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Leena Fagernäs

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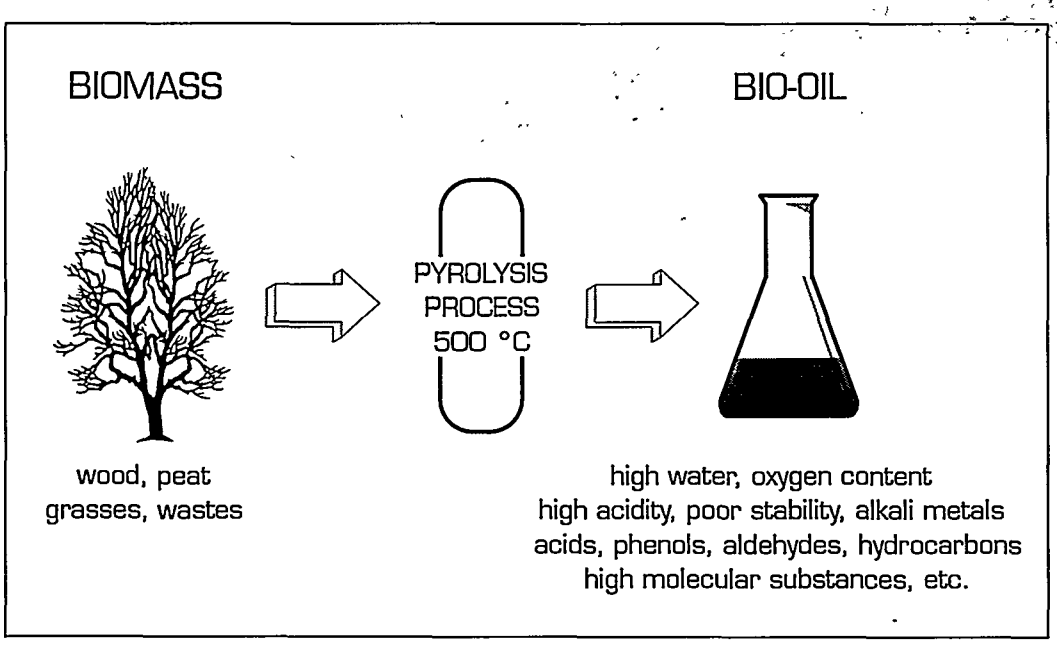
Literature review



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ABSTRACT

Biomass-based pyrolysis oils are complex mixtures of mainly organic compounds and water. The determination of their physical and chemical properties and chemical composition is a challenge for researchers. Characterisation of biomass pyrolysis oils has been studied at many universities in North America and Europe in the 1980s and 1990s. The existing literature on the analytical methods used for these oils is reviewed in this report.

The physico-chemical properties, such as water content, acidity, density, viscosity, heating value and stability, are important in terms of utilisation, storage and handling of oils. In the analyses, standard methods as such or as modified and, in addition, self-developed methods have been used. Standard fuel oil analyses are not often suitable as such for biomass-based pyrolysis oils.

For characterising the chemical composition, the bio-oils have first been mainly fractionated into different classes. Solvent extraction and adsorption chromatography are the most general methods used. In solvent extraction, the oils have often been divided into acidic, phenolic, basic, hydrocarbon and aqueous fractions or water-soluble and -insoluble fractions. In adsorption chromatography, the oils have been fractionated into different hydrocarbon and polar fractions. The fractions obtained have been analysed with various chromatographic and spectroscopic methods. Gas chromatography/mass spectrometry (GC/MS) technique is the analytical method most widely used and well adaptable for the fractions. For high-molecular-mass and highly polar compounds liquid chromatographic (LC) techniques as well as infrared (FT-IR) and nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectroscopies are more suitable due to the low volatility of pyrolysis oils.

For whole pyrolysis oils, LC techniques, primarily size exclusion chromatography and FT-IR and FT-NMR spectroscopies have proved to be useful methods, giving information on molecular weight, functional groups and aliphatic and aromatic structures and ratios. Direct mass spectrometric techniques (MS), such as molecular-beam MS and MS/MS, are rapid and interesting tools for the characterisation of the oils and for the investigation of the pyrolysis process.

In-depth characterisation of the complicated organic composition of pyrolysis oils requires the use of various techniques. The oils contain organic compounds such as acids, aldehydes, anhydrosugars, alcohols, phenolic compounds, esters and hydrocarbons, and, in addition, high-molecular, apparently lignin-derived substances, depending on feedstock, process conditions and recovery techniques.

PREFACE

Research into biomass pyrolysis is under way in the research field of Energy Production Technologies of VTT Energy. The work includes production, analysis, characterisation and handling of pyrolysis oils, and their use as fuels in boiler or diesel engine applications.

The report comprises the first part of research into chemical and physical characterisation of biomass-based pyrolysis oils. It takes a review of existing literature related to analytical methods used for pyrolysis oils. The work focuses on physical and chemical properties and behaviour as well as on chemical composition and safety and health aspects of the oils. The second part will include the test results of standard fuel oil analyses and their modifications for the oils, and in the third part, the applicability of chemical characterisation methods for rapid thermal pyrolysis oils will be discussed on the basis of experimental data.

The literature survey was carried out at VTT Energy in 1994 - 1995 within the project on "Production, properties and utilisation of pyrolysis oil". It was financed by Technology Development Centre Finland (TEKES) through the Bioenergy Research Programme (BIOENERGIA), and by the Finnish Corporations Neste Oy, Vapo Oy and Wärtsilä Diesel Ltd. The project was conducted by Prof. Kai Sipilä of VTT Energy. Prof. Raimo Alén of University of Jyväskylä, Jyväskylä, Finland, and Mrs. Eeva Kuoppala, Mr. Eero Leppämäki and Mrs. Anja Oasmaa, of VTT Energy, have made valuable comments on the report.

Many other persons have also contributed to this report by providing useful advice and latest information on the analytics of pyrolysis oils. My thanks are due to Dr. Douglas Elliott of Pacific Northwest Laboratories, Richland, USA; Prof. Esteban Chornet and Doctors Helena Chum, Thomas A. Milne, Foster Agblevor, David K. Johnson and Stefan Czernik of National Renewable Energy Laboratory, Colorado, USA; Prof. Charles Fuchsman of University of Bemidji, Minnesota, USA; Dr. Jan Piskorz of University of Waterloo, Ontario, Canada; Dr. Christian Roy and Dr. Hooshang Pakdel of Université Laval, Quebec, Canada; Prof. Dave Boocock of University of Toronto, Ontario, Canada; Dr. Dietrich Meier of Institute of Wood Chemistry and Chemical Technology of Wood, Hamburg, Germany; Dr. Rozanna Maggi of Université Catholique de Louvain, Brussels, Belgium, Dr. U. Balfanz and Dr. W. Baldauf of Veba Oel AG, Gelsenkirchen, Germany; and Dr. Rainer Ekman of Åbo Akademi University, Turku, Finland.

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CONTENTS

1 INTRODUCTION

Biomass can be converted into liquids, for example, by pyrolysis, high-pressure liquefaction, catalytic upgrading, or solvolysis. The main direct ways of thermochemical processing are pyrolysis and liquefaction [*Soltes & Milne* 1988: *Bridgwater & Kuester* 1988; *Anon.* 1989; *Mattucci et al.* 1989; *Hogan* 1992; *Bridgwater* 1994]. Considerable effort has been directed to these processes of upgrading biomass into liquid fuels. Pyrolysis is currently of greater interest than liquefaction due to lesser technical constraints and better economic feasibility [*Solantausta et al.* 1994a]. The pyrolysis liquids are typically produced at near-ambient pressures and at temperatures around 400 - 600 °C. The pyrolysis process produces solid char, gas and crude organic liquid known as bio-oil or tar. The proportions of these three products vary according to process conditions and feedstocks. There are a number of different pyrolysis processes for biomass. Pyrolysis processes differ from gasification processes, which use higher temperatures (800 - 1 100 °C) and produce gas (fuel gas, synthesis gas) as the main product containing tars only as impurities in the gas.

High liquid yields (60 - 80 % of dry feed) are obtained with rapid pyrolysis such as fast and flash pyrolysis, which have high heating rates (up to 1 000 °C/s), moderate temperatures (450 - 550 °C) and a short (<1 s) residence time of product vapours in the reactor. Several fast pyrolysis processes were developed in the 1980s. The main processes with liquid oil as the major product are the Fast Pyrolysis Process (WFPP) of the University of Waterloo [*Scott et al.* 1989, *Piskorz & Scott* 1988, *Scott et al.* 1988a, *Piskorz et al.* 1992], the Rapid Thermal Processing (RTP) of Ensyn Technologies Inc. [*Graham et al.* 1994, *Huffman et al.* 1994], Georgia Tech Entrained Flow Pyrolysis, the Vortex Ablative Pyrolysis of National Renewable Energy Laboratory (NREL) [*Chum* 1989, *Czernik et al.* 1993], and the Vacuum Pyrolysis Process of the University of Laval [*Roy et al.* 1988, 1989, 1992, *Pakdel et al.* 1992]. A wide range of biomass raw materials such as wood materials, peat, grasses, wood wastes, agricultural wastes, municipal solid wastes and also refinery wastes and scrap tires have been used in these processes.

Pyrolysis oils are studied with regard to their use as a resource for fuel products and chemicals. They rarely meet the standards required for fuels, but are nevertheless intended for use as such in direct combustion, in boilers or gas turbines. The chemical products of interest include petrochemicals, resins, specialty and commodity chemicals, polymers and co-polymers. The oils have the advantage of being easier to handle, store and transport than biomass, and have a much higher energy density. On the other hand, there are problems in handling, storing, and transporting of pyrolysis oils. They are highly acidic, very viscous, thermally unstable and not completely volatile. They are incompatible with petroleum products. They have high water, oxygen and alkali metal contents. They consist of a complex mixture of chemical compounds. Almost all oxygen containing

compound groups are present in the oils. The physical and chemical nature of bio-oils varies with feedstock, process conditions, and recovery techniques.

Adequate characterisation of bio-oils is very useful and important for the evaluation of use and upgrading alternatives. It is of great importance to know and understand the physical, chemical and biological properties of the bio-oils when solving the problems arisen. Standard methods generally used for petrol-based oils cannot often be applied for these oils. Due to the complicated nature of the oils their chemical composition is not known in detail. Modern analytical procedures for separation and analysis have to be used.

Characterisation of pyrolysis oils has been studied at many universities and institutes in the 1980s and 1990s. The major analytical efforts have been made in the United States, at Pacific Northwest Laboratories (PNL) in Richland [*Elliott* 1983, 1985, 1987, 1988, 1994a, *Elliott et al.* 1988] and at NREL in Golden, Colorado [*McKinley & Barrass* 1988, *Evans & Milne* 1988, *Johnson & Chum* 1988, *Chum* 1989, *Diebold* 1992, *Czernik et al.* 1994, *Pat. U.S.* 1993, *Czernik et al.* 1993]; in Canada, at the Universities of Laval [*Pakdel & Roy* 1987, 1988, 1990, 1992, *Pakdel et al.* 1989, 1994a and b, *Roy et al.* 1990], Waterloo [*Piskorz et al.* 1986, 1988a and b, *Radlein et al.* 1987, *Scott et al.* 1988a] and Saskatchewan [*Sharma & Bakhshi*, 1989, 1993a and b, *Adjaye et al.* 1992, *Bakhshi & Adjaye* 1994] and at B.C. Research in Vancouver [*McKinley & Barrass* 1988, *McKinley* 1989]; and in Europe, at Université Catholique de Louvain in Brussels [*Churin et al.* 1988, 1989, *Churin & Delmon* 1989, *Maggi & Delmon* 1994a, *Maggi et al.* 1991, *Laurent et al.* 1992], at the Institute of Wood Chemistry and Chemical Technology of Wood in Hamburg [*Meier et al.* 1994a, 1994b] and at Université Pierre et Marie Curie in Paris [*Desbene et al.* 1989, 1991a and b].

