading, the concentration of the metal oxide on slate was calculated as the ratio of the amount of substance of metal oxide and the mass of the slate. The catalyst used in experiment BRIKAT O employed the largest concentration of the metal oxide on slate (0.542 mmol manganese oxide per gram slate).

For regular experiments performed without a catalyst (BRIKAT A - BRIKAT L) a higher amount of feed resulted in a higher yield of pyrolysis oil. Conversely, experiments performed with a catalyst (BRIKAT M - BRIKAT V) did not show a similar dependence of the yield on the amount of feed.

The upgrading experiments denoted as BRIKAT T and BRIKAT U afforded the highest HHV of the pyrolysis oils obtained. The lowest HHV as well as the highest water content was calculated for the oils from experiments BRIKAT O and BRIKAT R. The pyrolysis oil obtained from experiment BRIKAT O exhibited a rather low viscosity, possibly because of a very high water content.

Experiment BRIKAT P was performed with sand in the first reactor and with manganese oxide on slate in the second reactor and afforded the highest yield of pyrolysis oil and the third lowest yield of gas of all upgrading experiments described here. The pyrolysis oil obtained possessed a reasonable HHV, small water content, and a low viscosity (even for the oil stored at 80 °C). In addition, the experiment BRIKAT P resulted in a large yield of pyrolysis oil and a small yield of gas. Hence, manganese oxide on slate in the second reactor in combination with sand in the first reactor may be a promising candidate for future catalytic upgrading experiments.

Conversely, a combination of slate in the first reactor and manganese oxide on slate in the second reactor as employed in experiments BRIKAT O and BRIKAT R, afforded a small yield of pyrolysis oil and a considerable increase in the gas production. Interestingly, manganese oxide on slate in the second reactor in combination with slate in the first reactor performs much worse compared to the combination of sand and manganese oxide on slate. The pyrolysis oils obtained from the other experiments performed with catalysts exhibited

minor improvements in their physico-chemical properties, for example quite low viscosity values. In total, the vapor phase upgrading with metal oxide on slate described in this work seems to be a promising method to improve the long-term stability of pyrolysis oils. The experiments performed show several leads that should be further exploited in future investigations.

4.2.3 Hydrogenation of pyrolysis oils

4.2.3.1 Introduction

For the hydrogenation investigations pyrolysis oils were treated at various temperatures and at different hydrogen pressures using a series of different catalysts. Hydrogen pressures up to 20 bar and temperatures up to 110 °C were used. Screening experiments were performed in a 1000 ml batch reactor at various reaction times. Extrudates prepared from powder catalysts were employed in most of the experiments while only one test was performed with a powdered catalyst. Because high speed stirrers tend to mechanically break catalyst extrudates into smaller fractions, a basket was used which contained the catalyst extrudates during the hydrogenation experiments. The construction of the basket is depicted in Figure 40.

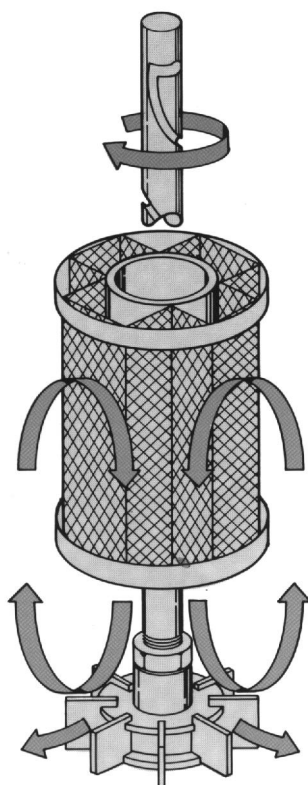


Figure 40: Schematic representation of the falling basket for mild hydrogenation experiments.

After each hydrogenation experiment the pyrolysis oils were analyzed by GC-FID and various physico-chemical methods to determine the viscosity, the density, and the pH value of the oils obtained. The conditions for the various hydrogenation experiments are described in the following parts. Mild hydrogenation experiments were performed with two different pine pyrolysis oils from VTT. The physical and chemical analyses data of VTT pine oil number 1 have already been depicted in chapter 4.1.

4.2.3.2 Reference hydrogenation experiments

Two mild hydrogenation experiments without catalysts were performed as reference runs to study the effect of hydrogen pressure and temperature on the pyrolysis oils obtained. The tests were carried out with VTT oil number 1 and were described in detail in section 4.1.3.1. A detailed study on the physico-chemical properties of these pyrolysis oils is presented in chapter 4.1.

4.2.3.3 Raney nickel

Raney nickel is experimentally used as an industrial hydrogenation catalyst because of its high activity. Since in industrial applications Raney nickel is often used as a powder, the following experiment was also performed with Raney nickel powder. Experiments were carried out with VTT pine oil number 2 (produced in May 1998 at VTT) under the following conditions: 8.5 wt.% catalyst, 2, 4, 6, and 8 hours at 80 °C, stirrer velocity of 1000 r.p.m., and H₂ pressure of 20 bar. The pyrolysis oils obtained after 2, 4, 6, and 8 hours from the experiments were denoted as hydrogenation C, hydrogenation D, hydrogenation E, and hydrogenation F, respectively. The viscosity data of the pyrolysis oils obtained are given in Table 20.

Table 20: Viscosity after hydrogenation experiments with Raney nickel.

Analysis method	VTT pine oil after hydrogenation with Raney nickel			
	C (2 h)	D (4 h)	E (6 h)	F (8 h)
Viscosity ¹ [cSt]	60.4	51.2	45.8	41.9
Viscosity ² [cSt]	n.a.	10.9	10.4	n.a.

¹ stored at 20 °C, ² stored at 50 °C, n.a. = not analyzed

It can be seen from Table 20 that the viscosity of the oils obtained decreased with reaction time. However, after storing the oils for several weeks phase separation occurred. The pyrolysis oils obtained were analyzed by gas chromatography (Figure 41). Evidently,

considerable differences can be noticed for retention times between 5 and 28 minutes. Interestingly, the amount of most of the corresponding compounds with bands in this region decreased with reaction time, indicating a decrease in the total amount of functional groups that are available for reaction during storage. Apparently, this observation confirms that the viscosity of the oils obtained decreased with reaction time.

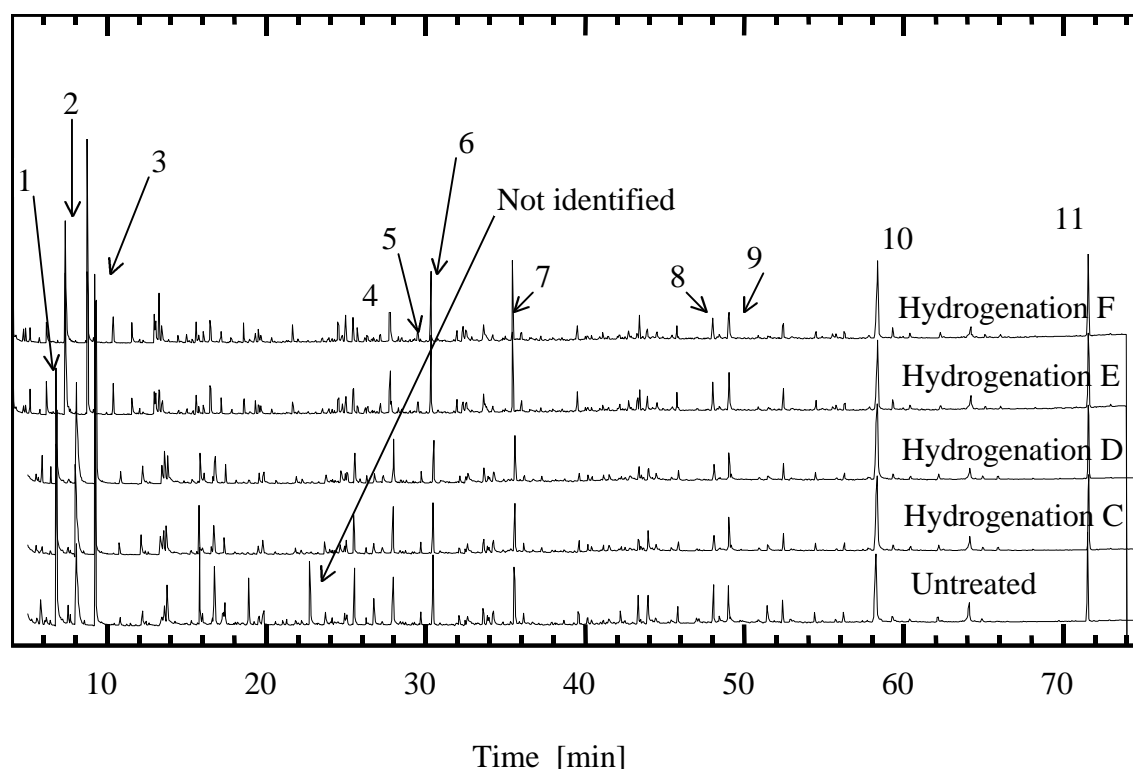


Figure 41: Gas chromatograms of hydrogenated VTT oil number 2. From bottom to top: pyrolysis oil before hydrogenation and hydrogenation C - F: increasing reaction time. [Identified peaks: (1) Hydroxyacetaldehyde; (2) Acetic acid; (3) Hydroxypropanone; (4) 2-Hydroxy-1-methyl-1-cyclopentene-3-one; (5) Phenol; (6) Guaiacol; (7) 4-Methylguaiacol; (8) trans-Isoeugenol; (9) Vanillin; (10) Levoglucosan; (11) Fluoranthene (internal standard).]

4.2.3.4 Nickel/nickel oxide

In addition to the experiments with Raney nickel several mild hydrogenation experiments with pyrolysis oils using a nickel/nickel oxide catalysts from SÜDCHEMIE were carried out. The hydrogenation tests were performed with VTT pine pyrolysis oil number 1 under the following reaction conditions:

(G) 1.3 wt.% catalyst, 20 hours at 22 °C, stirrer velocity of 1000 r.p.m., and H₂ pressure of 1.3 bar (denoted as hydrogenation G).

(H) 4.7 wt.% catalyst, 24 hours at 82 °C, stirrer velocity of 1000 r.p.m., and H₂ pressure of 5 bar (denoted as hydrogenation H).

(I) 3.4 wt.% catalyst, 19 hours at 50 °C, stir velocity of 1000 r.p.m., and H₂ pressure of 4 bar (denoted as hydrogenation I).

(J) 3 % catalyst, 5 hours at 60 °C, stir velocity of 1000 r.p.m., and H₂ pressure of 3 bar (denoted as hydrogenation J).

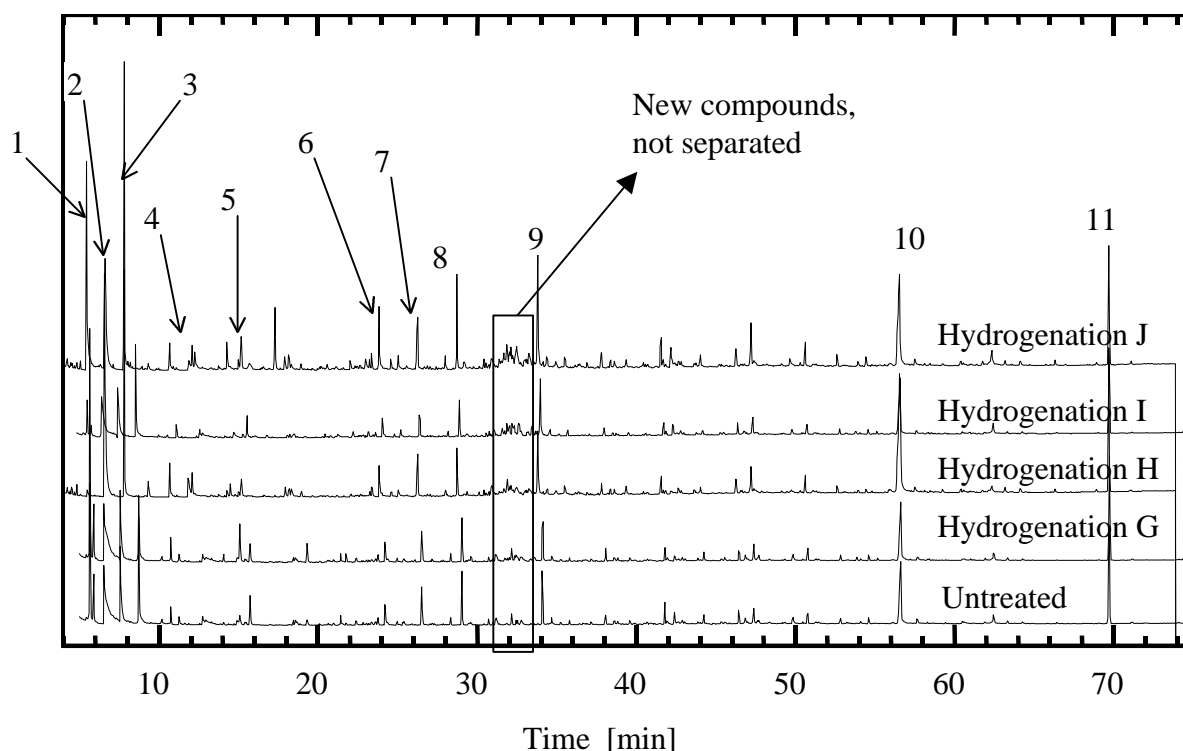


Figure 42: Gas chromatograms of hydrogenated VTT pine pyrolysis oil number 1. From bottom to top: pyrolysis oil before hydrogenation, hydrogenation G, hydrogenation H, hydrogenation I, and hydrogenation J. [Identified peaks: (1) Hydroxyacetaldehyde; (2) Acetic acid; (3) Hydroxypropanone; (4) 1,2 Ethanediol and 1-Hydroxy-2-butanone; (5) trans-2,5-Dimethoxytetrahydrofuran and 2-Furfural; (6) 2(5H)-Furanone; (7) 2-Hydroxy-1-methyl-1-cyclopentene-3-one; (8) Guaiacol; (9) 4-Methylguaiacol; (10) Levoglucosan; (11) Fluoranthene (internal standard).]