Two extensive projects on the characterisation of liquid products from different pyrolysis and high-pressure liquefaction processes were carried out in the United States and Canada in the 1980s. In one, which was co-ordinated by *Elliott* [1983] and constituted a part of the International Energy Agency (IEA) co-operative "Biomass Liquefaction Test Facility Project", a selection of biomass products derived from different processes were analysed with various analytical techniques at the Battelle Laboratory, United States. The other, co-ordinated by *McKinley* [1989], was the Centralised Analysis Project of the Canadian Liquefaction Program, which utilised the concept of a centralised laboratory to further understanding of liquefaction procedures in Canada. The B. C. Research performed and co-ordinated this project, in which different Canadian bio-oils were compared in a consistent manner. In addition, two IEA co-operative projects, "Voluntary standards" and "Standardised analytical methods", were carried out in the late 1980s. These projects focused on central analytical and quality-grading methods used worldwide for characterising feedstocks, by-products and end products of fuel conversion or chemical production. The usable methods were collected into a handbook [*Milne et al.* 1990]. *Elliott* [1994b] recently published a review on chemical analysis of biomass fast-pyrolysis oils.

This report reviews the existing literature on the analytical methods used for biomass-based pyrolysis oils. The review focuses on raw materials such as wood, bark, peat, straw, grass, lignite, oil shale, bituminous coal and waste paper, and on other different biomass residues and wastes. The pyrolysis methods comprise mainly flash, fast and rapid pyrolyses, because they produce organic liquid, bio-oil, as the main product. The work covers the physical and chemical properties and the behaviour as well as the chemical composition and the safety and health aspects of the oils. The methods reviewed are applied for bio-oils as such or for upgraded bio-oils. The intention was, on the basis of this review, to find and select the most suitable analytical methods for physical and chemical characterisation of rapid thermal pyrolysis oils at VTT and to test their applicability for this purpose. Physical properties - standard fuel oil analyses and their modifications - have already been applied for different oils at VTT and will be reported in the near future [*Oasmaa et al.* 1995].

2 BIOMASS FEEDSTOCKS

Wood materials were used as raw materials in most of the studies reviewed. Both conventional softwood (pine, oak, spruce) and hardwood species (aspen, birch, poplar, beech, red maple, hornbeam), energy crops and herbaceous species (acacia, eucalyptus, robinia, switchgrass) were included [*Elliott* 1983, 1985, *McKinley & Barrass* 1988, *Radlein et al.* 1986, *Piskorz et al. 1988a, Boocock et al.* 1988, *Pakdel et al.* 1988, *Pakdel & Roy* 1988, *Arpiainen & Lappi* 1989, *Maggi et al.* 1991, *Güell et al.* 1994, *Czernik et al.* 1994, *Elliott* 1994a, *Pakdel et al.* 1994a]. In addition, wood constituents such as lignin [milled wood lignin (MWL), organocell-lignin] and cellulose [*Piskorz et al.* 1986, *Scott et al.* 1988a, *Piskorz et al.* 1988b, *Desbene et al.* 1989, *Roy et al.* 1990, *Meier et al.* 1993, 1994, *Pakdel et al.* 1992], and also other forest biomass as peat and bark [*Karlsson & Björnbom* 1985, *Scott et al.* 1988b, *Arpiainen & Lappi* 1989, *Oasmaa & Boocock* 1992] were used.

The waste materials comprised forest residues (bark, sawdust), agricultural wastes (straw, wheat chaff, sugar cane bagasse, spent grain) [*Churin et al.* 1988, *Piskorz et al.* 1992, *Zemann & Bobleter* 1994, *Diebold* 1992] and industrial wastes (newsprint, pulp mill waste, kraft lignin, municipal solid waste, used tires, petroleum sludges) [*Helt & Agrawal* 1988, *Williams & Taylor* 1989, *Piskorz et al.* 1992, *Roy et al.* 1992, *Williams & Taylor* 1994].

3 PHYSICO-CHEMICAL PROPERTIES OF PYROLYSIS OILS

Physico-chemical parameters have been determined for bio-oils in order to know their nature and to understand their behaviour. The analyses are important in utilisation, storage and handling of oils. The physical and chemical nature of bio-oils varies with feedstock, process conditions and recovery techniques. The oils have been analysed for water content, acidity, density, viscosity, pour point, elemental analysis, heating value, solubility, char content, ash content, metals, flash point, stability and some other properties. In the measurements, mainly standard methods (ASTM, DIN, EN) as such or modified and, in addition, self-developed methods have been used.

Prior to analyses, bio-oil samples have generally been stored at room temperature and protected from light. In the Centralised Analysis Project [*McKinley* 1989] the samples were stored in a cold room at 5 °C.

3.1 WATER CONTENT

The pyrolysis oils are generally dark brown viscous liquids and their water content is typically high (15 - 30 %). The water in the oil comes from the original moisture of the feedstock, from the pyrolysis reaction or from the addition of extra water to condense pyrolysis vapours [*Laurent et al.* 1992]. When investigating RTP and WFPP oils, *Graham et al.* [1994] and *Radlein et al.* [1987] found, respectively, the water in the oils to be an integral part of the single-phase liquids. *Elliott* [1994a] evaluated the form of water in the oils of the Vortex Flash Pyrolysis reactor of NREL. No separate aqueous phase was recovered from or identified in the raw oil product. According to *Scott et al.* [1988a] water is dissolved in the organic phase, but the addition of more water to a certain level (about 60 % by weight) causes a phase separation.

The water content is important, as it affects other physical properties. It increases the pH, reduces the heating value and the viscosity, influences both chemical and physical stability, and can affect the subsequent upgrading processes.

For the determination of the moisture content of wood there are three main types of determination: oven or vacuum drying, titration with a selective reagent for water and distillation with a water-immiscible solvent [*Fengel & Wegener* 1984]. As regards petroleum oils, co-distillation with xylene in a Dean and Stark apparatus is applied for samples with higher levels of moisture, and Karl-Fischer (K-F) titration is employed for trace amounts of water [*Elliott* 1994b].

As to the bio-oils, water is difficult to measure and remove, since evaporation or distillation at normal temperatures of around 100 °C can cause significant and

potentially deleterious physical and chemical changes in the liquid [*Bridgwater & Double* 1989]. Lower-temperature drying is not successful. According to *Bridgwater* [1988], utilisation and consideration of oil on a "wet" basis may be more sensible than on a dry basis that is subject to uncertainty.

In the determination of the moisture content, the K-F titration method has mostly been applied and has been considered the method of choice [*Elliott* 1994b]. Due to the high amount of volatiles boiling below 100 °C in the oil, vacuum distillation, thermal drying or co-distillation with xylene cannot be used as such [*Elliott* 1983]. In the determination the material to be analysed is titrated with the standard K-F reagent to an electrometric end point. The K-F solution contains iodine, pyridine, sulphur dioxide and methanol and reacts almost quantitatively with water [*Fengel & Wegener* 1984]. The sample solvent is composed of methanol and chloroform (ASTM D 1774) or pyridine and ethylene glycol monomethyl ether (ASTM E 203). Titration can be performed best by potentiometric end-point determination. Standardised methods have mostly been applied for the bio-oils, either as such or as modifications, which concern mainly the composition of the reagent [*Elliott* 1985, *McKinley* 1989, *Arpiainen & Lappi* 1989, *Roy et al.* 1990, *Oasmaa & Boocock* 1992, *Maggi & Delmon* 1994a, *Maggi et al.* 1992, *Maggi & Delmon* 1994b]. In *Elliott's* studies [1983, 1985] the K-F titration was used by means of the Aquatest IV unit by Dow Chemical Co. The reagent is electrolytically generated in the presence of water. By means of a sensing electrode the instrument generates enough reagent to react with the water in the sample and calculates the water content integrating the current used in electrolysis [*Elliott* 1994a].

Generally, the K-F method has been found fast and reliable [*Fengel & Wegener* 1984]. *Czernik et al.* [1994] estimated the precision at ±0,2 % for bio-oils, when the water content was determined by K-F titration using a Metrohm 701 titrator and Baker's Hydra-Point Comp 5 titrant. This was in agreement with their results obtained for the triplicate analyses of the initial oil. According to *Chum and McKinley* [1988] water analysis by K-F titration can, however, be subject to systematic errors. Methanol used as a sample solvent may react with activated aldehyde/ketone groups present in the oils, and release water. The possibility of such systematic errors has been indicated by a preliminary comparison between K-F and gas chromatographic water determinations. A chromatographic method [*Chum* 1989] was employed using a glass column packed with Porapak QS. The chromatographs used were a Varian 3700 or a Hewlett Packard (HP) 5880. *Maggi et al.* [1991] used, in addition to the K-F method, azeotropic distillation in a Dean and Stark receiver. Both methods were found reproducible, the values obtained being 4.5 % (distillation) and 5 % (K-F).

3.2 ACIDITY

Pyrolysis oils are acidic. Their pH is low, ranging from 2.0 to 3.7 in the oils reported [*Radlein et al.* 1987, *Scott et al.* 1988a, *Graham et al.* 1994, *Roy et al.*

1992, *Bridgwater* 1988, *Czernik et al.* 1993, *Cuevas et al.* 1994]. The pH is dependent on the feed material. For example, according to *Czernik et al.* [1993], wood-based oils were more acidic than switchgrass-based oils. The oils contain organic acids. The acids found in pyrolysis oils and their analyses are discussed in Chapter 5. *Czernik et al.* [1993, 1994] has reported on the pH determination method; he used a Sentron model 2001 pH system with an ion sensitive field effect transistor as a sensor. The precision of the measurements was estimated at 0.1 units.

The bio-oils are corrosive, mainly due to acidity. Mild steel is not suitable for handling or storage [*Bridgwater* 1988]. Only special types of steels and packings have been found suitable for equipment. In addition, polypropylene piping has been used. *Baldauf and Balfanz* [1992] performed corrosivity tests on FeCrNi-steel (type 1,4541). Weight losses of the steel samples and an increasing concentration of the corresponding metal ions in the oil depending on time were found. The weight losses observed after a treatment of 7 days at 94 °C were 500 ppm. The corresponding corrosion rate was approximately 70 ppm/d. The concentrations of Fe, Ni and Cr in the oils increased in the treatment from 69, 4 and 2 ppm to 380, 47 and 210 ppm, respectively. At room temperature no corrosion was found.

3.3 DENSITY

Densities of bio-oils are high (1.11 - 1.28 g/cm^3). A pycnometer method has generally been used in density measurements. The sample weights, the pycnometer volumes and the temperatures used in the measurements vary in different studies. Room temperature has mostly been used. *Maggi and Delmon* [1994a] used a 20 ml pycnometer at room temperature, *Adjaye et al.* [1992] a 10 ml pycnometer at 25 °C and *Peacocke et al.* [1994] two 5 ml pycnometers over the temperature range 25 to 70 °C (Figure 1). In addition to Peacocke, *Graham et al.* [1994] measured the density as a function of temperature, changing the temperature from 25 to 70 °C. *Peacocke et al.* [1994], when using unfiltered samples, reported problems experienced with fine char particles present in the oils blocking the glass capillaries of pycnometers and producing erroneous results which were subsequently repeated.

3.4 VISCOSITY

With regard to the treatment of oil, the most significant characteristic is viscosity, which determines the treatment temperature. Viscosity is internal friction of flowing substances. Classification of fuel oils has traditionally based on kinematic viscosity at +50 °C. The kinematic viscosity is calculated by dividing the absolute (dynamic) viscosity by the density. The viscosity of fuel oil is highly dependent on the temperature and, in addition, on the nature and the water content of the oil.

The viscosity of biomass-based pyrolysis oils generally varies from about 10 to 500 mPa·s. The viscosity of a peat-based WFPP bio-oil has been measured to be considerably higher, 8 400 mPa·s at 63 °C [*Elliott* 1983]. Viscosities of different petroleum products and pyrolysis oils determined at 60 °C are shown in Figure 2.

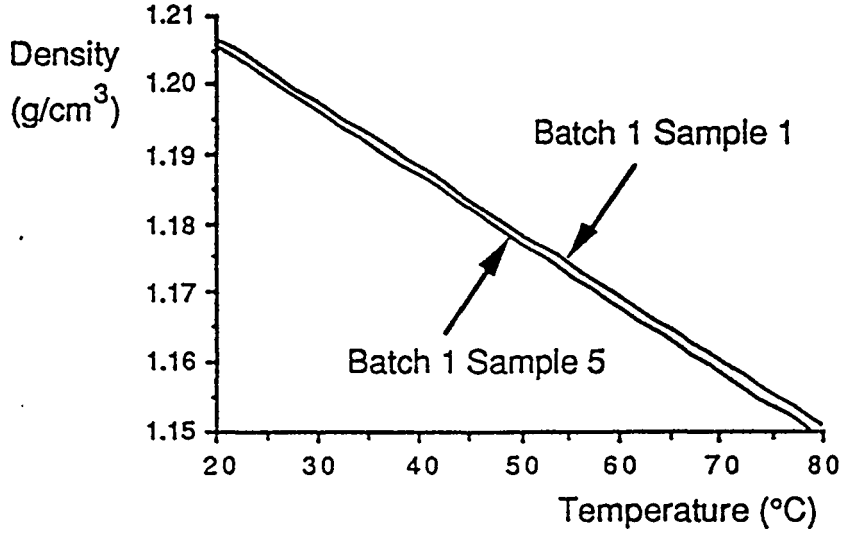

Figure 1. Variation in the pyrolysis liquid density of RTP bio-oil samples [Peacocke et al. 1994].

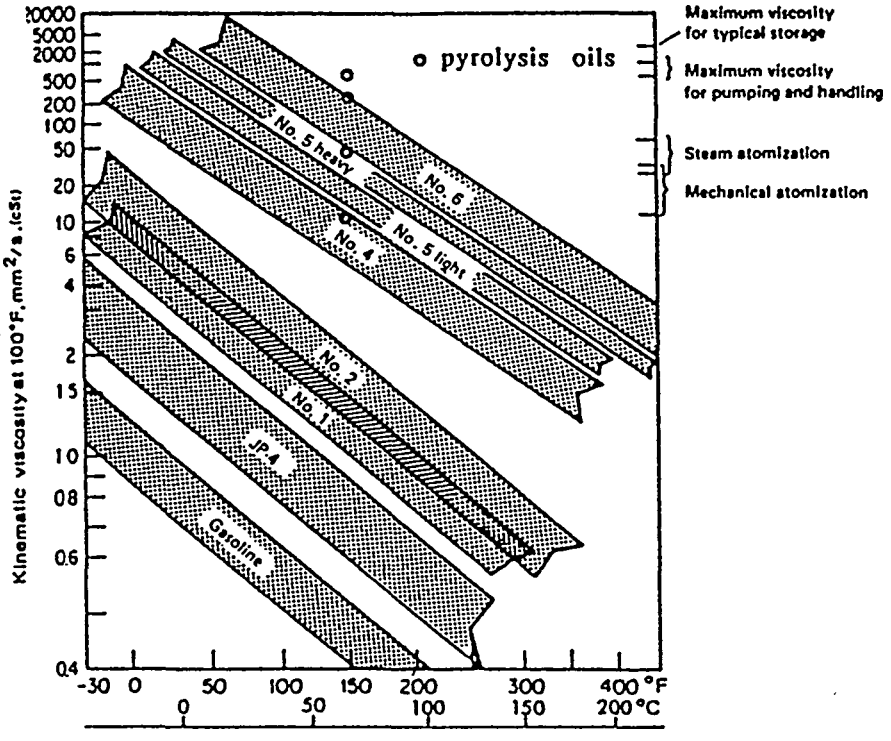

Figure 2. Viscosities of petroleum products and pyrolysis oils [Churin & Delmon 1989].

When determining the viscosity of pyrolysis oils, rotational viscometers have generally been used. Rotational viscometers are useful over a wide range of viscosity. For pyrolysis oils, Brookfield and Haake viscometers of different models are most commonly used.

Elliott [1983, 1985] used a Brookfield Synchro-Lectric Viscometer with a small sample adapter and a constant temperature water bath. The viscometer rotates a cylinder, called a spindle, in a fluid and measures the torque necessary to overcome the viscous resistance to the induced movement. This is accomplished by driving the immersed cylinder through a beryllium-copper spring. The degree to which the spring is wound is indicated by the position of a pointer on the viscometer dial and is proportional to the viscosity of the fluid for any given speed and spindle. The viscometer is able to measure over a number of ranges since, for a given drag, or spring deflection, the actual viscosity is proportional to the spindle speed and is also related to the spindle's size and shape.

Czernik et al. [1993] used a Brookfield Digital Model LVDT. The precision of the measurement was 2 % due to variations in fluid temperature. The values were measured at five temperatures and then linearly correlated using the variables log viscosity and 1/T (the correlation coefficient r^2 was always greater than 0.99). Chum et al. [*Pat. U.S.* 1993] used the same viscometer model. *Adjaye et al.* [1992] used a Brookfield cone and plate digital viscometer model RVTDCP. Haake's rotatory viscometer was used in the studies of Milne [*McKinley* 1989], *Maggi et al.* [1991], *Churin et al.* [1989] and *Peacocke et al.* [1994]. The viscometer uses various cup and rotor sensor systems, depending on the volume of available sample and viscosity range [*McKinley* 1989]. The measuring temperature varied from 21 to 70 °C in the studies.

3.5 POUR POINT

Oil is solidified while the temperature decreases. The pour point is the lowest temperature at which the oil is observed to flow and approximates the lower limit at which a fuel oil can be pumped from storage. For bio-oils the pour point has generally been low, for woody bio-oil -23 - -30 °C in the studies reviewed [*Radlein et al.* 1987, *Graham et al.* 1994, *Elliott* 1983, *Solantausta et al.* 1994b], while for peat-derived oils very high pour points, 42 and 51 °C, have been measured [*Elliott* 1985, *Scott et al.* 1988]. The high pour point indicates the semi-solid nature of peat oils. The water and wax contents and the viscosity of the oil affect the pour point. According to the standard (ASTM-D 97-87), after preliminary heating the sample is cooled at a specified rate and examined at intervals of 3 °C for flow characteristics. The lowest temperature at which movement of the oil is observed is recorded as the pour point.

3.6 ELEMENTAL ANALYSIS

Pyrolysis oil is thought to be a water-containing highly oxygenated hydrocarbon [*Bridgwater* 1988]. Consequently, the bio-oils contain mainly carbon, hydrogen and oxygen. Nitrogen and sulphur contents are very low. The elemental analysis of the bio-oil approximates that of feed material. The concentrations of the main elements in different bio-oils are reviewed in Table 1.

Table 1. The elemental composition of biomass pyrolysis oils. Variations in different studies.

Element	Concentration, wt% of organic matter
C	39 - 73
H	4.3 - 8.5
N	0.1 - 5.2
O	15 - 53
S	0.0 - 0.6

The oxygen content is very high due to the feedstock and the pyrolysis reaction mechanism. This determines the physical properties and chemical reactivity of the oils. For example, the viscosities and densities are high and the energetic content is low, because the C-O bonds do not release energy during combustion. In addition to oxygen contained in the structures of the molecules, pyrolytic oils contain oxygen in water [*Laurent et al.* 1992].

Elemental composition has been determined with different elemental analysers. *Elliott* [1983] and *Adjaye et al.* [1992] used Perkin-Elmer analysers 240 and 240B for analysing carbon, hydrogen, nitrogen and oxygen. Sulphur was not analysed with these instruments due to the low level of concentration [*Elliott* 1983]. The concentration of nitrogen in wood-derived samples was also at or below the limit of detectability, while nitrogen in peat-derived samples was easy to measure. The Perkin-Elmer 240 determines carbon, hydrogen and nitrogen by measuring their combustion products CO_2, H_2O and N_2. Combustion occurs in pure oxygen and the products are analysed by thermal conductivity (TC). Oxygen is measured by pyrolysing a separate sample in helium over platinised carbon so that oxygen is converted to carbon monoxide. Sulphur and other trace elements have been determined by energy-dispersive x-ray fluorescence using a combination of titanium and zirconium excitation sources. In *McKinley's* [1989] studies the analyses were performed on a Carlo Erba Model 1106 elemental analyser. CHN analysis consists of fast combustion in a tin capsule in the presence of oxygen and a catalyst. The conversion products are measured by gas chromatography using a TC detector. For oxygen analyses the sample is pyrolysed in a silver capsule and subsequently passed over a nickelised carbon to produce CO which is measured by gas liquid chromatography in a fashion similar to the CHN procedure. In studies by *Maggi et*

al. [1991] the elemental composition was determined in a Carlo Erba Analyser, and oxygen was calculated by difference. *Elliott* [1994a] also determined oxygen as difference. The standard error was 1.3 - 3.6 % in the difference determination and smaller than in the direct measurement according to the results of the Voluntary Standard Project's Round Robin [*McKinley et al.* 1994]. Other elemental analysers used and reported have been a Heraus analyser [*Meier et al.* 1994a] and a Leco CHN 600 instrument [*Arpiainen & Lappi* 1989].

3.7 HEATING VALUE

The heating value of bio-oils depends on the feedstock composition and, more closely, on the elemental composition. The water content of the oil reduces the heating value. The oil produced from dry or low-moisture biomass feed materials has a heating value typically a little above that of the feed, in the range of 15 - 25 MJ/kg [*Bridgwater & Double* 1989]. The heating values are generally reported as higher heating values (HHV). The bio-oil is readily combustible, and care has to be taken in storage, handling and atomisation.

Heating values have been measured with calorimeters according to standard methods. As to *Elliott* [1983], heating values were determined by combustion in a Parr oxygen bomb calorimeter. An adiabatic system was maintained by using a controlled temperature water bath. Combustion of the samples in the bomb was a straightforward procedure. Some difficulty was, however, noted with ignition of high-moisture-content samples. In these cases a fine cotton thread was used as a wick.

3.8 SOLUBILITY

The use of solubility for characterising bio-oils is based on heavy crude oil analyses. Heavy crude oil contains maltenes soluble in heptane, and asphaltenes insoluble in heptane. Pentane and hexane can also be used as solvents. Asphaltenes are usually soluble in aromatic solvents. In the characterisation of coal fluids pentane-solubility has been used as oil content.

Elliott [1983] chose hexane and toluene for the solvent when testing different bio-oils. *Maggi and Delmon* [1994a] measured solubility by solubilising oil samples in numerous solvents [cyclohexane, tetralin, BTX, tetrahydrofuran (THF), chloroform, methylene chloride and acetone] using an ultrasonic bath. *Baldauf and Balfanz* [1992] tried to find a suitable solvent for process pyrolysis oils together with refinery feedstocks. Pyrolysis oils were found to be unmiscible with crude petroleum oil, any petroleum cuts, and aromatics such as benzene and toluene.

Elliott [1983] found almost no (~1 %) hexane-soluble and little (~13 %) toluene-soluble material in wood pyrolysis oils. In peat pyrolysis oils, hexane and toluene soluble proportions were much higher, 26 % and 38 %, respectively [*Elliott* 1985, *Scott et al.* 1988b]. In studies by *Maggi et al.* [1992] on different bio-oils from the Basa carbonisation pilot unit (Switzerland) all oils behaved similarly; they were poorly (<10 %) soluble in cyclohexane and tetralin, weakly (<30 %) in BTX, and highly soluble (>75 %) in THF, chloroform, methylene chloride and acetone.

3.9 CHAR CONTENT

Pyrolysis oils contain solid char particles entrained by the pyrolysis vapours. Fine char particles are carried over and trapped in the condensed vapours. The char content varies from 0.5 to 5 % in the oils reported [*Maggi & Delmon* 1994a, *Maggi et al.* 1991, *Laurent et al.* 1991, *Graham et al.* 1994, *Elliott* 1994a]. The particle size range is about 1 - 100 μm.

Maggi and Delmon [1994a] and *Maggi et al.* [1992] determined the char content as the solid material retained by filters of 8 μ (SS 597 1/2) or 10 μ, when 1 % solution of oil in THF was filtered. *Elliott* [1994a] recovered char on a Whatman #42 paper (particle retention of 2.5 μm). The sample was mixed with methanol and stirred at room temperature. The solution was then filtered, washed with additional methanol, and air-dried. *Cuevas et al.* [1994] used a glass filter of 1.6 μm.

The solids in bio-oils are often defined as acetone insolubles [*Baldauf & Balfanz* 1992]. *Elliott* [1983] used hot acetic acid (with acetone) in the determination of actual char or solids in the liquids. Insolubility in this solvent was 0.13 - 0.16 % for maple-, poplar- and peat- based oils according to *Scott et al.* [1988b].