Table 21: Analysis results after hydrogenation tests with nickel/nickel oxide catalysts.

Analysis method	Hydrogenation G	Hydrogenation I	Hydrogenation J
Density ¹ [g/ml]	n.a.	1.251	1.247
PH value	2.22	2.77	2.72
Viscosity ² [cSt]	568.3	681.1	1087.7
Viscosity ³ [cSt]	56.7	69.6	87.5
Amount of Carbonyl groups [mol/kg]	4.00	3.78	4.12

¹ measured at 20 °C, ² stored at 20 °C, ³ stored at 50 °C, n.a. = not analyzed

Directly after each experiment, GC analyses of the pyrolysis oils obtained were performed. The corresponding chromatograms are presented in Figure 42. Differences can be noticed for retention times between 5 and 28 minutes. The amount of most of the corresponding compounds with peaks in this region increased with reaction temperature related to an increasing total amount of functional groups. This confirms that the viscosity of the oils obtained increased (from hydrogenation G via hydrogenation I to hydrogenation J) (see Table 22).

During the series of experiments described here, it became evident, that in order to obtain reliable results, all analytical tests need to be carried out directly after the hydrogenation experiments. However, this was not feasible in all cases. The analysis results obtained are shown in Table 21.

An additional mild hydrogenation experiment (hydrogenation K) was performed with VTT pine oil number 2 under the following reaction conditions: 1.1 wt.% catalyst, 24 hours at 100 °C, stir velocity of 1000 r.p.m., and H₂ pressure of 20 bar. Similar to hydrogenation experiment H an inhomogeneous pyrolysis oil was obtained that could not be analyzed with respect to its physico-chemical properties.

Polymerization reactions, for example via carbonyl groups, are a considerable part of the aging behavior of pyrolysis oils. Therefore, different amount and type of carbonyl groups of pyrolysis oils may indicate a different long-term stability and, hence, are an important property of the oils. For the crude VTT oil number 1 Figure 43 shows a considerable decrease

in the number of carbonyl groups with time at 80 °C, whereas at -20 °C the number of carbonyl groups decreased significantly less. This indicates again that the polymerization of various compounds in the oil is accelerated at higher temperatures.

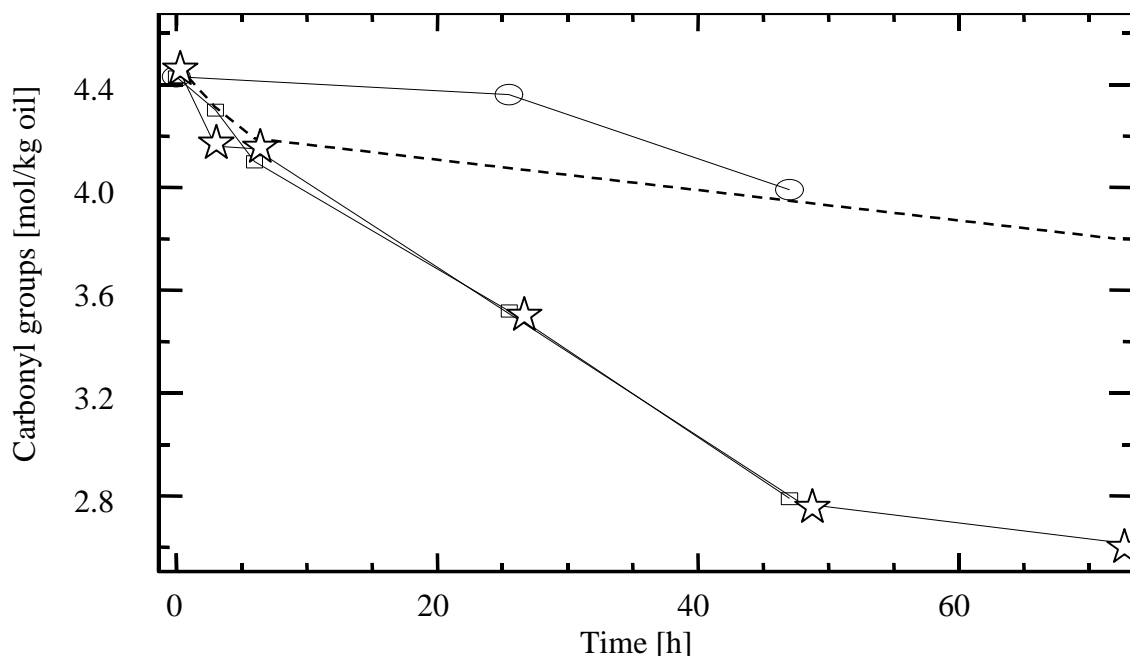


Figure 43: Evolution of the number of carbonyl groups with time at different temperatures. *Stars*: VTT oil stored at 80 °C; *dash*: VTT oil stored at -20 °C; *squares*: VTT oil (number 1) hydrogenated in the presence of Ni/NiO and stored at 80 °C; *circles*: VTT oil (number 1) hydrogenated in the presence of Ni/NiO and stored at -20 °C.

After hydrogenation G the oil obtained was stored at 80 °C and at -20 °C. Analysis of the amount of carbonyl groups in this oil as a function of storage time is also shown in Figure 43. Compared to the crude oil stored at -20 °C, smaller variations in the amount of carbonyl groups for the hydrogenated samples were found. Conversely, the samples stored at 80 °C exhibited the same decrease in the amount of carbonyl groups for untreated and hydrogenated VTT oil.

4.2.3.5 Palladium

Two hydrogenation experiments were performed with VTT pine pyrolysis oil number 1 under the following conditions:

(L) 1 % Pd catalyst, 3 hours at 60 °C, stir velocity of 1000 r.p.m., and H₂ pressure of 6 bar (denoted as hydrogenation L).

(M) 1.1 % pretreated Pd catalyst, 3 hours at 60 °C, stir velocity of 600 r.p.m.. and H₂ pressure of 6 bar (denoted as hydrogenation M).

Table 22: Analysis results after hydrogenation tests with palladium catalysts

Analysis methods	VTT pine pyrolysis oil number 1	VTT pine oil after hydrogenation with palladium	
	untreated	L	M
Moisture [%]	17.4	17.7	18.1
pH value	2.35	2.15	2.14
Density ¹ [g/ml]	1.24	1.24	1.25
Viscosity ² [cSt]	n.a.	529.5	527.8
Viscosity ³ [cSt]	35.0	49.6	49.0
Amount of carbonyl groups [mol/kg]	4.72	4.68	n.a.

¹ measured at 20 °C, ² measured at 20 °C, ³ measured at 50 °C, n.a. = not analyzed

Analysis results for these hydrogenation experiments are presented in Table 22. The viscosity for the untreated oil measured at 20 °C and at 50 °C was 532.7 cSt and 49.8 cSt, respectively. The amount of carbonyl groups in the untreated oil was 4.73 mol/kg. Apparently, hydrogenation of pyrolysis oil in the presence of a palladium catalyst under the selected conditions, affords pyrolysis oils with only minor difference in their physical properties compared to the untreated oil.

4.2.3.6 Copper/copper oxide/copper chromate/barium chromate

A mild hydrogenation experiment was performed with VTT pine oil number 2 using a mixed transmission metal catalysts (copper/copper oxide/copper chromate/barium chromate under iso-decanole from SÜDCHEMIE) under the following reaction conditions: 9.2 wt.% catalyst, 2, 4, and 6 hours at 80 °C, stir velocity of 1000 r.p.m., and H₂ pressure of 20 bar. The pyrolysis oils obtained after 2, 4, and 6 hours from the experiments were denoted as hydrogenation N, hydrogenation O, and hydrogenation P, respectively. The viscosity of the oils obtained from this mild hydrogenation experiment is given in Table 23. The viscosity

increased with experimental time. However, the pyrolysis oils obtained from these experiment were inhomogenous.

Table 23: Viscosity of VTT pine oil number 2 after hydrogenation using a copper/copper oxide/copper chromate/barium chromate catalyst.

Analysis method	VTT oil before hydrogenation	VTT pine oil after hydrogenation with copper/copper oxide/copper chromate/ barium chromate		
		N (2 h)	O (4 h)	P (6 h)
Viscosity ¹ [cSt]	109.7	135.3	127.6	157.9
Viscosity ² [cSt]	n.a.	18.9	19.3	n.a.

¹ measured at 20 °C, ² measured at 50 °C, n.a. = not analyzed

4.2.3.7 Concluding remarks

Improving the long-term stability of pyrolysis oils is one of the motivations of catalytic treatment of the oils after the pyrolysis process. Polymerization reactions and, hence, the resulting increase in the viscosity of the oils with time, seem to constitute a major problem with respect to the aging of pyrolysis oils and their industrial application. Because many polymerization reaction require particular functional groups such as C-C double bonds or carbonyl groups, hydrogenation of pyrolysis oils after production can be envisaged to reduce the number of these functional groups in the oils and, thus, to improve their long-term stability.

The results of mild hydrogenation experiments described in this work suggest that reaction temperatures above 80 °C are unsuitable for hydrogenation of bio oils. At temperatures above 80 °C, polymerization reactions in the oils proceed rapidly, resulting in pyrolysis oils with a high viscosity. In addition, the oils obtained tended to get phase separated with storage time yielding an undesired sludge at the bottom of the container. In general, the high viscosity and the inhomogeneity of the pyrolysis oils obtained after hydrogenation afford viscosity measurements that are difficult to interpret.

With respect to the experimental procedure it turned out that reliable investigations of physical and chemical properties of the oil after hydrogenation were possible only if catalyst extrudates had been used instead of powder catalyst. Fine catalyst powders seem to remain

well dispersed in the oils obtained and are extremely difficult to remove properly. Therefore, physico-chemical properties of these oils, for instance viscosity and chemical analysis, will be hardly comparable with the crude oil.

Hydrogenation experiments with Raney nickel as a powder catalyst at 80 °C yielded a homogeneous pyrolysis oil. However, after one day at room temperature an irreversible phase separation into a sludge and a less viscous oil occurred. Interestingly, the viscosity of the pyrolysis oils obtained and measured directly after the hydrogenation experiments decreased with reaction time. Apparently, the viscosity of the pyrolysis oils decreased with prolonged treatment under the conditions used. Conversely, hydrogenation experiment with Raney nickel as extrudate yielded pyrolysis oils with almost no variations in the viscosity. Therefore, if experimental precautions ensure that the catalyst powder remains well separated from the pyrolysis oils, Raney nickel may be a suitable candidate for further hydrogenation experiments.

The hydrogenation experiments using a nickel/nickel oxide catalyst from SÜDCHEMIE at reaction temperatures above 80 °C yielded an inhomogeneous pyrolysis oil. GC analysis of the resulting oils was performed directly after each experiment and afforded the largest changes in the product distribution for hydrogenation J. Here, new products seem to be formed during reaction, which are detected by GC in the retention time window between 32 and 37 minutes. However, because no preparative GC was used for the experiments described, those products could not be separated and identified.

Hydrogenation experiments using a palladium catalyst yielded pyrolysis oils with nearly the same physico-chemical properties as the original pyrolysis oil. Hydrogenation experiments employing a copper/copper oxide/copper chromate/barium chromate catalyst (SÜDCHEMIE) under iso-decanole produced only an inhomogeneous pyrolysis oil. Here, the viscosity of the resulting pyrolysis oils increased with reaction time.

In summary of the hydrogenation experiments performed in this work, none of the combinations of pyrolysis oils, heterogeneous catalysts, and experimental conditions employed resulted in more stable pyrolysis oils compared to the corresponding untreated oils. Because many of the commercial hydrogenation catalysts require rather high temperatures, they seem to be unsuitable for pyrolysis oil treatment. Polymerization reactions in the oils and hydrogenation of the corresponding functional groups are competing reaction pathways, and

conditions favorable for a successful upgrading of pyrolysis oils need to suppress the former while accelerating the latter. Therefore, for future upgrading experiments of pyrolysis oils by hydrogenation it will be of paramount importance to exploit reactive and selective catalysts that can operate already at temperatures well below 80 °C.

It is a capital mistake to theorise before one has data.
 Insensibly one begins to twist facts to suit theories,
 instead of theories to suit facts.

Sherlock Holmes
in Scandal in Bohemia

4.3 Pyrolytic lignin

4.3.1 Introduction

Pyrolytic lignins were obtained by adding pyrolysis oil dropwise to water under vigorous stirring using a 'turrax' (high speed stirrer). It has been noticed during the experiments described here that at temperatures above 20 °C the pyrolysis oil droplets could not be dissolved immediately, and that they tend to conglomerate and form a sticky mass. Consequently, certain components in the bio oil may not be completely dissolved and the yield of pyrolytic lignin increases. A slow increase of the temperature was observed applying the turrax. In this case the water had to be cooled during the entire experiment.

The rate of rotation is important for pyrolytic lignin production. Initial experiments were performed using a magnetic stirrer without cooling. Five different pyrolysis oils were employed for these experiments. Only two of them are shown in Table 24 because the other pyrolysis oils covered and blocked the magnetic stirrer and, hence, the experiments had to be aborted. The pyrolysis liquids used were selected because they were provided by various pilot plants and, thus, represented the to-be expected quality of pyrolysis liquids from future larger plants. Moreover, they were available in sufficient quantities.

Table 24: Origin of pyrolysis oil, yields, and color of pyrolytic lignin performed with magnetic stirrer.

Origin	Yield [wt. %]	Color
Union FENOSA (eucalyptus pyrolysis oil)	21.7	reddish-brown
University of Twente (mixed softwood pyrolysis oil)	9.2	beige

The largest amount of pyrolysis lignin as a fine powder was obtained from FENOSA eucalyptus pyrolysis oil. For all the other oils the pyrolytic lignin formed agglomerated using a magnetic stirrer. This happened even when the speed of adding oil was reduced to less than 1 ml/hour. Another experiment was performed in an automatic shaker. Pyrolysis oils and water (oil water ratio at least 1:10) were poured in a plastic bottle and shaken for about 3 hours. The results for two pyrolysis oils are presented in Table 25.

Table 25: Origin of pyrolysis oil, yields, and color of pyrolytic lignin performed with automatic shaker.

Origin	Yield [wt. %]	Color
Union FENOSA (pine pyrolysis oil)	25.2	dark brown
ENSYN Technologies Inc. (mixed hardwood pyrolysis oil)	30.6	light brown

Because it was found that only minor amounts of pyrolytic lignins could be precipitated at a slow rotation rate or by shaking pyrolysis oils with water, the following experiments were performed with an ultra turrax and rotation rates up to 6000 r.p.m. By using the ‘turrax method’ all investigated pyrolysis oils resulted in a fine homogeneous pyrolytic lignin powder. However, different compositions of pyrolytic lignins obtained by various methods have to be expected. This should be investigated in future studies.

4.3.2 Results

Pyrolytic lignins were dried at about 25 °C. It was observed, that temperatures above 40 °C caused the surface of pyrolytic lignin to turn black. Normally, the color of pyrolytic lignin varies between light and dark brown. The resulting homogeneous fine powder has a low density, and electrostatic charging of the fine powder is sometimes observed.

A systematic study on the precipitation and characterization of eight different pyrolytic lignins from different pyrolysis processes and feedstocks is presented in the following. The origin and physico-chemical data of the pyrolysis oils used are given in Table 26. Precipitation yields and colors on visual inspection of the pyrolytic lignins obtained are given in Table 27. It can be seen that the yield of pyrolytic lignin as determined for the different pyrolysis oils varies from 13.5 % to 27.7 % based on water free pyrolysis oils.

The lowest yield of pyrolytic lignin in this study was obtained from IWC pyrolysis oil. However, the high water content cannot sufficiently explain this behavior because VTT pyrolysis oil also yielded an amount of pyrolytic lignin below 20 % based on water free oil.

Table 26: Organization, feedstock, water content, elemental analysis, and higher heating value of pyrolysis oils.

Organization	Feedstock	Water content [wt. %]	Elemental Analysis ^a				HHV [MJ/kg]
			C [wt. %]	H [wt. %]	N [wt. %]	O [wt. %] ^b	
Federal Research Center for Forestry and Forest Products, Institute for Wood Chemistry (IWC), DE	beech	31.9	54.35	6.80	0.22	38.63	21.2
ENSYN Technologies Inc. (ENSYN), CA	mixed hardwood	26.4	59.89	5.98	0.34	33.79	22.8
Union Electrica FENOSA (FENOSA) I, ES	eucalyptus	25.6	54.44	6.10	0.39	39.07	20.2
Union Electrica FENOSA (FENOSA) II, ES	wheat/ straw	36.0	53.53	6.42	0.64	39.41	20.3
Aston University (ASTON), UK	poplar	16.1	53.55	6.50	0.35	39.60	20.3
National Renewable Energy Laboratory (NREL) ^c , US	poplar	16.3	56.20	6.64	0.30	36.86	21.9
Twente University (BTG), NL	mixed softwood	18.6	54.84	6.51	0.39	38.26	21.0
Technical Research Center of Finland (VTT), FI	pine	17.4	55.23	6.60	0.11	38.06	21.3

^a based on water free oil; ^b calculated by difference; ^c hot filtered oil

As shown in Table 27 colors of pyrolytic lignins varied between light and dark brown. Both ASTON and NREL pyrolysis oils are obtained from poplar by ablative processes. However, different reactor configurations were used. ASTON pyrolysis oil was produced with a 5 kg/h

ablative reactor, whereas NREL pyrolysis oil was obtained from a vortex reactor where the vapor was hot filtered before oil condensation. In addition, these two pyrolysis oils exhibited different degrees of aging. Interestingly, different colors for pyrolytic lignins obtained from ASTON and NREL oils were observed, possibly resulting from the age of the oils or the differing production parameters.

Table 27: Yield, color, and elemental analysis data of pyrolytic lignins and milled wood lignins.

Organization	Yield ^a [%]	Color	Elemental Analysis			
			C [wt. %]	H [wt. %]	N [wt %]	O [wt. %] ^b
IWC	13.5	reddish brown	66.91	6.19	0.27	26.63
ENSYN	24.1	light brown	66.18	6.02	0.23	27.57
FENOSA I	25.0	brown	63.68	5.79	0.19	30.34
FENOSA II	16.5	light brown	65.22	6.13	1.02	27.63
ASTON	24.0	light brown	66.03	6.11	0.21	27.65
NREL	23.0	brown	66.60	6.24	0.34	26.82
BTG	27.7	light brown	67.43	6.19	0.24	26.14
VTT	19.0	dark brown	70.56	6.64	0.15	22.65
MWL (beech)	-	-	58.84	5.92	0	35.24
MWL (eucalyptus)	-	-	60.20	6.21	0	33.59
MWL (poplar)	-	-	58.92	5.73	0	35.35
MWL (pine)	-	-	63.46	5.74	0	30.80

^a based on water free oil, ^b calculated by difference

Mean values for elemental analysis of pyrolytic lignins are given in Table 27. Because milled wood lignins are used to show lignin characteristics, elemental analysis data of milled wood lignins (MWL) [Fai99] are presented in Table 27 and are compared to pyrolytic lignin analysis data. Compared to milled wood lignins the elemental composition of pyrolytic lignin is in a similar range. The carbon content of pyrolytic lignin is between 3 and 8 %, higher than that of MWL produced from the corresponding wood. Elemental analysis data showed differences of 3 to 9 % and 0.3 to 0.9 % for oxygen content and hydrogen content, respectively. Pyrolytic lignin contains more carbon than wood (pyrolytic lignin: about 66.5 %, wood: about 49 %).

Because the hydrogen content in pyrolytic lignin and wood is similar, pyrolytic lignin has less oxygen than wood (pyrolytic lignin: about 26.9 %, wood: about 45 %).

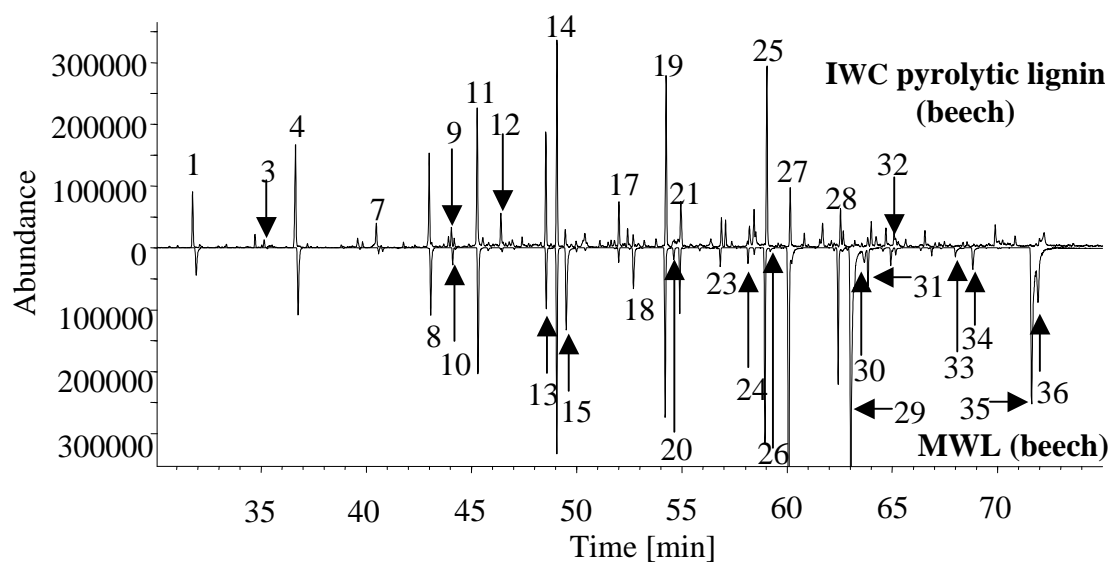


Figure 44: Pyrograms of pyrolytic lignin IWC and MWL (beech) mirrored at baseline. For peak identification according to the identification numbers see Table 28.

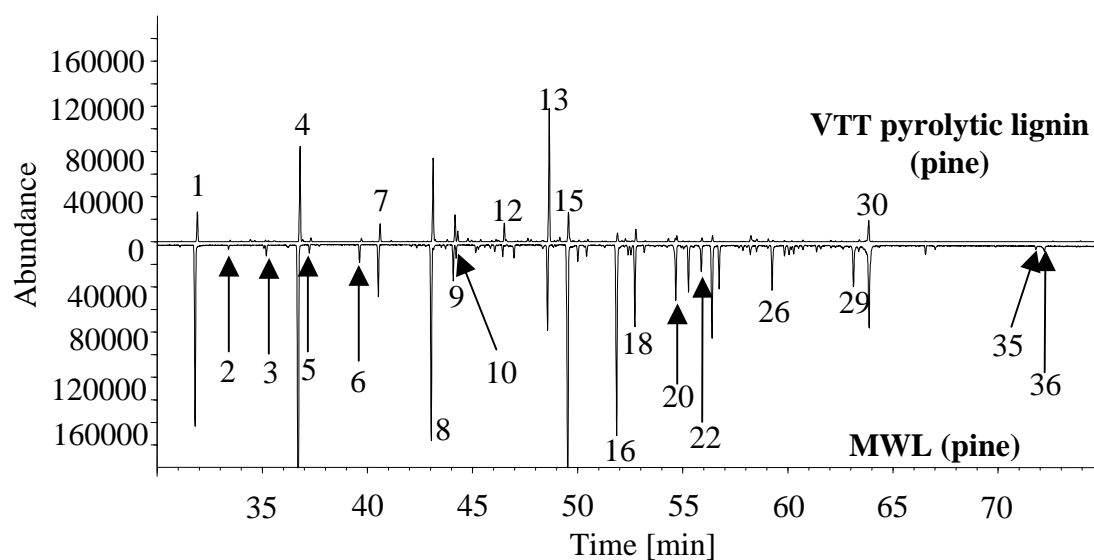


Figure 45: Pyrograms of pyrolytic lignin VTT and MWL (pine) mirrored at baseline. For peak identification according to the identification numbers see Table 28.

Table 28: Peak identification for pyrogram-GC/MS (Key: + weak, ++ middle, +++ strong, -absent or traces).

Peak Number	Intensity of MWL (Beech) Peaks	Intensity of Pyrolytic Lignin (Beech) Peaks	Intensity of MWL (Pine) Peaks	Intensity of Pyrolytic Lignin (Pine) Peaks	Compound
1	+++	+	+++	+	Guaiacol
2	-	-	-	-	o-Cresol
3	+	-	+	-	3-Methylguaiacol
4	++	+	+++	+++	4-Methylguaiacol
5	-	-	+	-	2, 4-Dimethylphenol
6	-	-	+	-	3-Ethylguaiacol
7	-	+	+	+	4-Ethylguaiacol
8	+	++	++	+	Vinylguaiacol
9	-	+	+	+	Eugenol
10	+	-	+	+	4-Propylguaiacol
11	++	++	-	-	Syringol
12	-	+	-	+	cis-Isoeugenol
13	+	++	+	++	trans-Isoeugenol
14	+++	+++	-	-	4-Methylsyringol
15	++	+	+++	+	Vanillin
16	-	-	+++	-	Homovanillin
17	-	+	-	-	4-Ethylsyringol
18	+	-	++	-	Acetoguaiacone
19	++	++	-	-	4-Vinylsyringol
20	-	-	+	-	Guaiacylacetone
21	+	+	-	-	4-Allyl and 4-Propylsyringol
22	-	-	+	-	Propioguiacone
23	+	+	-	-	cis-4-Propenylsyringol
24	+	+	-	-	6-Hydroxy-5,7-dimethoxy-indene
25	+++	+++	-	-	trans-4-Propenylsyringol
26	-	-	+	-	Dihydroconiferyl alcohol
27	+++	+	-	-	Syring aldehyde
28	++	+	-	-	Acetosyringone
29	+++	-	+	-	trans-Coniferyl alcohol
30	+	-	+	+	Coniferyl aldehyde
31	+	+	-	-	Syringyl acetone
32	+	+	-	-	Propiosyringone
33	-	-	-	-	Dihydrosinapyl alcohol
34	+	-	-	-	cis-Sinapyl alcohol
35	++	-	-	-	trans-Sinapyl alcohol
36	+	-	-	-	Sinap aldehyde

Composition of pyrolytic lignin was investigated by analytical pyrolysis-GC/MS. Peak identification was guided by a library, which includes all the major compounds that can be expected in pyrolysis oils. Figure 44 presents the pyrogram of pyrolytic lignin from IWC beech oil compared to that of MWL from beech wood.

In Figure 45 the pyrogram of pine MWL is depicted together with that of VTT pine pyrolytic lignin. Peak identification for all four pyrograms is given in Table 28. Since the use of the internal standard method for peak quantification of compounds determined with a Pyroprobe-GC/MS is still under investigation, quantitative comparison of different pyrograms is not yet possible. Therefore, only peak intensity ratios obtained for each pyrogram measured can be compared. One noticeable difference between the pyrograms is the low yield of vanillin and syring aldehyde in pyrolytic lignins. This can be explained by the absence of hydroxyl groups or ethers in alpha position of the propyl side chain.

Table 29: HGS-ratios for pyrolytic lignins and MWLs.

Origin of Oil for Pyrolytic Lignin Preparation	H-Units [wt. %]	G-Units [wt. %]	S-Units [wt. %]
IWC	0.2	27.2	72.6
ENSYN	2.8	34.6	62.6
FENOSA I	0.5	20.5	79.0
FENOSA II	6.0	73.0	21.0
ASTON	2.1	40.1	57.8
NREL	0.9	40.9	58.2
BTG	6.0	94.0	0
VTT	1.8	95.6	2.6
MWL beech	0	35.0	65.0
MWL aspen ¹	0	30.2	69.8
MWL pine	0.7	91.3	8.0
MWL pine ¹	0	100	0

¹ obtained from nitrobenzeneoxidation

Another remarkable difference is the very low amount of trans-coniferyl alcohol and coniferyl aldehyde as well as trans-sinap alcohol and sinap aldehyde in pyrolytic lignins. Normally, these are typical degradation products of lignin with an intact propyl side chains. Therefore, it

can be assumed that these side chains have been largely destroyed during the fast pyrolysis process.