Char constitutes a problem in applications. If the objective is to use bio-oil for turbine combustion, it must be low in inorganics, specially in alkali metals. The main source of alkalis in pyrolysis oils is believed to be the char [*Czernik et al.* 1993, *Elliott* 1994a]. *Elliott* [1994a] has recently studied forms of char, alkali and water in the oil. Alkalis in pyrolysis oils are discussed in further detail in chapter 3.12.

3.10 CARBON RESIDUE

The combustion property of heavy fuel oils is best described by carbon residue. The carbon residue of petroleum products is determined either with the Conradson [ASTM D 189] or Ramsbottom [ASTM D 524] method. The carbon residue designates the carbonaceous residue formed after evaporation and pyrolysis of a petroleum product. The carbon residue of bio-oils has scarcely been considered in the studies reviewed. According to *Kindelan* [1994] the available data on this

parameter for bio-oil are contradictory. The aromatic rings and low carbon number give opposite tendencies to this parameter.

3.11 ASH CONTENT AND INORGANICS

The ash content of biomass-based pyrolysis oils is typically in the range of about 0.03 to 0.20 %, and depends to a great extent on its content and composition in the feedstock. For switchgrass-based oil, a 0.45 % ash content has been reported [*Agblevor et al.* 1994]. Roughly two-thirds of the feedstock ash goes to the char and about one-third is contained in the oil [*Graham et al.* 1994].

The ash content is usually determined by incineration of organic material at 600 - 850 °C. Standard methods [ASTM D 1102-56, ASTM D-482-80] have mostly been used [*Elliott* 1983, 1985, *Roy et al.* 1990, 1992, *Baldauf & Balfanz* 1992]. Errors in the determination may be derived from some losses of volatile inorganic salts. *Elliott* [1983, 1985] determined combustion in a muffle furnace as specified in the ASTM method D-482-80, which covers determination of ash from distillate and residual fuels, crude oils and other petroleum products. Porcelain crucibles with lids were used throughout. In his recent studies, *Elliott* [1994b] reported that the samples were slowly heated over several hours to 500 °C to allow evolution of volatiles, and then ashed at 600 °C for 1 h and again at 700 °C for an additional 2 h.

Inorganic compounds present in the bio-oil have not been investigated until recently. As mentioned previously the bio-oil to be used for turbine combustion must be low in inorganics, alkali metals being particularly troublesome. The alkali oxides from combustion gases can condense on turbine blades causing unbalance, erosion and corrosion. Turbine fuel standards permit the total alkali content of 1 ppm in the oil [*Czernik et al.* 1993]. High concentrations of alkali metals in oils make them unsuitable for combustion in boilers as well. Char is believed to be the main source of alkalis in pyrolysis oils [*Czernik et al.* 1993, *Elliott* 1994a, *Agblevor et al.* 1994]. Thus, the removal of char is important. *Elliott* [1994a] has recently studied forms of char, alkali and water in the oil. Oil separations, including centrifugation, filtration, water dilutions, and phase separations, were carried out to confirm the site of the alkali in the oil. The probable mechanism of alkali metal deposition in pyrolysis oils has recently been discussed by *Agblevor et al.* [1994] and some of the proposed methods of alkali metal removal by *Diebold et al.* [1994].

In *Elliott's* [1994a] studies, trace elements were analysed by either atomic absorption spectroscopy (AAS) or inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Organic sample preparation for AAS involved acid digestion and the method for ICP-AES involved an alkali fusion by dissolution. The fusion was performed individually with both caustic sodium and potassium. Sodium was then measured in the sample fused in potassium and vice versa. However, there

was some cross contamination as Na and K numbers were by 1 or 2 orders of magnitude higher in all cases, and the ICP-AES numbers for Na and K were not reported. The AAS analyses were performed on aqueous samples prepared by nitric and hydrochloric acid dissolution of the oils or chars. The particle size of the oils was determined by computer evaluation of digitised images referenced to calibrated standards followed by appropriate statistical analyses. Neutron activation analysis has also been suggested for analysing alkalis [*Agblevor et al.* 1994].

The inorganic components in the oils include the same elements as those found in the biomass. The main alkali metals in the oils are calcium and potassium. High concentrations of potassium (160 - 300 ppm) and calcium (1 - 95 ppm) were found in herbaceous feedstock-based bio-oils [*Agblevor et al.* 1994]. There were also high concentrations of alkali metals in bio-oils derived from agricultural residues. High alkali metal concentrations (potassium 330, calcium 100 and sodium 38 ppm) and low vanadium concentrations (0.5 ppm) were also reported in wood-based oils by *Gros* [1995] *and Solantausta et al.* [1994].

The inorganic components are divided in both the homogeneous oil phase and the char [*Elliott* 1994a]. The char particulate was in the micrometer range, and was filtered with solvent dilution. However, the level of separation of the char (>2.5 μm in methanol wash) did not result in clean, ash-free oil. Significant levels of non-filterable alkali components were found in the methanol-soluble oils. Centrifugation of the oils removed less than half of the char. Water dilution of the oil caused a phase separation, but the fractionation of the inorganics to either phase was not complete. According to *Elliott* [1994a] more refined means of separating the inorganic components from pyrolysis oil need to be developed in order to make oils that meet current turbine fuel specifications. According to *Czernik et al.* [1993] it is possible that, prior to filtering, a substantial part of these metals can have already been leached out of the char particles due to the acidity of the oils. To remove char and alkali from the oils, a study of filtering vapours before condensing is presently under way at NREL. Optimisation of hot filtration conditions is being investigated using a hot baghouse of sintered stainless steel or ceramic fabric filter elements. *Agblevor et al.* [1994] suggest that hot gas filtration can effectively reduce the alkali metal contents of pyrolysis oils to acceptable levels with regard to their use as turbine and boiler fuels.

3.12 FLASH POINT

Flash point measures the tendency of the sample to form a flammable mixture with air under controlled laboratory conditions. According to the method ASTM D 93-90 (Flash point by Pensky-Martens closed-cup tester) the sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals. The flash point is the lowest temperature at which application of the test flame causes the vapour above the sample to be ignited.

Flash points of bio-oils have been determined only in a few studies [*Elliott* 1985, *Graham et al.* 1994, *Czernik et al.* 1993]. Czernik et al. obtained values ranging from 45 to 100 °C for the bio-oils of NREL, and Graham et al. 51 - 66 °C for RTP oils. Elliott determined flash and flame points in a Cleveland open cup test unit approximating ASTM D-92. The water in the liquefaction products interfered the measurement preventing it, even when heating the sample up to its boiling point. The boiling point was generally around 100 °C and indicated water evolution. Consequently, the minimum flash point (boiling point) and no flame point were given for the liquids.

3.13 STABILITY

Stability is of great importance regarding storage, transportation and processing of the oils. Pyrolysis oils are relatively unstable in both chemical and physical terms. Unstability with respect to time, light or temperature causes solidification during storage or in lines and injectors [*Laurent et al.* 1991]. Exposure to air affects at a slower rate than that of temperature rise. Temperatures above about 100 °C cause rapid deterioration of the liquid in terms of physical properties such as polymerisation, viscosity increase, phase separation, and deposition of a bitumen-like substance [*Bridgwater & Double* 1989, *Kindelan* 1994].

Stability of bio-oils has been studied only to a slight extent. Previously, *Scott et al.* [1988] reported briefly on the stability of WFPP oils. Recently, *Czernik et al.* [1994] published stability studies of wood pyrolysis oils from NREL Vortex reactor, and *Bakhshi and Adjaye* [1994] have studied stability characteristics of the Ensyn RTP oil and *Adjaye et al.* [1992] those of a high-pressure liquefaction oil. In addition, Chum et al. [*Pat. U.S.* 1993] have studied the stability of a phenol/neutral fractions containing extract (called P/N product) of a pyrolysis oil.

The WFPP bio-oils derived from different softwood and hardwood species have been reported to be quite stable at room temperature [*Scott et al.* 1988]. The water content was found to increase slightly over twelve months, presumably due to the slow processes of condensation-polymerisation even at room temperature. At higher temperatures, 120 °C and above, the oils became increasingly unstable and decomposed with evolution of gas, and finally with charification of a polymeric residue.

Czernik et al. [1994] studied the effects of storage conditions on physical and chemical properties of biomass pyrolysis oils exposed to elevated temperatures over extended periods of time. The oil was an oak pyrolysis oil obtained from the NREL reactor. Oil samples were placed in capped glass vessels and then stored at 37 °C for up to 12 weeks, at 60 °C up to 9 days, and at 90 °C up to 15 hours. Reference samples were stored in a freezer. Physico-chemical properties such as pH, water content and viscosity were measured for the samples. Structural changes in

3.14 OTHER PROPERTIES

Other physical characteristics determined for pyrolysis oils are thermal conductivity, specific heat capacity and refractive index. Their measurement has been reported only by *Peacocke et al.* [1994]. These properties, in addition to other physical ones, are important in the design and evaluation of transport units and in sizing process equipment. Characteristics like surface tension, vapour pressure and volatility of bio-oils have been discussed in a couple of studies [*Bakhshi & Adjaye* 1994, *Kindelan* 1994].

3.15 COMPARISON OF PYROLYSIS OILS AND FUEL OILS

The most important fuel oil characteristics reported for different biomass-based pyrolysis oils in the literature are compared with light and heavy fuel oil properties in Table 2. The water content, density and ash content are higher, and the pour point, heating value and flash point lower in pyrolysis oils than in both the light and heavy fuel oils. The alkali metal contents of bio-oils are high compared with those of the fuel oils, but the sulphur and vanadium contents are lower in bio-oils than in the heavy fuel oil. The high acidity of bio-oils is typical only for bio-oils.

Table 2. Comparison of important fuel characteristics of pyrolysis oils and light and heavy fuel oils. *[*Solantausta et al.* 1994b, *Gros* 1995]

Characteristic	Pyrolysis oils	Light fuel oil*	Heavy fuel oil*
Water content, wt%	15 - 30	0.02	0.04
Density, kg/dm^3	1.11 - 1.28	0.87	1.01
Viscosity, cSt, at 50 °C	10 - 500	6	175
Pour point, °C	-23 - -30	0	15
Heating value, HHV, MJ/kg	15 - 25	42.4	40.0
Ash content, wt%	0.03 - 0.20	0.01	0.05
Flash point, °C	45 - 100	70	100
Sulphur content, wt%	0.0 - 0.6	0.18	2.3
Acidity, pH	2.0 - 3.7	-	-

4 FRACTIONATION OF PYROLYSIS OILS

4.1 GENERAL

Fractionation of pyrolysis oils prior to analysis is very useful for in-depth chemical characterisation or for the determination of chemical composition, due to the complicated chemical nature of the oils. The complete chemical characterisation of the whole oil is almost impossible; while the fractionation allows a global identification of the different groups of chemical compounds [*Maggi & Delmon* 1994a]. The qualitative and quantitative analyses of individual components of pyrolysis oils can be simplified by prefractionated methods [*Chum & McKinley* 1988].

In crude oil refining the oil is fractionated by distillation, and the distillates are treated with conversion processes in order to obtain commercial oil products. Distillation is the most important physical method or unit process employed, but it is not particularly suitable for biomass oils. Hence, other fractionation methods must have been found for these oils. Two general methods are solvent extraction and chemical adsorption. They have been reported to be used for fractionating pyrolysis oils into various chemical classes.

Fractionation methods have been applied for bio-oils in many different ways. Various research groups have developed their own methods. The fractions obtained have then been subjected to a variety of chromatographic and spectroscopic methods to determine the composition of the oils.

4.2 DISTILLATION

In the refinery of petroleum crude oil the following products are obtained with distillation: gases (fuel gas, LPG), low-octane gasoline (cut temperature 30 - 150 °C), middle distillates, which are distillated to petrol (170 - 230 °C), diesel oil (220 - 300 °C) and light fuel oil (280 - 380 °C), heavy gas oil (360 - 480 °C) and undistillable bottom oil (>450 °C).

As a fractionation method of biomass-based oils, distillation has been studied by *Elliott* [1983, 1985], *Chornet and Overend* [1985], *Beaumont* [1985], *Adjaye et al.* [1992], *Baldauf and Balfanz* [1992], *Samolada et al.* [1993], *Bakhshi and Adjaye* [1994] and *Besler et al.* [1994]. Atmospheric, vacuum and steam distillations were applied.

Bakhshi and Adjaye [1994] performed atmospheric distillation for the Ensyn bio-oil and determined the composition of volatiles The amount of distillate, up to 100 °C was 8.6 wt% of bio-oil, and at 108 °C 25 wt% of bio-oil. In *Beaumont's* [1985] studies on the analysis of beech-derived flash pyrolysis oils, distillation

was abandoned after a few attempts, because the separation by volatility resulting from this technique did not facilitate further analysis by gas chromatography (GC). Even vacuum distillation of pyrolytic oil led to a tarry residue of about 15 %.

Baldauf and Balfanz [1992] investigated the feeding of raw biomass pyrolysis oil (RTP oil) to petroleum crude oil before or after the desalting unit. According to them both atmospheric and vacuum distillation are unsuitable processes to fractionate the pyrolysis oil separately or directly together with petroleum crude or any other petroleum fraction. The raw pyrolysis oil is not miscible with conventional distillation unit feedstocks, and the distillation products are likewise not compatible and are undesired in refineries. The products comprised nearly 50 light volatiles containing mainly water, acids, aldehydes and alcohols. The residue seemed to be coke, formed by thermal degradation and polymerisation of the unvolatiles (Table 3). As a pretreatment process for the oil they suggested upgrading in a preceeding hydrotreating step (Figure 3). After pretreatment the oil could be routed to atmospheric or vacuum distillation, from where it would end up very diluted in three distillate streams. It would also be possible to distil the hydrotreated oil separately and to feed the distillates to the corresponding conversion units.

Chornet and Overend [1985] have reported on the distillation of biomass liquefaction oils. For the TR-12 proto-oil obtained from the PERC mode initial boiling point (IBP) was 171 °C with 65 % of the oil distilling below 427 °C with no abrupt transitions at any temperature range. Although biomass liquefaction oils have been attempted to be distilled into hydrocarbon-like distillation cuts in view of the aromatic nature of the oils, a more appropriate fractionation should be followed. The following fractions have been suggested: IBP up to 170 °C (light ends and neutrals), 170 - 240 °C (monophenol fraction), 240 - 260 °C (catechol fraction) and 260 °C (pasting or recycle tar). Vacuum distillation at 100 mmHg (ASTM-D-1160) was used to separate the proto-oils into five to seven fractions which were individually analysed via gas chromatography/mass spectrometry (GC/MS). The mixture was a blend of carrier oil with derived phenolic and oxygenated cyclic components. Between 30 and 50 % of the oil could thus be routinely characterised.

Adjaye et al. [1992] used distillation characteristics of pyrolysis oil as basis for the stability monitoring of the oil. Fresh bio-oil (about 4 g) was distilled over the temperature range 85 - 250 °C in a Buchi GRK-50 distillation unit for 30 min under a fixed vacuum pressure of 172 Pa. The distillate was collected in a bulb immersed in liquid nitrogen and was analysed by GC. The amount of non-volatile residue after the distillation was determined. The amount of distillate increased from 21 wt% at 85 °C to 62 wt% at 200 °C before decreasing to 44 wt% at 250 °C (Table 4). The amount of residue decreased with an increase in temperature to a minimum of 38 wt% at 200 °C. For stability monitoring, the distillation temperatures

Table 3. Distillation characteristics of pyrolysis oil [Baldauf & Balfanz 1992].

	Atmospheric	Atmospheric and vacuum	Vacuum
Yields			
Distillates, %	49.7	55.6	51.2
- Boiling range, °C *	<120	<320	<320
- Pressure (vacuum), mbar		3.8 - 12	3.8 - 100
- Organic, %	16.2	22.5	29.2
- Water, %	33.5	31.1	22.0
Residue, %	45.5	31.6	30.7
- Elemental analysis of residue			
C, %	73.5	78.8	77.2
H, %	5.2	4.3	4.4
O, %	18.0	15.9	15.0
Gases and losses, %	4.9	12.8	18.1

** Atmospheric or atmospheric equivalent temperature*

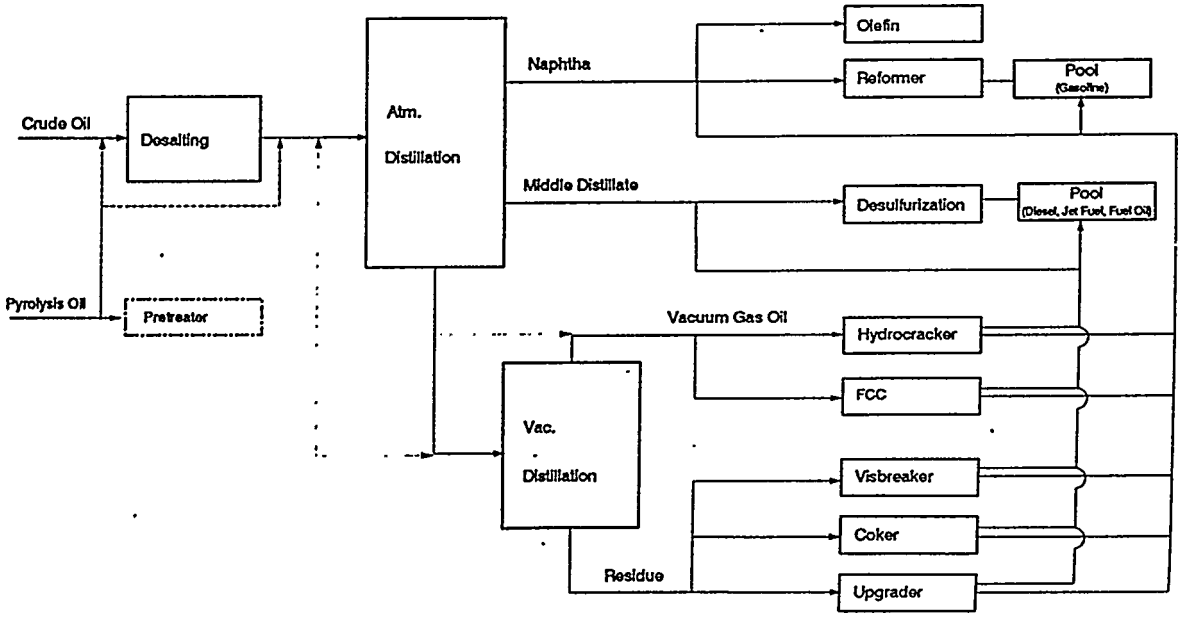

Figure 3. Scheme of a refinery with possible inputs of pyrolysis oil [Baldauf & Balfanz 1992].

were at 175, 200 and 250 °C. The distillation characteristics and the distillate composition were measured after 1, 16 and 31 days (Chapter 3.13).

Table 4. The amount and composition of bio-oil distillate at different temperatures, wt% [Adjaye et al. 1992].

Parameter	Temperature, °C								
	85	115	140	165	175	190	200	220	250
Distillation characteristics									
Distillate	21	22.5	30.0	35.0	38.5	47.0	62.3	52.6	43.5
Residue	79.0	77.5	70.0	65.0	61.5	53.0	37.7	47.4	56.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Distillate composition									
Acids	4.3	4.4	3.7	2.8	2.6	2.5	2.5	2.5	2.3
Alcohols	7.2	10.3	8.6	3.8	3.5	3.6	6.6	5.3	5.2
Aldehydes + ketones	9.1	11.0	9.0	12.4	14.2	10.0	7.8	7.7	7.5
Aliphatic hydrocarbons	11.1	10.3	7.6	6.5	6.4	6.0	5.5	5.5	5.5
Aromatic hydrocarbons	19.2	20.8	21.8	23.8	23.7	23.7	21.6	21.3	21.1
Ethers	4.9	6.2	5.4	3.1	3.8	3.5	2.5	2.6	2.5
Furans	4.0	4.0	3.8	2.2	3.0	3.2	3.4	3.4	3.6
Naphthenes	9.2	9.8	12.4	13.0	13.7	12.1	12.0	12.0	11.9
Phenols	12.6	11.0	16.8	19.0	21.4	24.7	28.1	29.8	35.2
Unidentified fraction*	18.5	12.3	10.1	13.3	7.7	11.7	9.9	9.8	4.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

**Determined by difference*

Elliott [1983, 1985] applied vacuum distillation for different pyrolysis and liquefaction oils. When enough sample was available, modified ASTM-D-1160 apparatus and procedure were used. With lesser amounts of oil a conventional, short-path micro still was used. The D-1160-77 method specifies both a procedure and an apparatus for the distillation, which provides approximately one theoretical plate fractionation. The apparatus comprised an alternate column assembly including a vacuum jacketed reflux column, a mercury thermometer instead of the specified thermo-couple, and a vacuum manifold receiver, which allowed the collection of separate product fractions without interruption of the vacuum or distillation.

Vacuum distillation data was converted to atmospheric pressure using a petroleum hydrocarbon vapour pressure chart with allowance made for the difference

between the water and phenolics of wood oil and hydrocarbons of petroleum. The distillation curves of pyrolysis oils, describing only the organic material in the oils, are shown in Figure 4. When using the short-path micro still distillation apparatus, similar results were obtained.

As can be seen from Figure 4, the pyrolysis oils from wood contained a high percentage of low-boiling material in addition to the water. Hence, separation of the light organics from the water and water from the pyrolysis oils as well is not feasible by fractional distillation without loosing a significant portion of the organic product. In addition to the largest fraction of low-boiling organics of all the products tested, the vacuum pyrolysis wood oil of Sherbrooke had a relatively low temperature for the onset of decomposition. At about 170 °C smoke began to carry over through the water-cooled condenser and to collect in the dry ice trap. If the distillation was suspended at this temperature the residual material could still be handled as a liquid and have a melting point of 66 °C. The distillation range of the peat oil from the Sherbrooke vacuum pyrolysis was at much higher temperatures and the onset of thermal decomposition was at 271 °C. There remained a large amount of non-distillable residue (57 %).

The flash pyrolysis poplar oil of Waterloo contained less light end material than the vacuum pyrolysis oil. There was, however, a substantial distillate (50.3 %) up to thermal decomposition at 233 °C. The residual material was a coke which did not melt (MP >300 °C). For the maple oil thermal decomposition occurred at

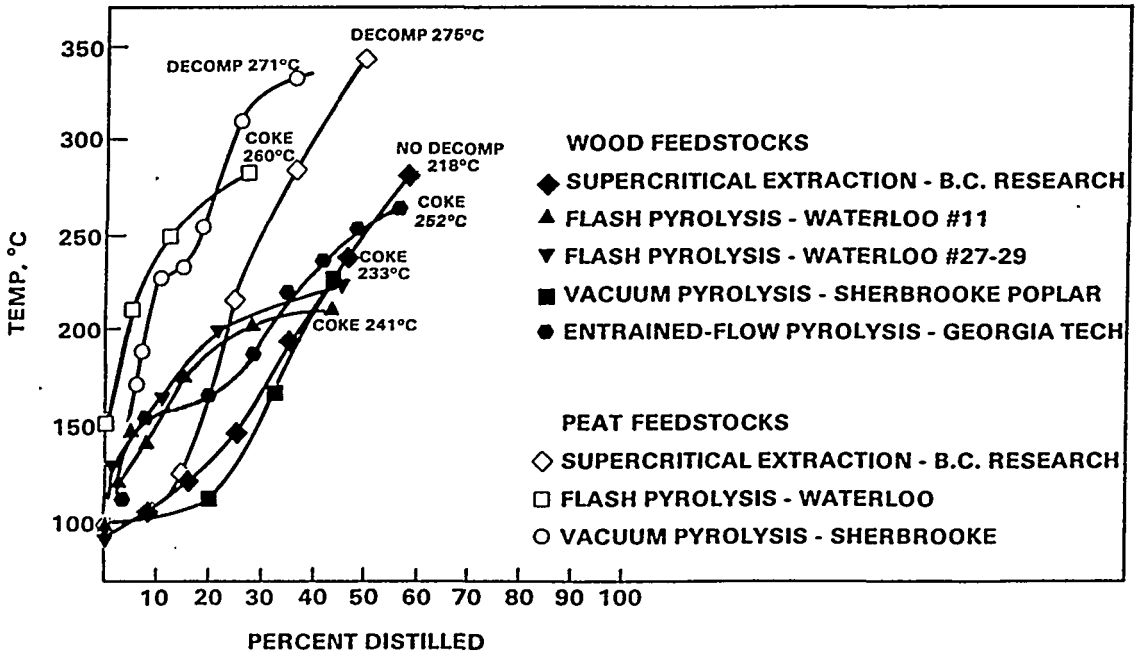

Figure 4. Distillation curves of biomass pyrolysis products [Elliott 1985].

lower temperatures. Distillation of the peat oil resulted in a clear water phase, a two-phased second fraction and a waxy fraction, which continued to the end of distillation. The distillation was discontinued when a light yellow solid began to collect in the secondary condenser and the residue coked at 260 °C.