From the chromatograms measured from the various pyrolytic lignins compounds were identified by both matching product retention times with those of known compounds and comparison of mass spectra. GC analysis was done as follows: Peak areas of all identified compounds were summed up and set to 100. Afterwards, areas of hydroxyphenyl (H), guaiacyl (G), and syringyl (S) compounds were added and their amount compared to the total peak area calculated in percent. H/G/S-ratios were also calculated for milled wood lignins and compared to those obtained for pyrolytic lignins. Results are given in Table 29. G-units for softwood samples are above 90 %, similar to that of pine MWL. The values for S-units and G-units of hardwood pyrolytic lignin samples are in the range from 58-79 % and 21-41 %, respectively. The average of the values of S -, and G-units (66 % and 33 %, respectively) from hardwood pyrolytic lignins are in the same range as the values for beech MWL (S-unit = 65 %, G-unit = 35 %). The FENOSA pyrolytic lignin obtained from wheat/straw pyrolysis oil contains 73 % G-units and 21 % S-units. Compared to the values of G-units, those of S-units are larger than expected from previously performed methoxyl group determination. Here, parallel demethoxylation of G- and S-units is a possible explanation. In addition, the detected syringyl compounds seem to be related to S-units from oligomers instead of S-units from original β -O-4-compounds.

For milled wood lignin, HGS ratios can be calculated from FTIR data [Fai91]. Nevertheless, well characterized MWLs are necessary to calibrate the system. In this work, some samples of pyrolytic lignins were also analyzed by this method. Compared to HGS values calculated from GC data, deviations up to 20 % were obtained in some cases. However, provided a sufficient amount of pyrolytic lignins were used for calibration, calculating HGS values of pyrolytic lignins from FTIR data may become a useful method. In the work presented here, FTIR analysis is preferred because it is less time consuming and currently more reliable than calculating HGS values from GC data.

The pyrolytic lignin samples were prepared as self-supporting pellets and measured by FTIR spectroscopy. The spectra obtained are presented in Figure 46. In the fingerprint region of a FTIR spectrum absorption features from different components superimpose and a detailed interpretation of absorption bands is rendered difficult. Absorption bands above 1510 cm^{-1} result from carbonyl and aromatic skeletal vibrations. Below 1500 cm^{-1} all bands are complex

and have their origin in a variety of vibrational modes. Because absorption bands above 1600 cm^{-1} , associated to conjugated C=O groups, are often broadened by aromatic skeletal vibrations and, hence, exhibit a considerable overlap, experimental spectra were fitted with gaussian profile functions using a conventional least-squares algorithm (software package used: WinXAS by T. Ressler [Res98]). As a typical example fit results for ASTON and NREL pyrolytic lignin are depicted in Figure 47 and Figure 48, respectively.

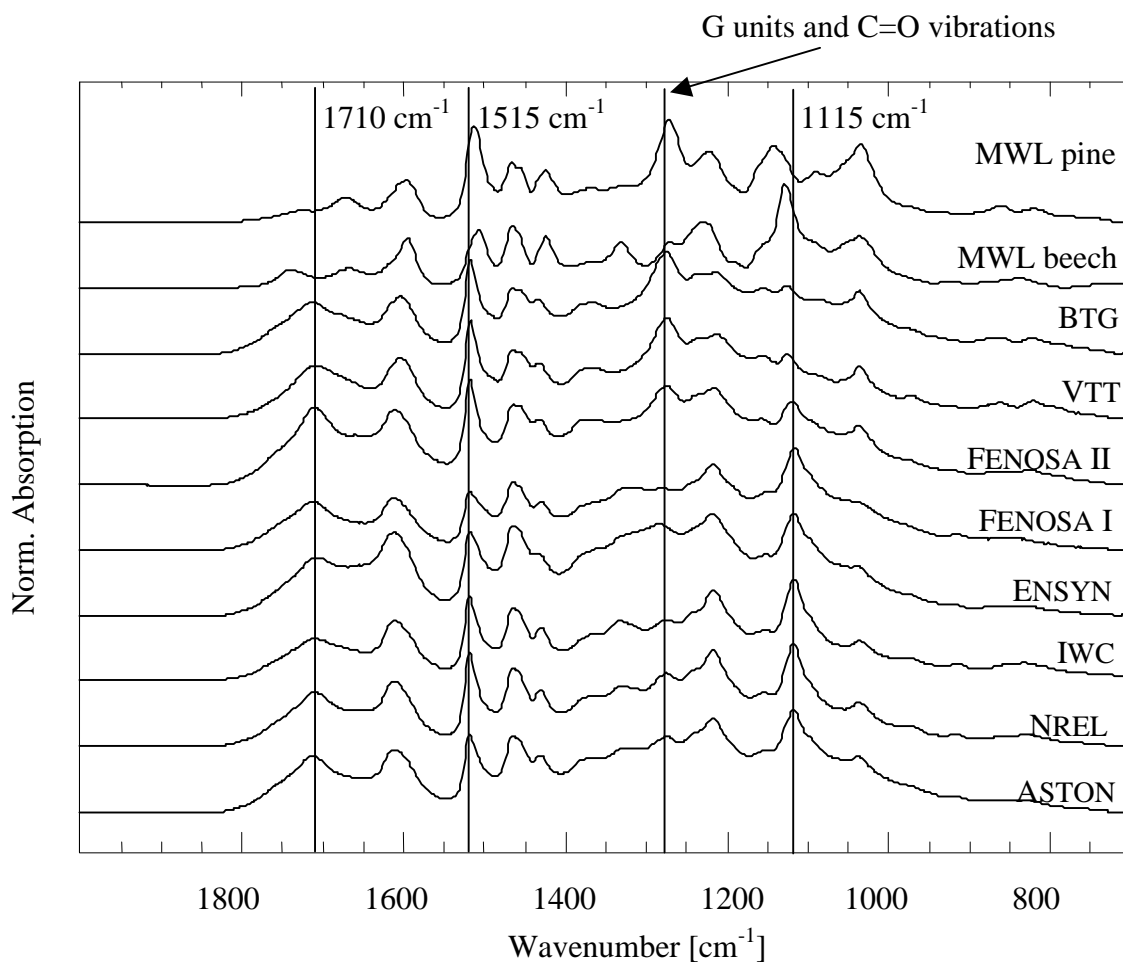


Figure 46: FTIR spectra of eight different pyrolytic lignins investigated in the fingerprint region between 2000 cm^{-1} and 700 cm^{-1} .

FTIR data for different MWL samples were published by Faix [Fai92]. The author described the origins for different bands and assigned the corresponding wavenumbers. With respect to these wavenumbers, FTIR data in the region between 2000 cm^{-1} and 700 cm^{-1} of all eight pyrolytic lignins obtained by the ‘turrax method’ described in this work are given in Table 30.

The absorption intensities are normalized with respect to the intensity of the highest band in this region.

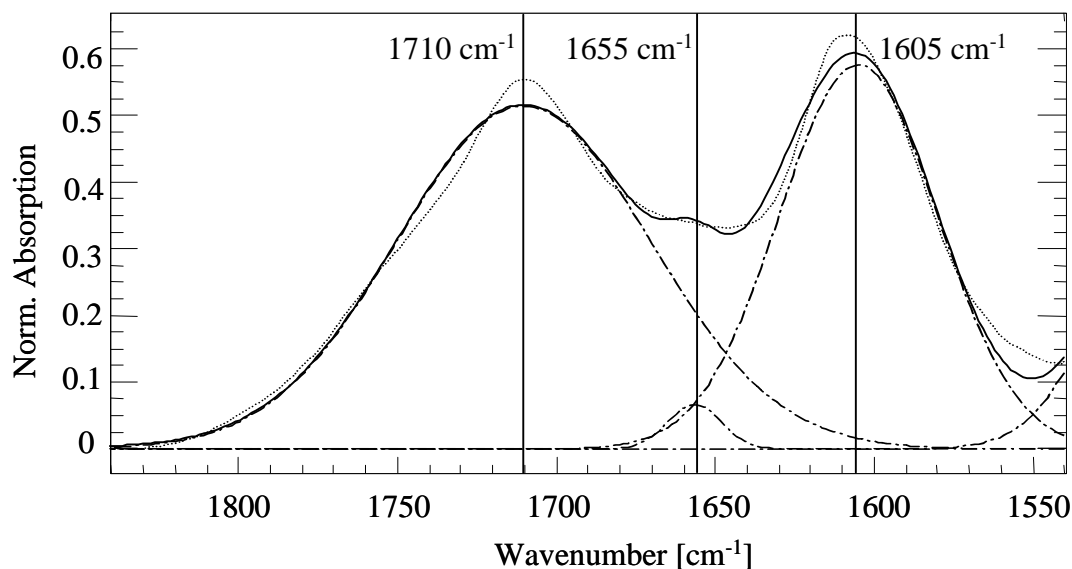


Figure 47: FTIR spectra of ASTON pyrolytic lignin (dot) fitted with gaussian profile functions (single functions: dash-dot; resulting function: connect).

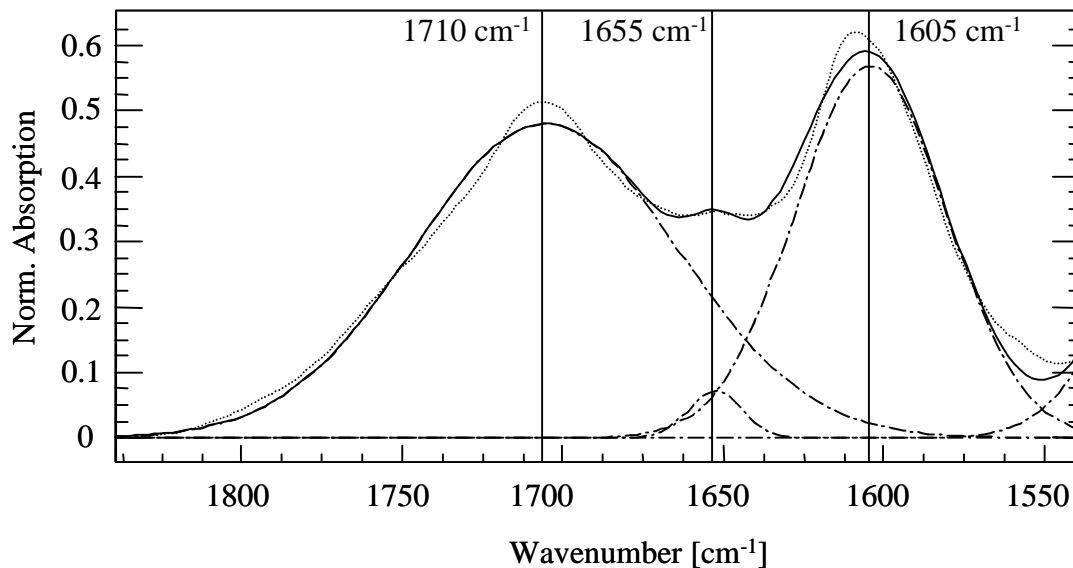


Figure 48: FTIR spectra of NREL pyrolytic lignin (dot) fitted with gaussian profile functions (single functions: dash-dot; resulting function: connect).

In order to reveal correlations between absorption bands and other pyrolytic lignin properties, the absorption bands of the FTIR spectra measured were depicted as a function of the elemental analysis data and heating values. For all lignins with carbon contents between 67.5 % and 65.2 % a correlation of the elemental analysis results with the absorption bands at

1701 cm^{-1} , 1652 cm^{-1} , and 1600 cm^{-1} was observed. Elemental analysis data and the resulting linear regression for the absorption band at 1701 cm^{-1} are depicted in Figure 49. The three absorption bands investigated originate from carbonyl groups.

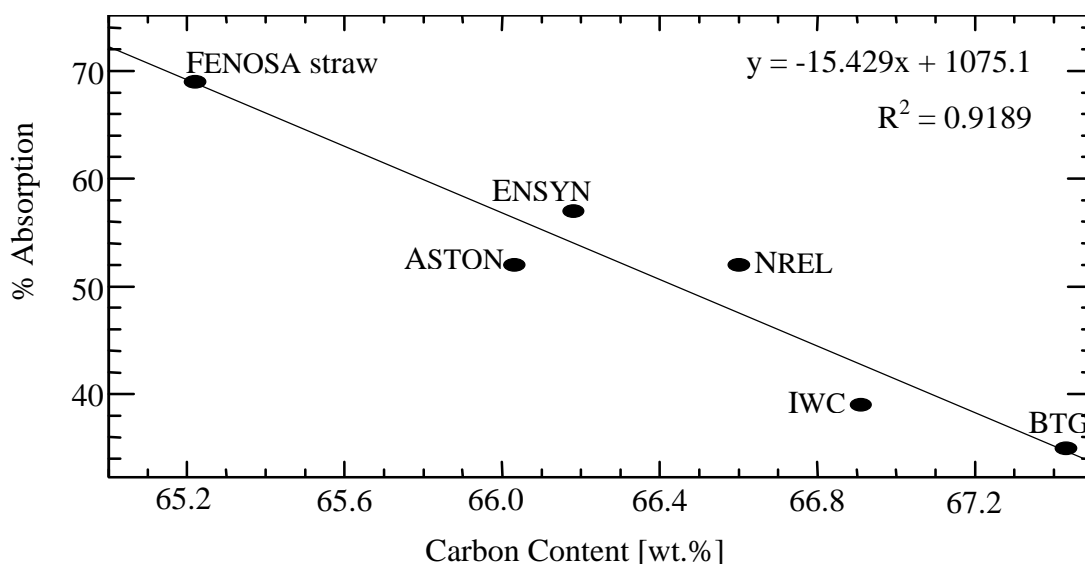


Figure 49: FTIR absorption at 1701- 1712 cm^{-1} versus carbon content of different pyrolytic lignins.

A correlation between the amount of carbonyl groups and the carbon content can be derived. Figure 49 shows that a larger carbon content is weakly correlated with a smaller intensity in the three carbonyl absorption bands (1701 cm^{-1} , 1652 cm^{-1} , and 1600 cm^{-1}). Therefore, it can be assumed that the alteration in oxygen content mainly indicates different amounts of carbonyl groups in the system. Other oxygen related bands, such as hydroxyl and methoxyl bands, are less affected.