Fractionation of the phenolic mixture obtained from the Ensyn oil with liquid-liquid extraction was tried by *Samolada et al.* [1993] for phenols recovery by applying vacuum distillation. Three fractions were collected. A great difficulty in maintaining a constant vacuum value was reported. At 5 - 20 mbar degradation and gasification of the phenolic mixture was detected at temperatures higher than 120 °C. The first and the second fractions (light and middle) contained the bulk of phenol and light phenols (up to xylenols), while the (heavy) third fraction contained mainly syringyl derivatives and eugenol as well. The operating problems resulted in a considerable carbonisation of the heavy phenols contained in the phenolic fraction (~50 wt%). According to Samolada et al., the method seemed to be proper for the fractionation of the phenolic fraction, if large sample amounts are used in a standard vacuum distillation apparatus. The steam distillation procedure was applied for the phenolic fraction also in these studies (Figure 5). The fraction was used instead of phenol in alkylation experiments.

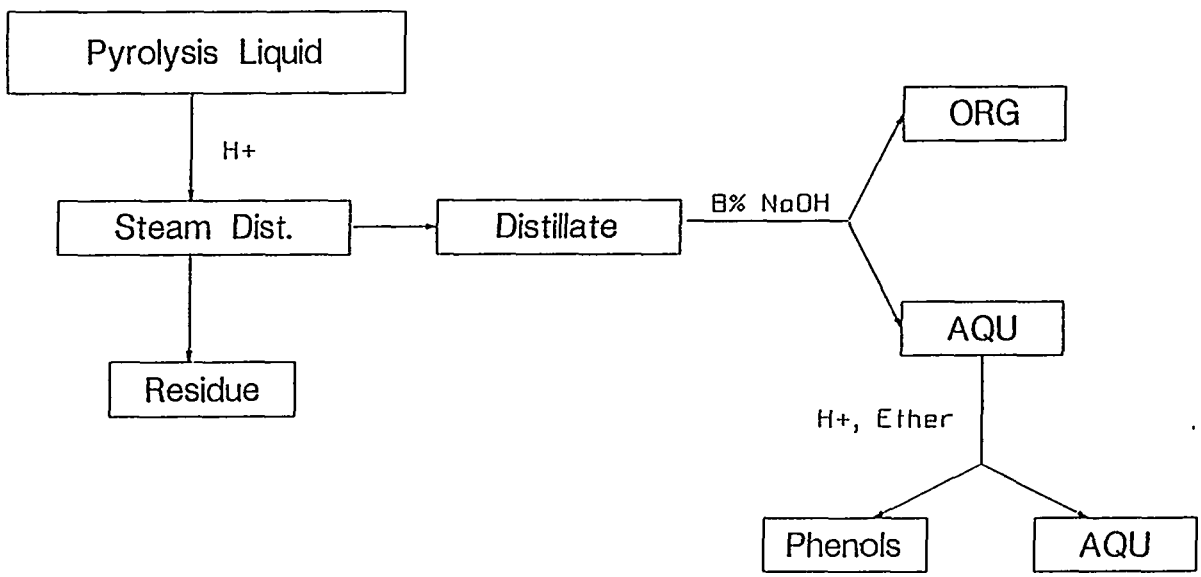

Figure 5. Steam distillation scheme of pyrolysis liquid [Vasalos et al. 1993].

Simulated distillation is an analytical technique generally used to determine the boiling point range of petroleum products by GC. A simulated distillation GC programme based on ASTM procedure D2887-73 was used in the Centralised Analysis Project reported by *McKinley* [1989]. *Besler et al.* [1994] performed fractional distillation for pyrolysis oil obtained from *Euphorbia rigida* according to ASTM D256-62 in the ranges of <140 °C, 140 - 240 °C, 240 - 350 °C and >350 °C. Fractions boiling at 140 - 240 °C and 240 - 350 °C were subjected to simulated distillation (ASTM D2887-84) and compared with kerosene and diesel fuel to assess the compatibility of the oil with conventional transport fuels (Figure 6). The pyrolysis oils derived from different wastes were subjected to simulated distillation using a modified method incorporating pyroprobe GC by *Williams and Taylor* [1989]. The system was a PE 8320 capillary GC coupled to a CDS Pyroprobe. The results, representing the simulated distillation range only for those compounds that are volatilised below 500 °C, showed that ranges similar to petroleum oil were found for wood and municipal waste. Rubber tyre and crop oil had higher ranges. However, the simulated distillation is not suitable for polar compounds or oils, because they are not correctly calibrated. The boiling temperature scale is calibrated to the retention times of *n*-paraffins, which is suitable for separating non-polar hydrocarbons in boiling point order.

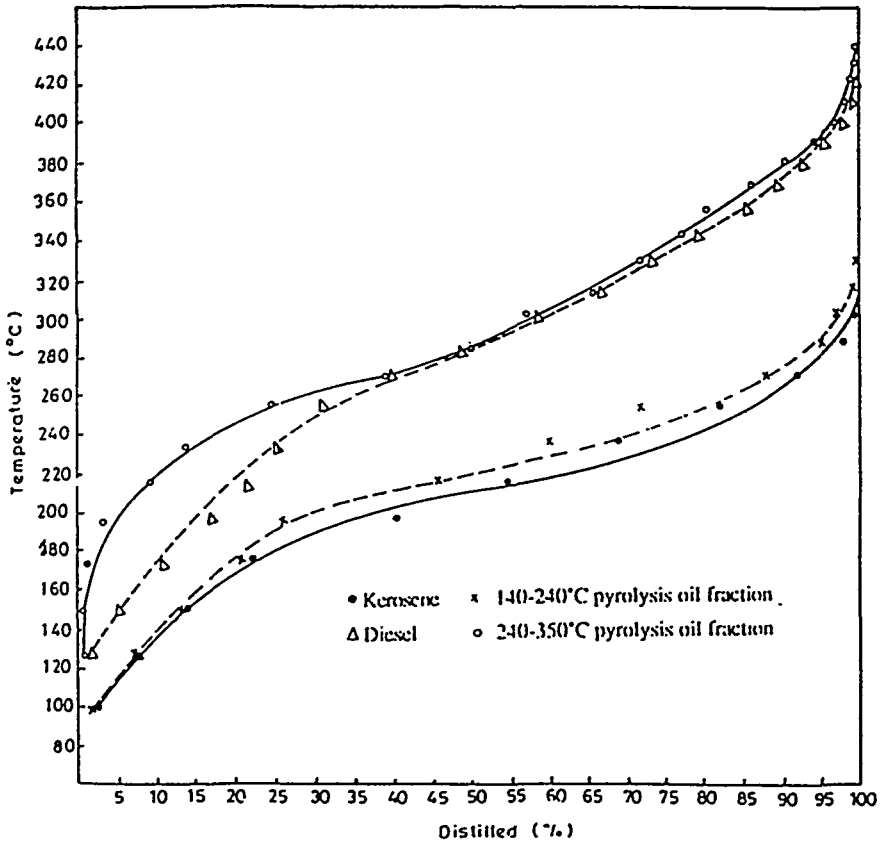

Figure 6. Comparison of the boiling ranges of E. rigida pyrolysis oil fractions and some common fuels measured by simulated distillation [Besler et al. 1994].

Distillation by GC has many advantages over the classical vacuum distillation procedure because of the small sample quantity required and the speed and ease of operation [*McKinley* 1989]. The procedure has also some limitations. The distillation profile applies only to the portion of the sample that reaches the detector at the end of the chromatographic column. The computer program that controls the output of the results does not give any indication of the percentage of the sample that eluates through the GC column. Another limitation is that the procedure is not conducted under reduced pressure and, consequently, the components are subjected to elevated temperature. The higher temperatures may change the chemical composition of the bio-oil. McKinley recommends that the technique and software ought to be modified so that the amount of sample distilled is reported, and the profiles ought to be compared with those obtained from vacuum distillation.

4.3 SOLVENT EXTRACTION

4.3.1 General

In the solvent extraction method the oils are extracted with different solvents to remove different phases from the oil. Solubility has long been used in the characterisation of heavy crude oil. The 'oil' fraction of coal fluids is typically defined as the portion extractable, for example, into pentane. Adaptation of this approach to biomass-derived liquids is based on the work initially conducted by the MOBIL group [*Chornet & Overend* 1985, *Whitehurst et al.* 1980]. One of the first methods used to characterise bio-oils was simple solubility measurements in solvents of different polarity. In the measurement of the yields of proto-oils, extraction of the organic phase is used. According to Chornet and Overend, common solvent systems for extraction are chloroform, methanol-chloroform, acetone, benzene and tetrahydrofuran (THF).

Elliott [1985, 1988] carried out the first fundamental and overall analysis of tars obtained from the carbonisation of various species of softwood and hardwood in different processes. He used capillary GC and MS to qualitatively and quantitatively determine components after simplifying the organic matrix by extraction with dichloromethane (CH_2Cl_2). However, this extraction method has later been found to be of limited use and somewhat biased due to the low solubility of highly polar compounds in this solvent.

The solvent extraction method has been reported to have been used in the fractionation of bio-oils mainly by the research groups of the Universities of Louvain [*Churin et al.* 1989, *Maggi et al.* 1992, *Maggi & Delmon* 1994a, 1994b], Waterloo [*Scott et al.* 1988, *Piskorz & Scott* 1988, *Piskorz et al.* 1988b, *Radlein et al.* 1987], Saskatchewan [*Sharma & Bakhshi* 1993a] and Laval [*Pakdel & Roy* 1990, *Pakdel et al.* 1988, 1989, *Pakdel & Roy* 1988] and by the groups of NREL [*Pat. U.S.* 1993, *Diebold* 1992, *Chum* 1989, 1991, *Johnson & Chum* 1988] and of Chemical

Process Engineering Research Institute (CPERI), Greece [*Vasalos et al.* 1994]. The solvents and the order of the solvents vary greatly in the methods used.

4.3.2 Fractions soluble in organic solvents

The most general way of fractionating bio-oils by solvent extraction has been to divide them into acid, basic and neutral fractions with organic solvents.

Maggi et al. [1991] and *Maggi and Delmon* [1994a, 1994b] fractionated slow and flash pyrolysis oils by a liquid-liquid partition scheme. The method was a modification of a method developed for separating coal tars. This partition fractionates the bio-oil dissolved in an adequate organic solvent by extractions based, in the first steps, on the acidity-basicity properties of the molecules, and later on polarity. The method is relatively easy allowing simple, reproducible and inexpensive characterisation. The preparative liquid chromatography technique previously used by *Churin et al.* [1988] (Chapter 4.4) was, although providing very good results, abandoned because it was long and expensive [*Maggi et al.* 1992, *Maggi & Delmon* 1994b].

The oil samples used by *Maggi and Delmon* [1994b] originated from the BASA carbonisation process produced from eucalyptus, robinia, oak, pine bark and acacia, and from the Ensyn rapid pyrolysis process from a mixed hardwood sawdust (maple-oak). The samples were weighed and evaporated to eliminate free water and most volatile compounds. The remaining product was diluted in THF and then filtered to separate remaining char particles. THF was evaporated, the samples were weighed and then dissolved in CH_2Cl_2. The insoluble compounds were filtered and weighed, and the solvent was evaporated. The samples were then subjected to a partition procedure shown in Figure 7. Four fractions were obtained: phenols and acidic compounds (I), bases (II), 'polar' neutrals (III) and hydrocarbons or 'non-polar' neutrals (IV). All fractions were dried with Na_2SO_4, filtered, evaporated, weighed and analysed by FT-IR and GC/MS. The precipitates formed during the partition were collected and weighed. The yields of the fractions, when cumulated, did not reach 100 %. The difference corresponds to very polar molecules retained in the aqueous layer, obtained during the separation of the acidic fraction (I). This aqueous layer was re-extracted with chloroform in a continuous extraction apparatus yielding an 'aqueous fraction' (V). The yields obtained for the oils studied with this procedure are given in Table 5.

Fahmy et al. [1982] used solvent extraction when studying the chemical composition of the pyrolytic tar obtained from cotton stalks by rapid continuous pyrolysis. The volatile products of the pyrolysis were received in several condensors. The condensation zones were washed out with peroxide-free ether. The obtained solution containing some char residue was subjected to Soxhlet extraction after addition of fresh ether. The ether solution containing the extractives, i.e., tars and oils, was then washed and worked up for phenols, acids, and neutral components.

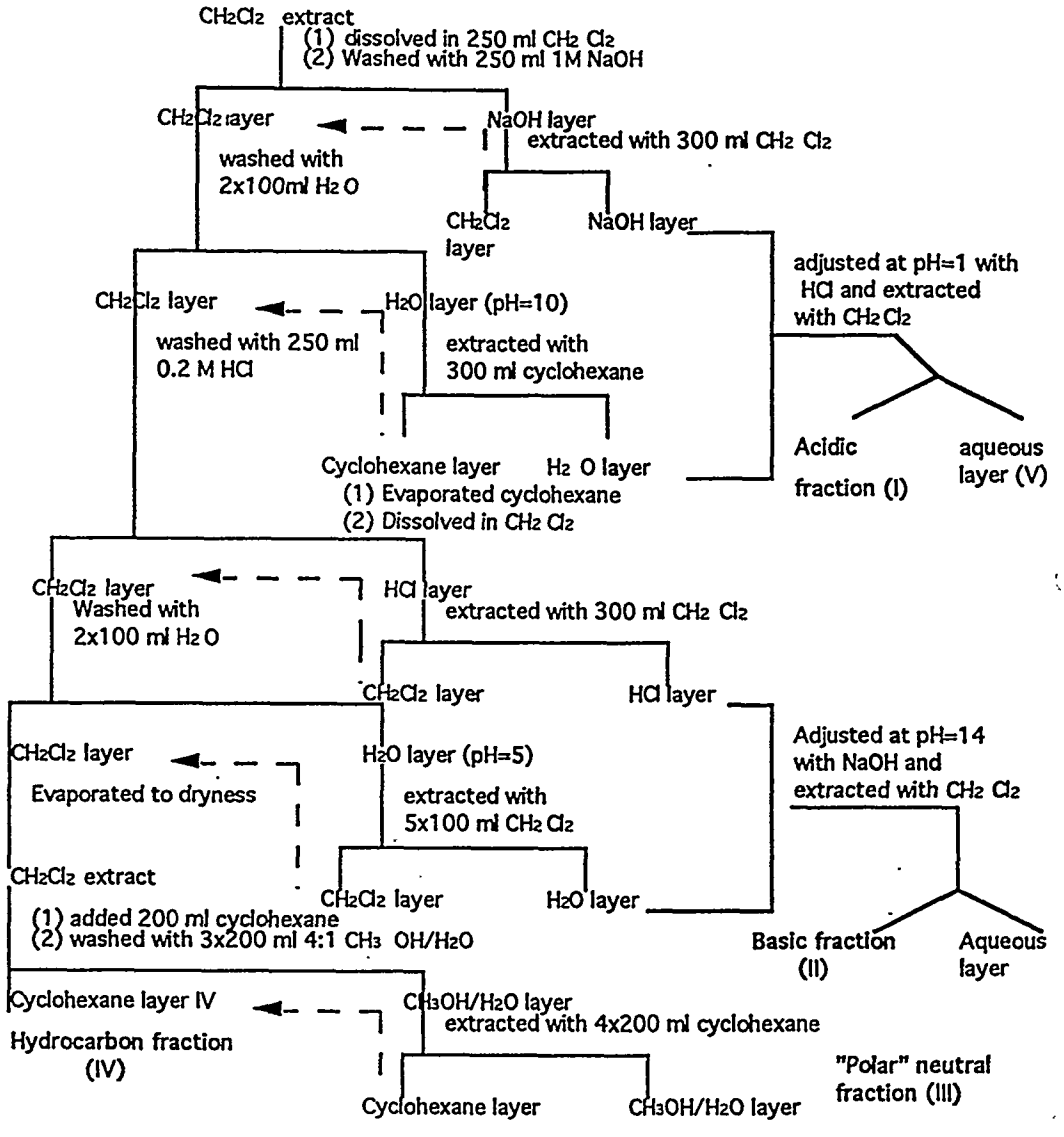

Figure 7. Liquid-liquid fractionation scheme for bio-oils [Maggi & Delmon 1994b].

After shaking the etheric solution five times with saturated bicarbonate solution, the obtained aqueous phase was acidified with a concentrated sulphuric acid and percolated for 24 hrs with peroxide-free ether to obtain the acids. The ether solution was dried over sodium sulphate, filtered and evaporated in vacuum under nitrogen. The ether-soluble acids were precipitated. The ether phase remaining after bicarbonate extraction was shaken three times with aqueous sodium hydroxide solution to precipitate the phenols as sodium phenolate in the aqueous phase. After acidification the free phenols were obtained through percolation with ether; they were then dried and purified. The group of neutral products was obtained as residue after the alkaline treatment of the remaining ether solution. The phenols representing the largest group were then separated by GC. The yields of different product groups of the ether extractives are presented in Table 6.

Table 5. Yields of various fractions obtained in liquid-liquid partition from bio-oils of different origin [Maggi & Delmon 1994b].

Fraction	Oil, wt%				
	Acacia	Oak	Eucalyptus	Pine bark	RTP
I (acidic)	40.0	43.08	26.6	21.8	34.5
II (basic)	0.7	0.39	0.57	0.8	0.4
III (neutral)	6.7	4.96	6.82	5.6	6.0
IV (hydrocarbon)	10.0	11.02	7.95	11.9	2.7
V (aqueous)	22.7	12.0	-	-	17.0
Precipitates	13.3	9.12	13.57	11.3	18.9
Yield	93.4	80.57	55.51	51.4	79.5

Table 6. Yields of different product groups of the ether extractives of the oil obtained at 400 °C and 600 °C pyrolysis temperatures [Fahmy et al. 1982].

Particle size	Less than 0.5 mm		More than 0.5 mm	
Experiment No.	1	2	3	4
Pyrolysis temperature, °C	400	600	400	600
Yield of tar, mg (ether extractives)	1 877.5	1 252.0	1 955.0	1 221.5
Crude phenols mixture, mg	1 401.5	927	1 258	767.5
Identified phenols in the crude phenols mixture, mg	188.5	129.8	288.3	146
Neutrals, mg	238.5	250	450	350
Acids, mg	237.5	75	247	104

Input in all experiments was 25 grams air dry cotton stalks with 8 % moisture content.

Beaumont [1985] studied flash pyrolysis products of beech wood. He used liquid-liquid extraction as pretreatment of the pyrolytic oil after abandoning distillation (Chapter 4.2) (Figure 8). The oil was first neutralised with highly concentrated sodium hydroxide. Then the oil was extracted with diethyl ether in a continuous apparatus over one night. The organic fraction was dried and evaporated; a neutral fraction was obtained amounting to 11 % of the crude oil. The aqueous phase was acidified to pH 1 and re-extracted with diethyl ether in the same way. The acid fraction (9.8 %) was obtained after drying and evaporation of the solvent. A portion of the oil (12.5 %) was totally insoluble in ether. Analysis of the fractions was performed by GC, MS and chemical derivation.

Vasalos et al. [1993] studied separation of phenols from Ensyn pyrolysis oils. They used three separation techniques; liquid-liquid extraction, open-column chromatography and steam distillation. Liquid-liquid extraction yielded a sufficient 65 - 75 wt% recovery of phenols. The phenolic content of Ensyn oil was 11 wt%. Eucalyptus bio-oil from Union Fenosa was fractionated according to

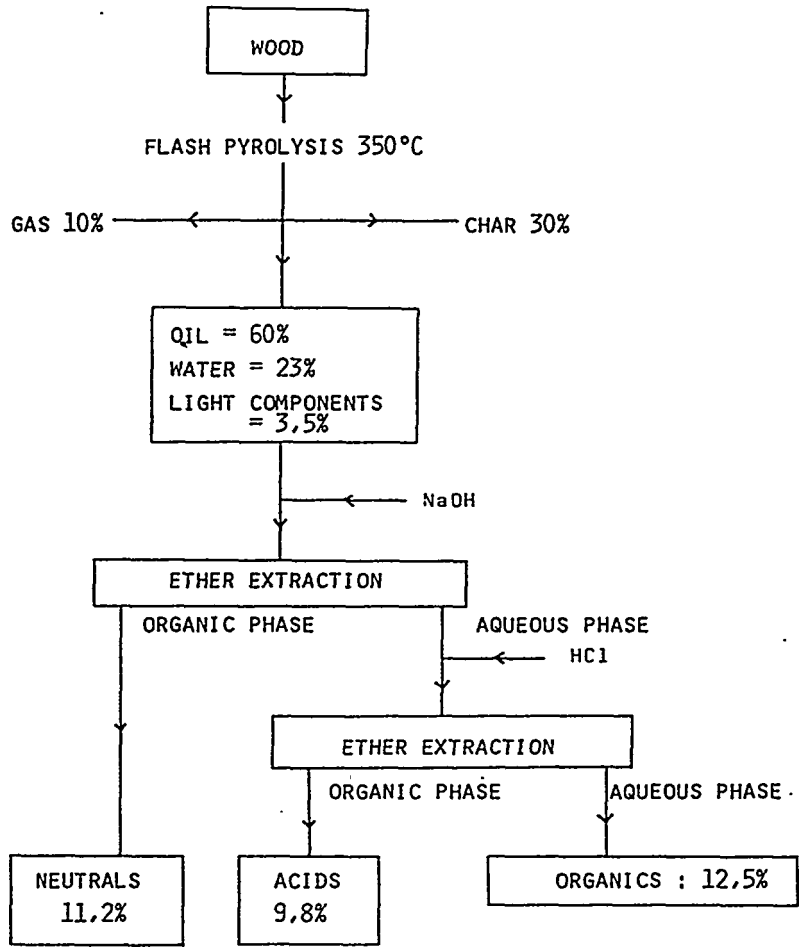

Figure 8. Pretreatment of pyrolysis oil [Beaumont 1985].

Figure 9 [*Vasalos et al.* 1994]. The content of tar, water, as well as total aqueous, phenolic, acidic, neutral and basic compounds were estimated. Each fraction was analysed qualitatively by GC/MS.

A method for the production of phenolics has been developed at NREL by Chum et al. [*Chum* 1989, 1991, *Diebold* 1992, *Pat. U.S.* 1993]. The goal of the fractionation of the pyrolysis oils was to concentrate the phenolic fraction sufficiently so that it could replace a portion of the phenol in phenol-formaldehyde resins. The phenolics has the potential to replace at least 50 % or more of the phenol in phenol-formaldehyde (PF) thermosetting resins. Waste resources, such as sawdust and bark, and kraft lignins are converted into phenolics through fast pyrolysis employing a Vortex reactor and a very fast heat transfer to depolymerize biomass into monomeric and oligomeric components. A liquid extraction system to produce the phenol-rich extractive from the oil has been developed at NREL on a small-batch scale, and then set up and operated on a continuous basis by a local company, Hazen Research, Inc., Golden, Colorado.