From FTIR data of pyrolytic lignins it can be concluded that an alteration in the oxygen content is mainly visible in a change of the intensity of carbonyl absorption bands. Other oxygen related bands, such as hydroxyl and methoxyl bands, are less affected. If these results could be verified also for pyrolysis oils, FTIR analysis might be used as a fast technique to determine the number of carbonyl groups. Furthermore, these investigations may reveal further results connected with the aging of pyrolysis oils.

Table 30: FTIR data of pyrolytic lignins.

Wavenumbers [cm ⁻¹]	Band origin	IWC % Abs.	ENSYN % Abs.	FENOSA euc. % Abs.	FENOSA straw % Abs.	ASTON % Abs.	NREL % Abs.	MWL beech % Abs.	MWL pine % Abs.	BTG % Abs.	VTT % Abs.
1701-1734 ^a	C=O stretch in unconj. ketones, carbonyl and ester groups	39	57	46	69	52	52	53	82	35	36
1652-1666 ^a	C=O stretch in conj. p-subst. aryl ketones	2	14	5	12	7	8	68	59	5	5
1593-1609 ^a	aromatic skeletal vib. plus C=O stretch	60	74	48	68	58	61	46	40	43	40
1510-1515	aromatic skeletal vib.	85	84	58	100	77	94	47	95	93	98
1443-1463	C-H deformations, asym. in -CH ₃ and -CH ₂ -	74	90	68	78	76	79	61	60	65	69
1422-1431	aromatic skeletal vib. combined with C-H in -plane deformation	53	61	47	64	56	56	51	51	54	55
1214-1233	C-C plus C-O plus C=O stretch	93	99	85	94	94	97	66	69	80	80
1033-1037	arom. C-H in-plane def., plus C-O def. in prim. alcohols, plus C=O stretch (unconj.)	41	49	49	58	55	45	50	78	63	53
914-919	C-H out-of-plane, arom.	17	11	16	13	16	13	7	no	no	no
852-859	C-H out-of-plane in Pos. 2, 5 and 6 of Guaiacol units	16	10	11	13	13	12	7	16	15	16

^a after fitting

The results from the methoxyl group determination of pyrolytic lignins are given in Table 31. For methoxyl groups an index is calculated from the ratio of methoxyl groups of pyrolytic lignins and methoxyl groups of milled wood lignins. The methoxyl group index (OMe_i) is calculated according to Equation 1. The mean values of the amount of methoxyl groups in hardwood MWLs and in pine MWL were taken for the calculation of the indices of hardwood and softwood pyrolytic lignins, respectively.

$$OMe_i = \frac{\% OMe PyLig}{\% OMe MWL} \quad \text{Equation 1}$$

Table 31: Methoxyl groups, hydroxyl groups, calculated indices, and higher heating values of pyrolytic lignins.

Origin of oil for pyrolytic lignin	OMe [wt.%]	OMe_i	OH [wt.%]	OH_i	HHV [MJ/kg]
IWC	15.8	0.77	10.7	0.88	26.8
ENSYN	8.5	0.41	13.6	1.12	26.1
FENOSA I	11.0	0.54	12.0	0.99	24.4
FENOSA II	7.5	0.47	11.9	0.81	25.9
ASTON	10.4	0.51	11.4	0.94	26.2
NREL	12.6	0.61	11.3	0.93	26.7
BTG	6.9	0.43	11.9	0.81	27.0
VTT	7.7	0.48	12.0	0.82	29.4
MWL (beech)	19.8	-	12.0	-	22.1
MWL (eucalyptus)	21.7	-	12.2	-	23.3
MWL (poplar)	20.0	-	12.2	-	21.8
MWL (pine)	15.9	-	14.7	-	24.2

In comparison to MWL, the number of methoxyl groups in pyrolytic lignin is reduced by pyrolysis. Number of methoxyl groups in MWL from hardwood and softwood are given by Fengel and Wegner [FW84] as 18-22 % and 12-16 %, respectively. Demethoxylation may be caused by conversion of methoxyl groups to methanol during thermal degradation. Except for the ENSYN sample, methoxyl indices of hardwood pyrolytic lignins exhibit larger values than those of softwood samples indicating a smaller degree of demethoxylation reactions.

The content of hydroxyl groups (10.7 % - 13.6 %) in pyrolytic lignin is similar to that of MWLs (12.0 % - 14.7 %). According to the procedure for calculating a methoxyl index, an index for hydroxyl groups is defined. The hydroxyl group index (OH_i) can be calculated according to Equation 2:

$$OH_i = \frac{\% OH \text{ PyLig}}{\% OH \text{ MWL}} \quad \text{Equation 2}$$

Hydroxyl group data as well as postulated indices are shown in Table 31. As opposed to MWL, pyrolytic lignin samples contain a smaller amount of hydroxyl groups. Splitting of propyl side chains could be a possible explanation for this behavior.

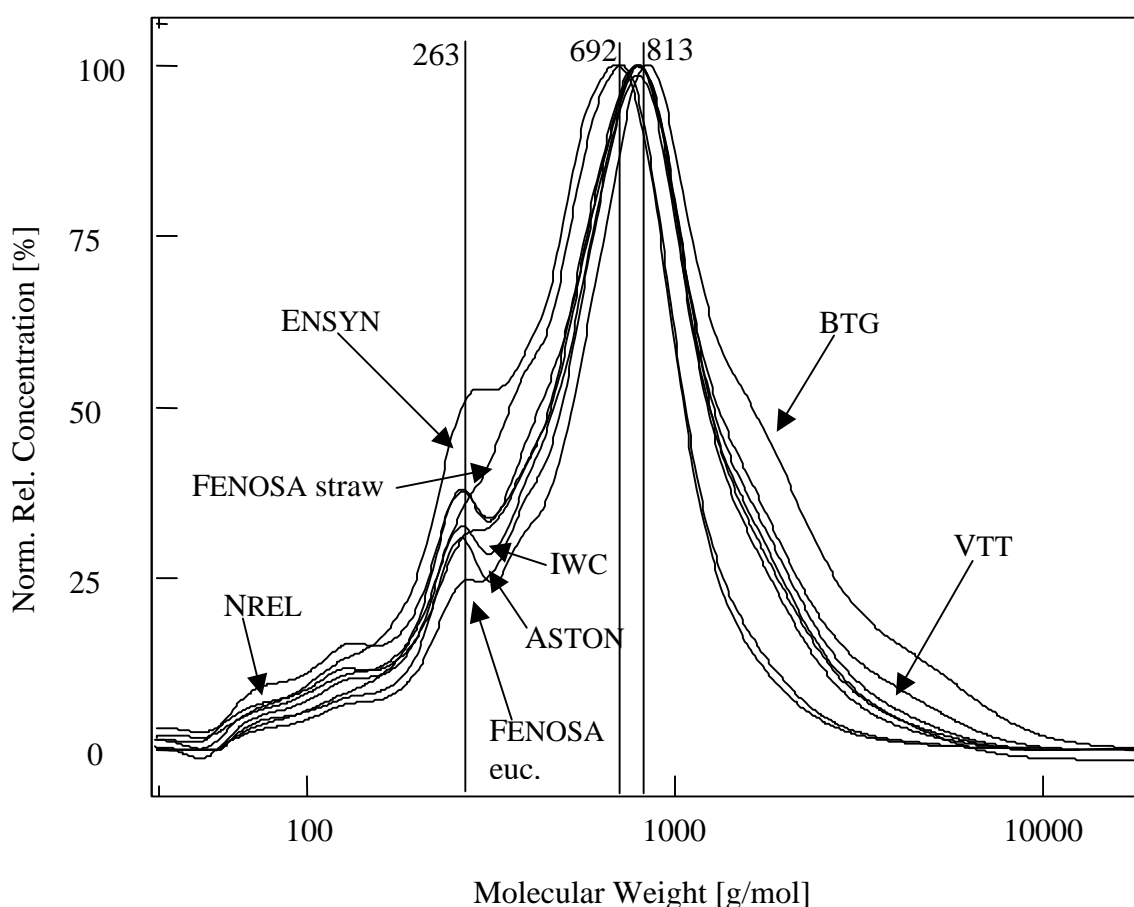


Figure 50: Gel permeation chromatograms (measured with RI detector) of the pyrolytic lignins obtained from pyrolysis oils of IWC, ENSYN, FENOSA (eucalyptus), FENOSA (straw), ASTON, NREL, BTG, and VTT.

Heating values of pyrolytic lignins were calculated from elemental analysis and yield values in the range between 24.4 MJ/kg and 29.4 MJ/kg (Table 31). As expected from the smaller

amount of oxygen in the corresponding samples, the heating values decrease in the following order: pyrolytic lignin > MWL > pyrolysis oil.

The structure of pyrolytic lignin was investigated by gel permeation chromatography (GPC). The molecular weight distribution (MWD) can provide first insight into the polymeric nature of pyrolytic lignin. In contrast to conventional lignin samples, for example milled wood lignin, pyrolytic lignin is entirely soluble in THF. Therefore, acetylation of the samples prior to the GPC measurements is not necessary. MWDs of the eight pyrolytic lignins obtained by the 'turrax method' are presented in Figure 50.

For the measurements of the MWD of the pyrolytic lignin, the GPC system was calibrated with commercial polystyrene samples. Various molecular weight numbers were calculated from the experimental data. The mass average (M_w) and the number average (M_n) of the molecular weight of pyrolytic lignins are shown in Table 32.

Table 32: The different molecular weight numbers and the dispersity (D) for pyrolytic lignins.

Pyrolytic lignin 6 mg/ml in THF	RI detector			UV detector		
	M_w [g/mol]	M_n [g/mol]	D (M_w/M_n)	M_w [g/mol]	M_n [g/mol]	D (M_w/M_n)
IWC	871	418	2.1	895	434	2.1
ENSYN	649	376	1.7	621	305	2.0
FENOSA I	903	529	1.7	869	412	2.1
FENOSA II	692	397	1.7	684	382	1.8
ASTON	922	394	2.3	875	337	2.6
NREL	882	408	2.2	831	304	2.7
BTG	1317	592	2.2	1319	550	2.4
VTT	1007	518	1.9	958	475	2.0
MWL beech ^a	10680	4900	2.2	10100	4200	2.4
MWL spruce ^a	5720	3270	1.8	5500	3000	1.8

^a published by Choi [Cho99]

Table 32 presents the molecular weight of 2 different MWL as determined by Choi [Cho99]. Furthermore, the ratio of M_w and M_n is presented as dispersity (D), which is a measure of the homogeneity of the fragments. Because there were no significant differences in the M_w and

molecular weight of softwood samples is larger than that of hardwood samples. This can be explained by the free C5 (see Figure 51) position in softwood lignins, which is prone to polymerization reactions.

The average molecular weight of MWL is about 10 times larger than that of pyrolytic lignins. This indicates a high degree of thermal splitting during pyrolysis as is also visible in the corresponding ^{13}C -NMR spectra. From the M_w and M_n values it can be concluded that pyrolytic lignin consists mainly of tri- and tetramers of HGS units.

Pyrolysis products of biomass include a large number of compounds containing carbonyl groups. Thermal splitting during the pyrolysis process generates most of them. To date little can be found in the literature regarding carbonyl group content of pyrolytic lignins. In this work the amount of carbonyl groups in pyrolytic lignin was determined by wet chemical oximation. Results are presented in Table 33. It can be seen that the amount of carbonyl groups of pyrolytic lignins is spread over a large range (1.8 to 5.1 mol/kg).

In order to compare different pyrolytic lignins with each other, a ' C_8 formula' is defined using elemental analysis and methoxyl group data. The results obtained are displayed in Table 34. Out of the eight pyrolytic lignin samples studied, the VTT pyrolytic lignin exhibits the lowest molecular weight per C_8 unit. The FENOSA eucalyptus pyrolytic lignin shows the highest molecular weight per C_8 unit. The following order presents pyrolytic lignin samples with decreasing molecular weight per C_8 unit:

FENOSA (eucalyptus) > IWC > NREL > ASTON > FENOSA (straw) > ENSYN > BTG > VTT

The ratio of M_w determined by GPC and the calculated molecular weight per C_8 unit yields an average degree of polymerization (DP) in the range of 4 – 9 (see Table 34). Evidently, pyrolytic lignins produced from softwood show the highest DP values.

Table 34: Origin of the pyrolysis oils for pyrolytic lignin preparation, elemental analysis, methoxyl groups, hydroxyl groups, calculated C₈ formula, mass average of the molecular weight per C₈ formula, and average degree of polymerization of pyrolytic lignins.

Origin of the oils	Elemental analysis			OMe [wt. %]	OH [wt. %]	C ₈ Formula	Mw/C ₈ [g/mol]	DP (Mw _{GPC} /Mw _{C8})
	C [wt.%]	H [wt.%]	O [wt.%]					
IWC	66.91	6.19	26.63	15.8	10.7	C ₈ H _{6.3} O _{0.83} (OH) ₁ (OCH ₃) _{0.8}	157.55	5.5
ENSYN	66.18	6.02	27.57	8.5	13.6	C ₈ H _{6.65} O _{0.99} (OH) _{1.22} (OCH ₃) _{0.42}	152.41	4.3
FENOSA (eucalyptus)	63.68	5.79	30.34	11.0	12.0	C ₈ H _{6.43} O _{1.35} (OH) _{1.14} (OCH ₃) _{0.57}	161.25	5.6
FENOSA (straw)	65.22	6.13	27.63	7.5	11.9	C ₈ H _{7.18} O _{1.21} (OH) _{1.08} (OCH ₃) _{0.37}	152.55	4.5
ASTON	66.03	6.11	27.65	10.4	11.4	C ₈ H _{6.8} O _{1.12} (OH) _{1.04} (OCH ₃) _{0.52}	154.69	6.0
NREL	66.60	6.24	26.82	12.6	11.3	C ₈ H _{6.7} O _{0.94} (OH) _{1.04} (OCH ₃) _{0.63}	155.12	5.7
BTG	67.43	6.19	26.14	6.9	11.9	C ₈ H _{7.08} O _{1.06} (OH) _{1.04} (OCH ₃) _{0.33}	148.11	8.9
VTT	70.56	6.64	22.65	7.7	12.0	C ₈ H _{7.31} O _{0.66} (OH) ₁ (OCH ₃) _{0.35}	141.89	7.0

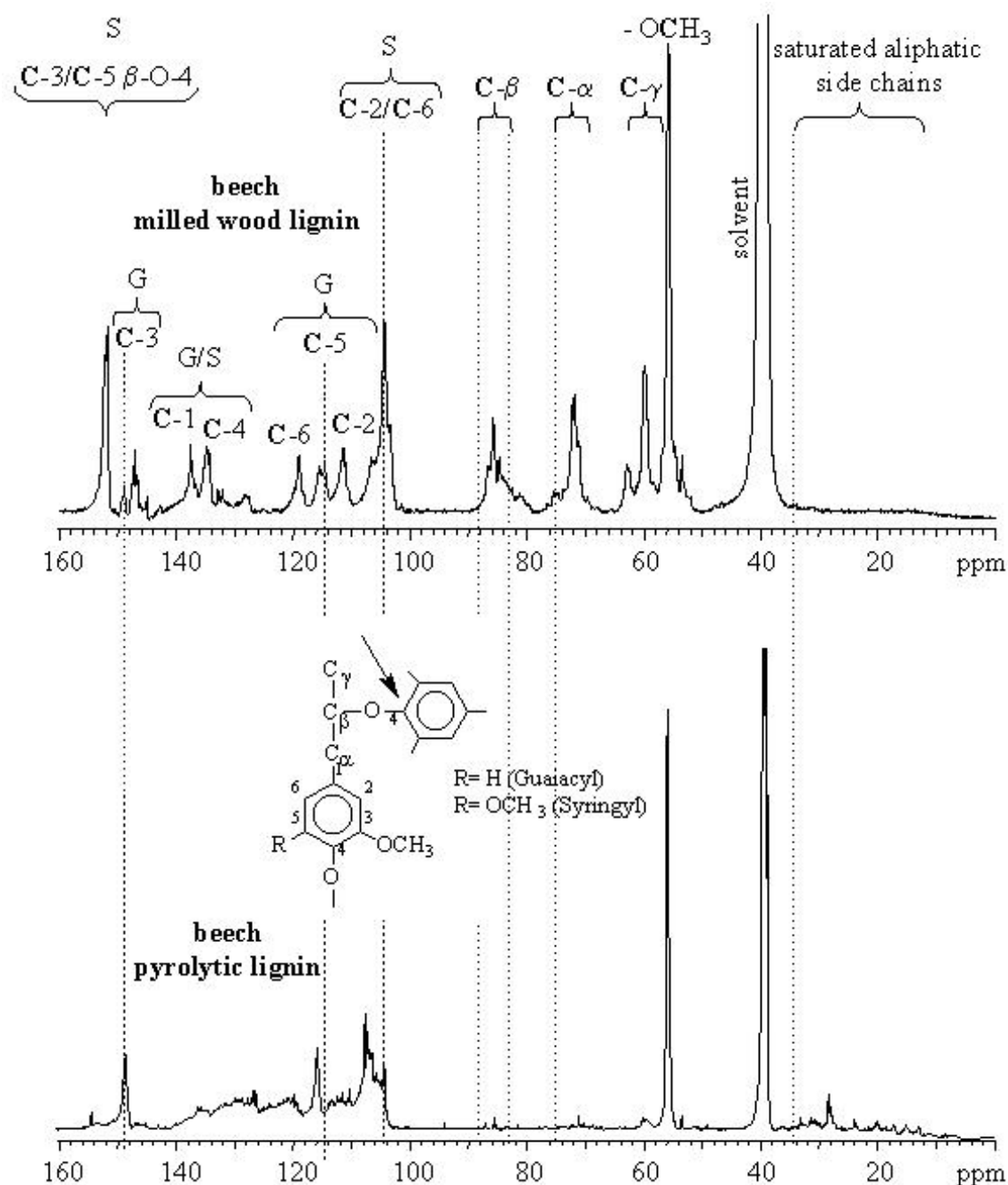


Figure 52: ^{13}C -NMR spectra of beech MWL and beech pyrolytic lignin.

The eight different pyrolytic lignin samples were investigated by ^{13}C -NMR spectroscopy to obtain additional structural information. The spectrum of beech pyrolytic lignin was compared to that of beech MWL. As can be seen in Figure 52 the main signal in the spectra of pyrolytic lignin and MWL at 55 ppm is assigned to methoxyl groups.

In $\beta\text{-O-4}$ structural units, peaks in the ranges of 86, 72, and 60 ppm in MWL are derived from carbon atoms β , α and γ , respectively. These signals are very weak in the

spectrum of beech pyrolytic lignin, indicating both the high degree of thermal depolymerization caused by splitting of the main ether bonding in lignin (see arrow in Figure 52) and the presence of some structural units that are still intact after pyrolysis.

Typical signals for G/S units in the spectrum of MWL (152-104 ppm) are very small, in contrast to signals from pyrolytic beech lignin. This indicates a substantial amount of demethoxylation reactions occurring during pyrolysis. This result is in line with the wet chemical methoxyl group determination showing that the $-\text{OMe}_3$ content of beech pyrolytic lignin is reduced by 21 % based on beech MWL.

In contrast to MWL, a multitude of newly developed saturated aliphatic carbons are evident in the spectra of the pyrolytic lignins from chemical shifts in the region between 35-10 ppm. The formation of saturated alkyl side chains (sp^3 -hybrides) in pyrolytic lignins demonstrates the degree of cracking reactions followed by protonation and hydrogenation at the alkyl side chains.

The overlapping aromatic region between 155 ppm and 100 ppm in the pyrolytic lignin spectrum indicates fundamental structural changes and possible formation of new C-C bonds. The drastic depolymerization is in line with the GPC results, which reveal the thermal splitting of lignin into much smaller fragments. The formation of new bondings, for example the formation of C-C bonds at former syringyl C5 (after $-\text{OCH}_3$ splitting in C5), is highly probable. Using lignin model compounds, Lüdemann and Nimz [LN74] assigned signals from several guaiacylic and syringylic compounds with olefenic and carboxylic side chain that fall into this region. The overlapping signals in the aromatic region indicate possible reaction during pyrolysis comprising rearrangements, eliminations, condensations and additions. The missing C1/C4 signals of syringyl units at 137/134 ppm in the pyrolytic lignin spectra also points towards structural changes.

Figure 53 shows the ^{13}C -NMR spectra of eight different pyrolytic lignins in the range from 160-0 ppm. As with ^{13}C -NMR of MWL, ^{13}C -NMR spectra of pyrolytic lignins permit the classification according to their character of different aromatic nuclei. Hence, signals from syringyl residues (C-2/C-6 at 108-104 ppm) in hardwood and straw pyrolytic lignins are clearly discernible, but are completely lacking in the spectra of pine and mixed softwood. Although differences in the spectra in the range from 35 to 10 ppm are visible, further interpretation is not yet possible.

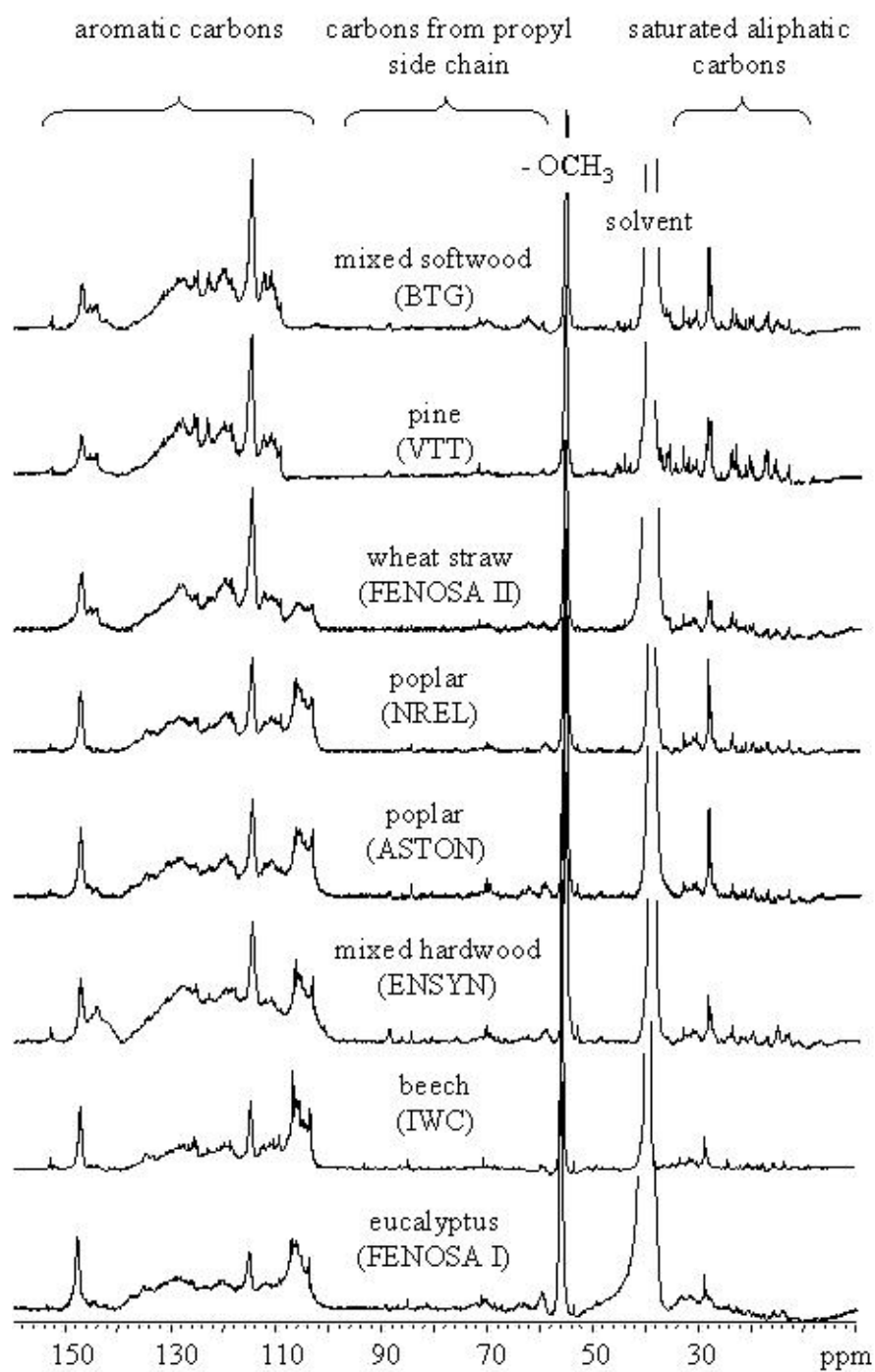


Figure 53: ^{13}C -NMR spectra of various pyrolytic lignins from pyrolysis oils of IWC, ENSYN, FENOSA (eucalyptus), FENOSA (straw), ASTON, NREL, BTG, and VTT.

4.3.3 Summary

Currently two alternative methods for preparation of pyrolytic lignin exist. In contrast to the method described by Czernik and Piskorz [CP99], the precipitation method, using an ultra turrax, presented in this work affords a fine powder without inclusions of water soluble compounds. For future studies we [SM01] recommend using the ‘turrax method’, because fine homogeneous pyrolytic lignin powder is obtained. A homogeneous powder is of paramount importance to obtain reproducible and comparable analysis results. In addition, for investigations and applications a homogeneous sample is to be preferred.

FTIR measurements of pyrolytic lignin showed a correlation of carbonyl absorption bands intensities between on the one hand oxygen content and on the other hand carbon content. These results are most promising for a future development of a fast analysis technique of pyrolytic lignins and pyrolysis oils.

Whether large lignin molecules are products from recombination reactions occurring after pyrolysis or are being directly desorbed as molecular aggregates from wood and transported to the condensation system as part of the aerosols is one subject of this investigation.

Using GPC the average molecular weight of pyrolytic lignin was determined to be between 650-1300 g/mol, which indicates that pyrolytic lignin consists mainly of tri- and tetramers. For pyrolytic lignins the M_w of softwood samples is larger than that of hardwood samples, hence, softwood samples may be more prone to polymerization reactions. The M_w of MWL is about 10 times larger than that of the pyrolytic lignins, which can be explained by a large degree of thermal cracking during the pyrolysis process.

Assuming that the basic structure of pyrolytic lignins consists of phenyl ethane units, a C_8 -formula was calculated from the analysis data. In addition, the average molecular weight per C_8 -unit was calculated. These data were combined with GPC measurements and resulted in an average degree of polymerization (DP) between 4 and 9. Pyrolytic lignins obtained from softwood show the highest DP values.

^{13}C -NMR spectra of pyrolytic lignins also indicated the formation of new bondings, for example the formation of C-C bonds at former syringyl C5. Thus, pyrolytic lignin mainly consists of alkylated aromatic units linked together by newly formed bonds, different from alkyl-aryl-ethers. Detailed analysis of ^{13}C -NMR spectra of pyrolytic lignins showed that some structural units of lignin are still intact after pyrolysis. This corroborates the thermal ejection

theory postulated by Piskorz et al. [PMR99]. The presence of weak signals in the ^{13}C -NMR spectra of beech pyrolytic lignin at 86, 72, and 60 ppm also corroborates the thermal ejection theory.

Therefore, we conclude, that oligomeric molecules in pyrolysis oils are desorbed from the feedstock by thermal ejection. Large molecules, for example C_8 -units, are combined by formation of new bondings, whereas recombination of smaller molecules to the complex pyrolytic lignin structure appears to be unlikely.

In contrast to different MWL spectra, the data obtained for pyrolytic lignin indicate, that the basic characteristics are less pronounced because of the severe thermal treatment. Fractionation of pyrolytic lignin and further investigations, such as liquid chromatography, are necessary to elucidate the detailed structure of pyrolytic lignins.

Change is inevitable,
except from a vending machine.

Z. Sardar and I. Abrams
in 'Introducing Chaos', 1999,
by Totem Books, New York

5 Summary

Because the fossil fuels are limited and their unrestricted use in the past exhibits a severe influence on our environment ('greenhouse effect'), renewable energy sources that could be substitutes for the conventional fossil fuels are attracting ever-increasing interest. Wood and other forms of biomass represent some of the most promising candidates for a renewable energy source.

In this framework the pyrolysis of biomass and the pyrolysis oils obtained from this process become of increasing interest. However, in order to establish and promote the use of pyrolysis oil as a fuel or a source for fine chemicals, several important improvements of the oils obtained and the pyrolysis process itself have to be achieved.

- Because pyrolysis oil exhibits an inferior long-term stability compared to conventional petroleum fuels, detailed knowledge is required on how the physico-chemical properties of pyrolysis oil change with storage time. Eventually, knowing the reasons for the undesired ageing behavior of pyrolysis oils will enable to recommend how pyrolysis oils should be properly stored.
- If the aging behavior of pyrolysis oils is because of certain compounds or functional groups in the oils, it should be possible to tailor the characteristics of pyrolysis oils by employing particular catalysts during the pyrolysis process or by a special treatment of the pyrolysis oils after production.
- It should be possible to obtain a well-defined (with respect to structure and composition) fraction of the pyrolysis oils that can be used for further technical applications.

5.1 Stability and storage of pyrolysis oils

Several authors have reported that the physico-chemical properties of pyrolysis oils change as a function of time under regular storage conditions. In this work, the investigations regarding the aging of pyrolysis oils were divided in three parts:

- Storage of four different pyrolysis oils from pilot plants (FENOSA, ENSYN, and IWC).
- Storage of untreated and hydrogenated VTT pine pyrolysis oil.
- Storage of different fractions of IWC beech pyrolysis oil.

The investigations of the aging behavior of the pyrolysis oil from FENOSA, ENSYN, and IWC afforded the following results: Pyrolysis oil samples stored at -20 °C were still homogeneous after 6 months (or even longer), whereas samples stored at 50 °C developed varying amounts of sludge at the bottom of the container. Less sludge formation was observed in the IWC oil samples compared to ENSYN and FENOSA pyrolysis oil samples stored under similar conditions. After more than two years of storage time, the thick and gummy sludge at the bottom of the storage vessels of the FENOSA and the ENSYN samples was estimated to amount to about 90 weight-% of the entire original samples.

The FTIR data of the pyrolysis oils investigated showed that the ratio of the maximum of the carbonyl bands at 1715 cm⁻¹ and 1650 cm⁻¹, and the maximum in the region from 1500 to 700 cm⁻¹ ranges from 0.6 to 1. The ratio approaches unity with increasing age of the oils. This method turned out to be very useful to monitor changes within an oil sample, however it may not be suitable to compare different bio oils. The GPC data showed an increase towards a larger molecular weight average with storage time for the pyrolysis oils investigated. Apparently, polymerization processes play an important role in the aging behavior of pyrolysis oils under the storage conditions studied. Interestingly, the acid numbers of FENOSA and ENSYN oil samples increased with storage time, whereas the acid number of the IWC oil decreased with storage time.

The most important result of this part of the investigations performed in this work is the high stability of the IWC beech pyrolysis oil. Even samples stored at 50 °C for an extended period of time exhibited a considerable stability. After more than two years only a thin film but no sludge had developed at the bottom of containers. For the IWC oil, the special handling of the oil after the production may account for the superior long-term stability observed. After production the oil was diluted with methanol and subsequently distilled. Apparently, light

reactive components were removed together with methanol resulting in a more stable pyrolysis oil.

The investigations of the aging behavior of untreated and treated VTT pine pyrolysis oil focused on the evolution of the number of carbonyl groups and the viscosity. All samples showed a considerable decrease in the number of carbonyl groups with storage time, while samples stored at -20 °C exhibited the smallest decrease in the number of carbonyl groups compared to samples stored at 80 °C. Hydrogenated oils showed a smaller decrease of the number of carbonyl groups than the crude VTT pyrolysis oil. This decrease in the amount of carbonyl groups observed together with the increase in viscosity, substantiates the assumption that polymerization is a key reaction in the aging of bio oils. Viscosity is another important parameter of pyrolysis oils, which may be employed to indicate polymerization in pyrolysis oils. The systematic rheological study performed with hydrogenated and crude oil showed an increase of viscosity after storage time. It was found, that the increase in viscosity is more pronounced for samples stored at higher temperatures.

The studies on the aging behavior of different fractions of IWC beech pyrolysis oil cannot be easily compared to previous aging investigations. Earlier studies had shown an extremely high viscose sludge attached to the bottom of containers, while the aging studies considered the entire pyrolysis oil. Also in the work described here, the IWC oil fractions exhibited a rapid sludge formation. However, the sludge was obtained in one piece and not attached to the container walls. All of IWC pyrolysis oil samples showed either a high viscosity or a phase separation. The assumption that one of the fractions may contain less reactive compounds or a lower amount thereof and, thus, may be more stable was not confirmed.

5.2 Catalytic upgrading of pyrolysis oils

Vapor phase upgrading experiments during the pyrolysis process and mild hydrogenation experiments of pyrolysis oils were performed in this work with respect to potentially improving the physico-chemical properties of pyrolysis oils by '*catalytic upgrading*'. For vapor phase upgrading experiments, various metal oxides supported on slate were chosen as catalysts. In order to compare the catalysts used with respect to their metal loading, the

concentration of the metal oxide supported on slate was calculated as the ratio of the amount of substance of metal oxide and the mass of the slate.

For regular pyrolysis experiments performed without a catalyst, a higher amount of feed resulted in a higher yield of pyrolysis oil rather than char and gas. Conversely, experiments performed with a catalyst did not show a similar dependence of the yield on the amount of feed.

Experiment BRIKAT P was performed with sand in the first reactor and with manganese oxide supported on slate in the second reactor and afforded the highest yield of pyrolysis oil and the third lowest yield of gas of all the upgrading experiments described here. The pyrolysis oil obtained from this experiment possessed a reasonable HHV (higher heating value), a small water content, and a low viscosity. Hence, manganese oxide on slate in the second reactor in combination with sand in the first reactor may be a promising candidate for future catalytic upgrading experiments.

Interestingly, manganese oxide on slate in the second reactor in combination with slate in the first reactor performed much worse compared to the combination of sand and manganese oxide supported on slate. In general, the pyrolysis oils obtained from the various other experiments performed with catalysts exhibited minor improvements in their physico-chemical properties, for example lower viscosity values.

In total, the vapor phase upgrading with metal oxide on slate described in this work seems to be a promising method to improve the long-term stability of pyrolysis oils. The experiments performed show several leads that should be further exploited in future investigations.

Hydrogenation of pyrolysis oils after production was performed both with and without various heterogeneous catalysts in order to investigate the evolution of the number of carbonyl groups and the viscosity. The results of mild hydrogenation experiments described in this work suggest that reaction temperatures above 80 °C are unsuitable for hydrogenation of bio oils. At temperatures above 80 °C, polymerization reactions in the oils proceed rapidly, resulting in pyrolysis oils with a high viscosity. In addition, the oils obtained tended to phase separation with storage time yielding an undesired sludge at the bottom of the container. With respect to the experimental procedure, it turned out that reliable investigations of physical and chemical properties of the pyrolysis oils after hydrogenation were possible only if catalyst extrudates

had been used instead of powder catalyst. Fine catalyst powders seem to remain well dispersed in the oils obtained and are extremely difficult to remove properly.

The hydrogenation experiments performed showed that none of the combinations of pyrolysis oils, heterogeneous catalysts, and experimental conditions employed resulted in more stable pyrolysis oils compared to the corresponding untreated oils. Because many of the commercial hydrogenation catalysts require rather high temperatures, they seem to be unsuitable for pyrolysis oil treatment. Polymerization reactions in the oils and hydrogenation of the corresponding functional groups are competing reaction pathways, and conditions favorable for a successful upgrading of pyrolysis oils need to suppress the former while accelerating the latter. Therefore, for future upgrading experiments of pyrolysis oils by hydrogenation it will be of paramount importance to exploit reactive and selective catalysts that can operate already at temperatures well below 80 °C.

5.3 Pyrolytic lignin

Currently two alternative methods for preparation of pyrolytic lignin are described in the literature. In contrast to the preparation method reported by Czernik and Piskorz [CP99], the precipitation method presented in this work, by using an ultra turrax, affords a fine powder without inclusions of water-soluble compounds. For future studies on the preparation of pyrolytic lignin, using the ‘turrax method’ should be preferred, because fine homogeneous pyrolytic lignin powders are obtained which is of paramount importance for both obtaining reproducible and comparable analysis results, and technical applications.

From GPC measurements the average molecular weight (M_w) of pyrolytic lignin was determined to be between 650 g/mol and 1300 g/mol, which indicates that pyrolytic lignin consists mainly of tri- and tetramers. For pyrolytic lignins the M_w of softwood samples is larger than that of hardwood samples, hence, softwood samples may be more prone to polymerization reactions. The M_w of MWL (milled wood lignin) is about 10 times larger than that of the pyrolytic lignins, which can be explained by a large degree of thermal cracking during the pyrolysis process.

Assuming that the basic structure of pyrolytic lignins consists of phenyl ethane units, a C_8 -formula was calculated from the analysis data. In addition, the average molecular weight per C_8 -unit was calculated (e.g. for IWC pyrolytic lignin $C_8H_{6.3}O_{0.83}(OH)_1(OCH_3)_{0.8}$). These

data were combined with GPC measurements and resulted in an average degree of polymerization (DP) between 4 and 9. Pyrolytic lignins obtained from softwood show the highest DP values.

^{13}C -NMR spectra of pyrolytic lignins also indicated the formation of new bondings, for example the formation of C-C bonds at former syringyl C5 units. Thus, pyrolytic lignin mainly consists of alkylated aromatic units linked together by newly formed bonds, different from alkyl-aryl-ethers. Detailed analysis of ^{13}C -NMR spectra of pyrolytic lignins showed that several structural units of the original lignin are still intact after pyrolysis. This corroborates the thermal ejection theory postulated by Piskorz et al. [PMR99]. The presence of weak signals in the ^{13}C -NMR spectra of beech pyrolytic lignin also corroborates the thermal ejection theory. It seems that oligomeric molecules in pyrolysis oils are desorbed from the feedstock by thermal ejection. Large molecules, for example C_8 -units, are combined by formation of new bonds, whereas recombination of smaller molecules to the complex pyrolytic lignin structure appears to be unlikely.

In contrast to different MWL, the data obtained for pyrolytic lignin indicate, that the basic characteristics (e.g. average molecular weight) are less pronounced because of the severe thermal treatment. Fractionation of pyrolytic lignin and further investigations, such as liquid chromatography, are necessary to elucidate the detailed structure of pyrolytic lignins.

6 Zusammenfassung

Da der Vorrat an fossilen Brennstoffen auf der Erde begrenzt ist und deren uneingeschränkter Gebrauch in der Vergangenheit heute bereits schwerwiegende Einflüsse auf unsere Umwelt hat ('Treibhaus Effekt'), steigt das Interesse an erneuerbaren Energiequellen (nachwachsende Rohstoffe), welche als Ersatz für konventionelle fossile Rohstoffe verwendet werden können. Als aussichtsreichste Kandidaten für erneuerbare Energiequellen bieten sich Holz und andere Formen von Biomasse an.

In diesem Zusammenhang kommt der Pyrolyse von Biomasse und den dabei entstehenden Pyrolyseölen eine stetig wachsende Bedeutung zu. Um die Verwendung von Pyrolyseölen als Brennstoff oder als Quelle zur Gewinnung von Chemikalien zu etablieren, müssen die heute erhaltenen Öle und der Pyrolyseprozess selbst noch entscheidend verbessert werden.

- Weil im Vergleich zu konventionellen Petroleumölen Pyrolyseöle eine schlechtere Langzeitstabilität besitzen, muss detailliert erforscht werden in wie weit sich die physikalisch-chemischen Eigenschaften von Pyrolyseölen im Laufe der Lagerung verändern. Wenn die Gründe für das unerwünschte Alterungsverhalten von Pyrolyseölen bekannt sind, ist es möglich eine Empfehlung auszusprechen, wie Pyrolyseöle gelagert werden sollten.
- Wenn die geringe Langzeitstabilität der Pyrolyseöle bedingt ist durch die im Öl enthaltenen vielen verschiedenen Verbindungen mit ihren verschiedenen funktionellen Gruppen, sollte es möglich sein, die Eigenschaften von Pyrolyseölen durch Einsatz geeigneter Katalysatoren während des Pyrolyseprozesses oder durch eine spezielle Behandlung der Öle nach der Produktion zu beeinflussen und den Erfordernissen anzupassen.

- Aus der Vielzahl von chemischen Verbindungen im Pyrolyseöl sollte es möglich sein, definierte (in bezug auf Struktur und Zusammensetzung) Fraktionen zu erhalten, welche dann für weitere technische Anwendungen benutzt werden können.

6.1 Stabilität und Lagerung von Pyrolyseölen

Verschiedene Autoren haben berichtet, dass sich die physikalisch-chemischen Eigenschaften von Pyrolyseölen im Laufe der Zeit ändern, wenn die Öle unter normalen Bedingungen gelagert werden. In der vorliegenden Arbeit wurden die Alterungsuntersuchungen an Pyrolyseölen in drei Teile unterteilt:

- Lagerung von vier verschiedenen Pyrolyseölen aus diversen Pyrolyseanlagen (FENOSA, ENSYN, and IWC)
- Lagerung von unbehandeltem und hydriertem VTT Pyrolyseöl (Kiefer)
- Lagerung von verschiedenen Fraktionen von IWC Pyrolyseöl (Buche)

Die Untersuchungen zum Alterungsverhalten der Pyrolyseöle FENOSA, ENSYN, und IWC ergaben die folgenden Resultate: Pyrolyseöle, die bei -20 °C gelagert wurden, bestehen nach 6 Monaten (in einigen Fällen sogar länger) noch aus einer homogen Phase. Im Gegensatz dazu bilden Proben, die bei 50 °C gelagert wurden, unterschiedliche Mengen eines zähen Schlammes auf dem Boden der Probenbehälter. Eine geringere Schlamm Bildung wurde bei den IWC Proben beobachtet, im Vergleich zu den unter gleichen Bedingungen gelagerten ENSYN und FENOSA Pyrolyseölen. Nach mehr als 2 Jahren Lagerung wurde der gebildete Schlamm in den Behältern der FENOSA und ENSYN Öle auf ungefähr 90 Gewichtsprozent der eingesetzten Öle geschätzt.

Die FTIR-Untersuchungen der Pyrolyseöle haben gezeigt, dass das Verhältnis der Maxima der Carbonylbanden bei 1715 cm^{-1} und 1650 cm^{-1} und des Maximums in dem Bereich $1500 - 700\text{ cm}^{-1}$ zwischen 0.6 und 1 liegt. Mit zunehmendem Alter der Öle geht das Verhältnis gegen 1. Diese Methode erwies sich als sehr nützlich, um die Änderungen innerhalb eines Öles mit der Zeit zu verfolgen. Für den Vergleich von verschiedenen Pyrolyseölen ist die Methode allerdings nur bedingt anwendbar. Die GPC-Untersuchungen der Pyrolyseöle zeigten einen Anstieg des durchschnittlichen Molekulargewichtes mit zunehmender Lagerungszeit. Offensichtlich spielen Polymerisationsprozesse bei dem Alterungsverhalten der Pyrolyseöle unter den untersuchten Lagerungsbedingungen eine

entscheidende Rolle. Interessanterweise stiegen die Säurezahlen der FENOSA und ENSYN Ölproben im Laufe der Lagerungszeit an, wohingegen die Säurezahl des IWC Öles im Laufe der Zeit abnahm.

Das wichtigste Ergebnis dieses Abschnittes der Arbeit ist die hohe Stabilität des IWC Pyrolyseöls aus Buchenholz. Sogar Proben, die für eine längere Zeit bei 50 °C gelagert wurden, zeigten eine beträchtliche Stabilität. Nach mehr als zwei Jahren befand sich nur ein dünner Film auf dem Boden des Probenbehälters, Schlamm hatte sich während dieser Zeit keiner gebildet. Diese ausgezeichnete Stabilität des IWC Öls kann eventuell auf die Behandlung nach der Produktion zurückgeführt werden. Nach der Produktion wurde das Öl mit Methanol versetzt, welches anschließend wieder abdestilliert wurde. Offensichtlich wurden dabei leichtflüchtige reaktive Verbindungen mit abdestilliert, wodurch ein stabileres Öl entstand.

Die Untersuchungen zum Alterungsverhalten von unbehandeltem und behandeltem VTT Pyrolyseöl aus Kiefernholz waren auf die zeitliche Änderung der Anzahl von Carbonylgruppen und der Viskosität ausgerichtet. Alle Proben zeigten eine beträchtliche Abnahme der Anzahl von Carbonylgruppen im Laufe der Lagerungszeit. Proben, die bei -20 °C gelagert wurden, zeigten eine geringere Abnahme als die Proben, die bei 80 °C gelagert wurden. Hydrierte Ölproben zeigten eine geringere Abnahme der Anzahl von Carbonylgruppen als das unbehandelte Öl. Diese Abnahme der Anzahl von Carbonylgruppen und die gleichzeitig beobachtete Zunahme der Viskosität unterstützen die Annahme, dass Polymerisationsreaktionen eine wichtige Rolle während der Alterung von Pyrolyseölen spielen. Die Viskosität ist ebenfalls eine wichtige Eigenschaft von Pyrolyseölen, welche den Grad der Polymerisation in Pyrolyseölen anzeigt. Eine systematische rheologische Studie wurde mit hydriertem und unbehandeltem Öl durchgeführt und zeigte einen Anstieg in der Viskosität mit zunehmender Lagerungszeit. Es stellte sich heraus, dass für Proben, die bei höheren Temperaturen gelagert wurden, der Viskositätsanstieg größer war.

Die Untersuchungen zum Alterungsverhalten von verschiedenen Fraktionen des IWC Pyrolyseöls aus Buchenholz sind schwer mit vorangegangenen Studien zu vergleichen. Frühere Untersuchungen, die sich auf das gesamte Pyrolyseöl bezogen, haben gezeigt, dass sich ein hochviskoser Schlamm am Boden der Probenbehälter bildet. Auch in dieser

Untersuchung zeigten die IWC Ölfractionen eine schnelle Schlamm Bildung. Allerdings bestand der Schlamm hier aus einem 'Stück' und klebte nicht an den Wänden des Behälters. Alle IWC Pyrolyseölproben hatten eine hohe Viskosität oder wiesen mehrere Phasen auf. Die ursprüngliche Annahme, dass eine der Fraktionen weniger reaktive Verbindungen oder einen geringeren Gehalt an reaktiven Verbindungen enthält und daher stabiler sein könnte, konnte nicht bestätigt werden.

6.2 Katalytische Verbesserung von Pyrolyseölen

In der vorliegenden Arbeit wurden Katalysatoren in der Gasphase während des Pyrolyseprozesses eingesetzt, sowie milde Hydrierungsversuche von Pyrolyseölen durchgeführt. Durch dieses sogenannte 'catalytic upgrading' sollte eine Verbesserung der physikalisch-chemischen Eigenschaften von Pyrolyseölen erhalten werden. Für die Katalyseversuche in der Gasphase wurden verschiedene Metalloxid-Katalysatoren auf Blähschiefer als Trägermaterial ausgewählt. Um die Katalysatoren in bezug auf ihre Metallbeladung zu vergleichen, wurde die Konzentration des Metalloxides auf Blähschiefer aus dem Verhältnis von Stoffmenge des Metalloxides und Masse an Blähschiefer berechnet.

Für die Pyrolyseexperimente, die ohne Zusatz von Katalysatoren durchgeführt wurden, führte eine größere Eintragsmenge zu einer erhöhten Ölausbeute und einer verringerten Kohle- und Gasausbeute. Im Gegensatz dazu zeigten die Experimente, die mit Katalysatoren durchgeführt wurden, keine gleichartige Abhängigkeit der Ausbeute von der Eintragsmenge.

Experiment BRIKAT P wurde mit Sand im ersten Reaktor und mit Manganoxid auf Blähschiefer im zweiten Reaktor durchgeführt. Dieses Experiment hatte von allen Experimenten die größte Pyrolyseölausbeute und die drittkleinste Ausbeute an Gas. Das entstandene Pyrolyseöl hat einen guten Heizwert (HHV, 'higher heating value'), einen kleinen Wassergehalt und eine geringe Viskosität. Manganoxid auf Blähschiefer im zweiten Reaktor in Kombination mit Sand im ersten Reaktor scheint daher ein vielversprechender Ausgangspunkt für katalytische Verbesserungsexperimente.

Dagegen ergab Manganoxid auf Blähschiefer im zweiten Reaktor in Kombination mit Blähschiefer im ersten Reaktor ein Pyrolyseöl mit deutlich schlechteren Eigenschaften. Die Pyrolyseöle, die aus den anderen Experimenten erhalten wurden, zeigten generell weniger

Verbesserungen in den physikalisch-chemischen Eigenschaften, wie zum Beispiel der Viskosität.

Insgesamt scheinen die in dieser Arbeit beschriebenen Gasphasenexperimente mit Metalloxiden auf Blähschiefer eine vielversprechende Methode zu sein, um die Langzeitstabilität von Pyrolyseölen zu verbessern. Die Ansätze, die in dieser Arbeit aufgezeigt sind, sollten nun in nachfolgenden Experimenten weiter verfolgt werden.

Um die zeitliche Änderung der Anzahl von Carbonylgruppen und die Änderung der Viskosität zu untersuchen, wurden Hydrierexperimente mit Pyrolyseölen nach der Produktion mit und ohne Katalysatoren durchgeführt. Die milden Hydrierungsversuche dieser Arbeit zeigen, dass Reaktionstemperaturen über 80 °C für die Hydrierung von Pyrolyseölen ungeeignet sind. Bei Temperaturen über 80 °C findet rasche Polymerisation statt, und es entsteht ein Pyrolyseöl mit hoher Viskosität. Außerdem neigen die entstandenen Pyrolyseöle mit zunehmender Lagerungszeit zu einer Phasentrennung und es entsteht ein unerwünschter Schlamm auf dem Boden des Probenbehälters. In bezug auf das experimentelle Verfahren zeigte sich, dass zuverlässige Untersuchungen der physikalischen und chemischen Eigenschaften nach der Hydrierung nur möglich waren, wenn die Katalysatoren als Extrudate anstatt als Pulver eingesetzt wurden. Katalysatoren aus feinem Pulver scheinen hoch-dispers in dem erhaltenen Pyrolyseöl zu verbleiben und sind sehr schwer zu entfernen.

Die durchgeführten Hydrierungsversuche haben gezeigt, dass keine der Kombinationen von Pyrolyseöl, heterogenem Katalysator und Reaktionsbedingung zu einem Pyrolyseöl führten, das stabiler war als das unbehandelte Öl. Da viele der kommerziellen Hydrierkatalysatoren recht hohe Temperaturen benötigen, scheinen sie für die Behandlung von Pyrolyseöl ungeeignet zu sein. Reaktionsbedingungen für ein erfolgreiches ‚catalytic upgrading‘ müssen die Polymerisationsreaktionen im Pyrolyseöl unterdrücken, während gleichzeitig die Hydrierung von funktionellen Gruppen beschleunigt wird. Für zukünftige Verbesserungsexperimente von Pyrolyseölen durch Hydrierungen müssen daher reaktive und selektive Katalysatoren entwickelt werden, die auch schon bei Temperaturen unterhalb von 80 °C funktionieren.

6.3 Pyrolyselignin

In der Literatur werden zwei alternative Methoden zur Herstellung von Pyrolyselignin beschrieben. Im Gegensatz zu der von Czernik und Piskorz [CP99] beschriebenen Präparationsmethode, wurde in der Methode, die in dieser Arbeit beschrieben wird, ein 'Ultraturrax' verwendet. Das dabei entstehende feine Pulver zeigt keine Einschlüsse von wasserlöslichen Verbindungen. Für zukünftige Untersuchungen zur Herstellung von Pyrolyselignin wird die 'Turax-Methode' empfohlen, da ein feines homogenes Pyrolyseligninpulver entsteht, welches reproduzierbare und vergleichbare Analysenergebnisse liefert, sowie für technische Anwendungen wichtig ist.

Aus GPC-Messungen wurde für Pyrolyselignin ein durchschnittliches Molekulargewicht (M_w) zwischen 650 g/mol und 1300 g/mol bestimmt, was darauf schließen lässt, dass Pyrolyselignin hauptsächlich aus Tri- und Tetrameren besteht. Die mittleren Molekulargewichte M_w der Pyrolyselignine aus Weichhölzern sind größer als die M_w der Pyrolyselignine aus Harthölzern, was vermuten lässt, dass Pyrolyselignine aus Weichhölzern bei der Produktion vermehrt Polymerisationsreaktionen eingehen. Das durchschnittliche Molekulargewicht M_w von MWL (*milled wood lignin*) ist ungefähr 10 mal so groß wie das von Pyrolyselignin. Dieses ist durch den hohen Grad an thermischen Zersetzungsreaktionen während des Pyrolyseprozesses zu erklären.

Unter der Annahme, dass die Grundstruktur von Pyrolyselignin aus Phenylethan-Einheiten besteht, wurde aus den Analysendaten eine C_8 -Formel berechnet. Außerdem wurde das mittlere Molekulargewicht pro C_8 -Einheit berechnet (z.B. für IWC Pyrolyselignin $C_8H_{6,3}O_{0,83}(OH)_1(OCH_3)_{0,8}$). Diese Zahlen wurden kombiniert mit GPC-Messungen und ergaben für die untersuchten Pyrolyselignine einen mittleren Polymerisationsgrad (DP) zwischen 4 und 9. Pyrolyselignine, die aus Weichhölzern produziert wurden, hatten den höchsten DP Wert.

^{13}C -NMR Spektren von Pyrolyseligninen zeigten ebenfalls die Bildung neuer Bindungen, zum Beispiel die Bildung von C-C Bindungen an früheren 'syringyl' C_5 Einheiten, schließen. Pyrolyselignin besteht hauptsächlich aus alkylierten aromatischen Einheiten, die durch neu gebildete Bindungen, und zwar keine aryl-alkyl-Ether, verknüpft sind. Eine detaillierte Analyse der ^{13}C -NMR Spektren der Pyrolyselignine zeigte, dass

mehrere strukturelle Einheiten des ursprünglichen Lignins auch nach dem Pyrolyseprozess noch intakt sind. Diese Beobachtung unterstützt die sogenannte 'thermal ejection theory', die durch Piskorz et al. postuliert wurde [PMR99]. Die zusätzlichen schwachen Signale, die in den ^{13}C -NMR-Spektren von Pyrolyselignin aus Buchenholz gefunden wurden, unterstützen ebenfalls die 'thermal ejection'-Theorie. Anscheinend werden Oligomere durch 'thermal ejection' aus den eingetragenen Pyrolyseölen herausgeschlagen. Große Moleküle, zum Beispiel C_8 -Einheiten, werden durch Bildung neuer Bindungen kombiniert, wohingegen die Rekombination von kleineren Molekülen zu der komplexen Pyrolyseligninstruktur unwahrscheinlich ist.

Im Gegensatz zu MWL, deuten die Daten, die für die Pyrolyselignine erhalten wurden, darauf hin, dass die Grundstrukturen (z.B. das mittlere Molekulargewicht) aufgrund der thermischen Behandlung weniger erhalten geblieben sind. Fraktionierung von Pyrolyseligninen und weitere Untersuchungen (zum Beispiel mittels HPLC), sind notwendig, um die Struktur von Pyrolyselignin genauer zu bestimmen.

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Goethe, an die Fürstin Gallitzin, 06.02.1797

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Curriculum vitae

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04.09.2000	birth of son Cedric Florian Ressler

**Pooh began to feel a little more comfortable,
because when you are a Bear of Very Little Brain,
and you Think of Things, you find sometimes that a Thing
which seemed very Thingish inside you
is quite different when it gets out into the open and
has other people looking at it.**

A.A. Milne 1882-1956

The House at Pooh Corner (1928)