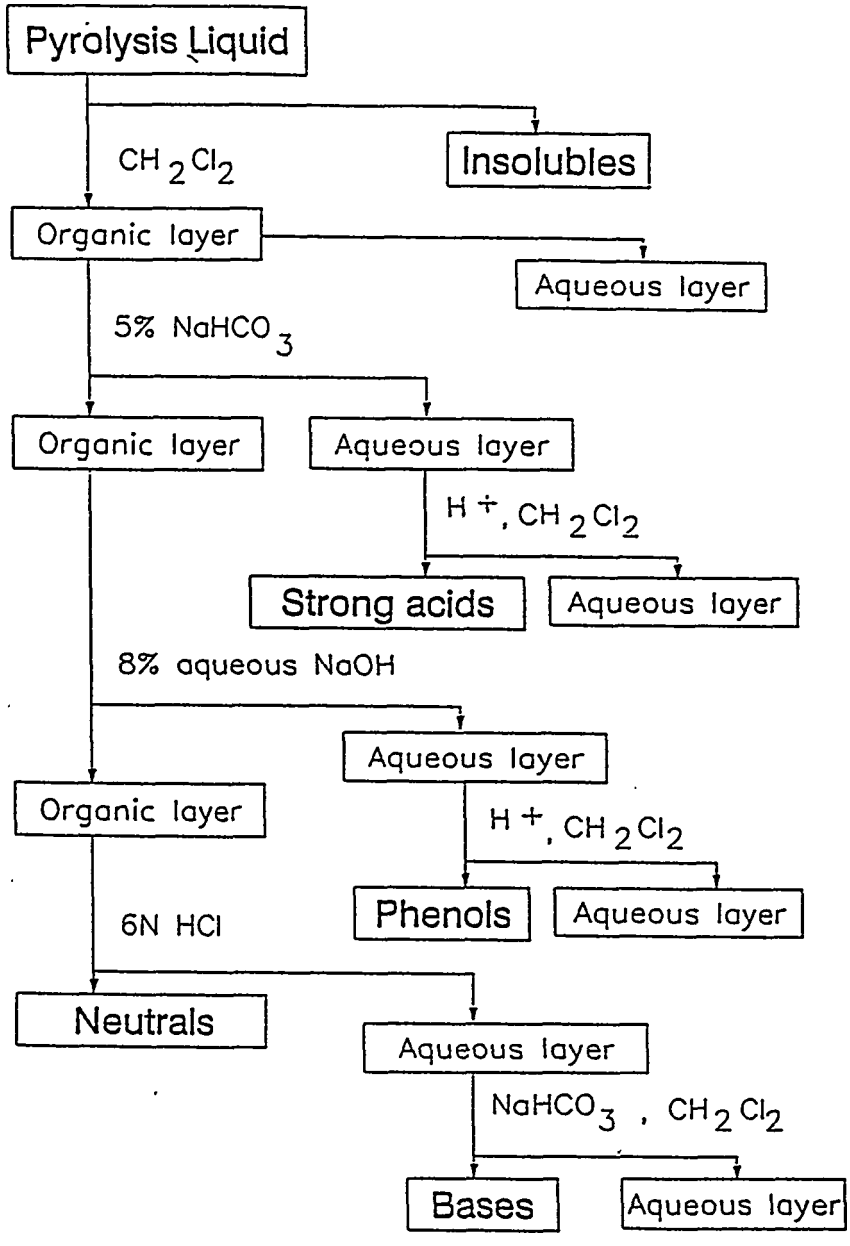

Figure 9. Liquid-liquid extraction of pyrolysis oils [Vasalos et al. 1994].

According to the method the pyrolysis oils were collected in a series of condensers followed by a coalescing filter to remove residual aerosols. The oil was fractionated according to the scheme shown in Figure 10. Whole oil (1 kg) was dissolved in ethyl acetate (EA) (1:1, w/w). The oil was then vacuum-filtered through filter paper to remove fine char. When standing, the oil separated into two phases: an organic rich, EA-soluble phase and an EA-insoluble phase. Most of the water formed in pyrolysis was contained in the EA-insoluble phase. The EA-soluble portion of the oil was washed with water (2 x 75 ml) to remove the remaining water-soluble derived products.

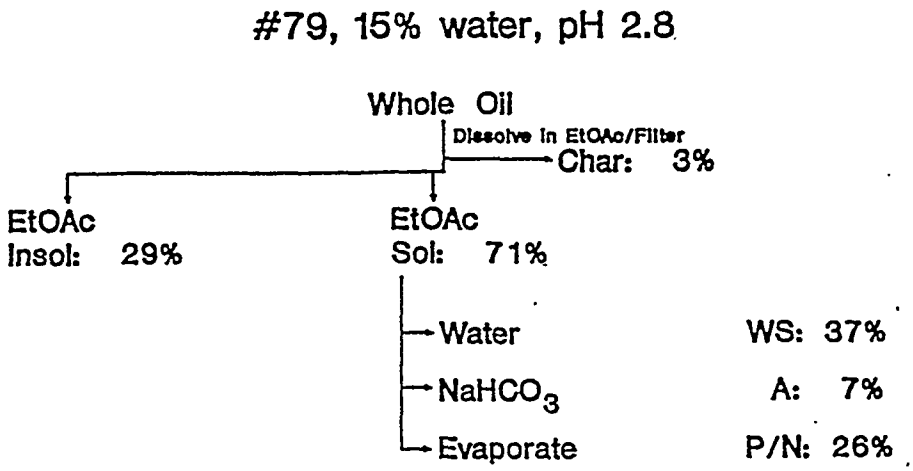

Figure 10. The fractionation scheme of pyrolysis oils to produce a phenolic/ neutral fraction. Yields are on a dry basis [Chum 1989].

The EA-soluble phase was then extracted with $NaHCO_3$ (5 wt%, 10 x 200 ml) and the aqueous layer was saved for isolation of the organic acids fraction. The solvent was removed from the remaining EA-soluble fraction, which contained the phenolic and neutrals (P/N) fractions. The final water content of each fraction was 0.5 to 1.0 wt%. The organic acids fraction was isolated by acidifying the aqueous layer (pH 2) with 50 % H_3PO_4, saturating the solution with NaCl, and extracting the organic layer with fresh EA. The solvent was removed by evaporation. The water-soluble and EA-insoluble fractions were also isolated by evaporation. Recently Chum et al. [*Diebold*, 1992, *Pat. U.S.* 1993] reported on the neutralisation of bio-oils prior to solvent extraction. $NaHCO_3$ was used to neutralise the organic acids present in the oils. The P/N fraction was then extracted with the EA solvent. In liquid-liquid partition of smoke condensates *Toth and Potthast* [1984] found EA to be an excellent solvent for separating phenolic constituents from the aqueous phases. The extraction was carried out at pH 6.5 - 6.7 since phenols are not degraded at these pH values. The isolation and fractionation of phenolic constituents from smoke condensates are illustrated in Figure 11.

The fractionation method of *Chum et al.* [1989, 1991] removes the water-soluble carbohydrates and derived polar compounds, and the EA-soluble strong organic acids from the remaining EA-soluble P/N fraction through water and aqueous bicarbonate extractions, respectively. The P/N product is useful in making PF thermosetting resins. About 30 % of the pine sawdust oil was extracted into useful P/N products. This fraction consisted of 73 % phenolics, extractable by aqueous sodium hydroxide solution from an EA solution, and 27 % neutrals. The various fractions were subjected to a variety of analytical techniques to determine the best extracts for replacement of phenol in PF resins or other high-value applications. The techniques included, e.g., conductimetric titrations, NMR spectrometry, FT-IR spectrometry, high-performance size exclusion chromatography (HPSEC) and molecular-beam mass-spectrometry (MBMS).

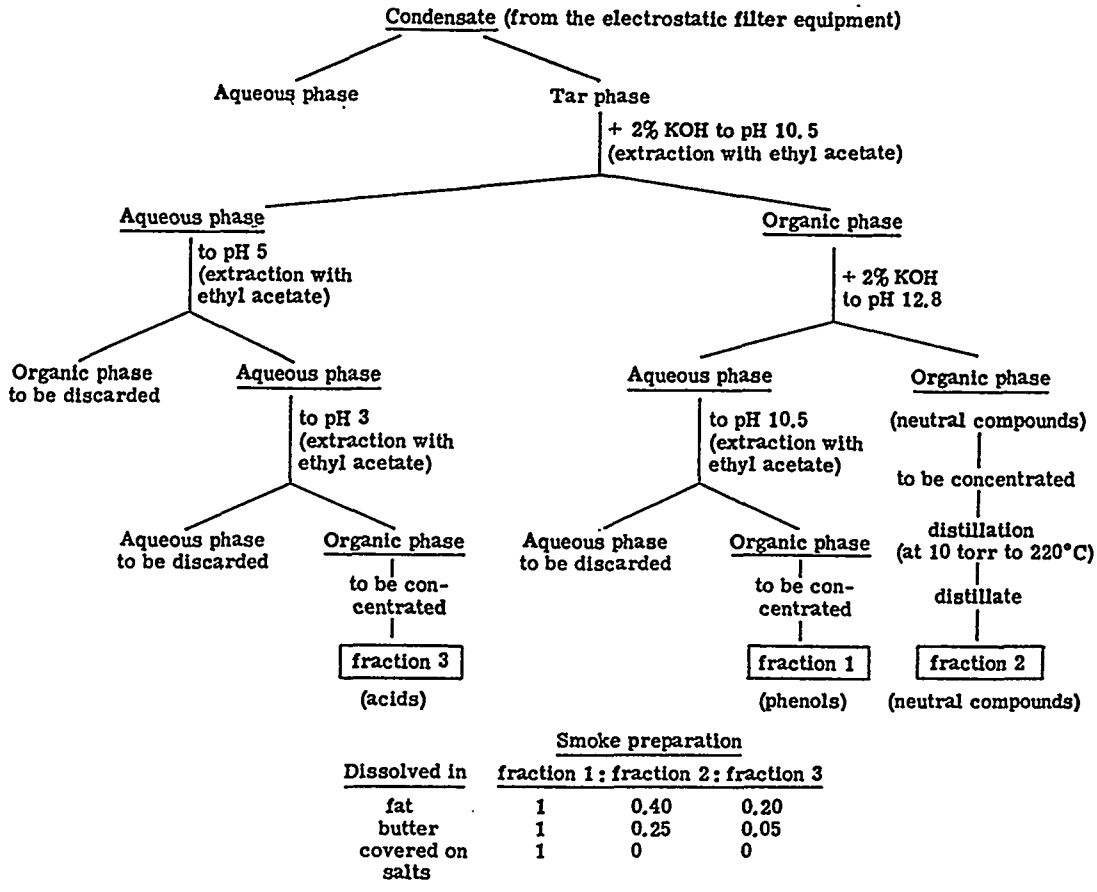

Figure 11. Fractionation scheme for smoke condensates [Toth & Potthast 1984].

When studying oils from steam liquefaction of poplar chips *Boocock et al.* [1988] separated the oils using diethyl ether, chloroform and acetone. According to them ether essentially dissolves monomeric material, while chloroform and acetone dissolve successively higher-molecular-weight materials. Phenols, quaiacols and syringols were found in the ether-soluble fraction along with aliphatic acids (pentanoic acid and higher) and various benzoic acids. The carboxylic acid fraction appeared to be twice as prevalent as the phenolic fraction. The neutral fraction showed spectral characteristic of straight-chain aliphatic protons and may contain extractives such as mono-, di-, and triglycerides.

4.3.3 Water-soluble and water-insoluble fractions

In many studies the water-soluble fraction of bio-oil has been separated. The research group of the University of Waterloo [*Scott et al.* 1988a, *Piskorz & Scott* 1988, *Piskorz et al.* 1988b, *Radlein et al.* 1987] characterised their WFPP oils with the method developed by them. In the oils, water is dissolved in the organic phase. Addition of more water to the level of about 60 % by weight causes a phase separation. Utilising this behaviour and water extraction they divided the oils into

water-soluble and water-insoluble fractions. The method was used for pyrolysis oils from different woods (spruce, maple, poplar) [*Scott et al.* 1988a, *Radlein et al.* 1987], peat [*Piskorz & Scott* 1988] and different celluloses [*Piskorz et al.* 1988b]. Liquid yields from wood were 70 to 80 % of the dry feed in optimal conditions, the organic liquid yields being 60 to 65 % of the feed. The water-soluble fraction was analysed by HPLC. It contained sugars and anhydrosugars, carbonyl and hydroxycarbonyl compounds and acids. The yields of different fractions and the HPLC analysis data are presented in Table 7 [*Scott et al.* 1988].

Table 7. The yields and analysis of different fractions separated from WFPP oils of different origin [Scott et al. 1988a].

	Brookville poplar	White spruce	Red maple	IEA poplar
Run #	58	43	63	A-2
Temperature, °C	504	500	508	504
Yields, wt% of feed, m.f.				
Organic liquid	62.9	66.5	67.9	62.6
1. Oligosaccharides	-	-	-	0.70
2. Cellobiosan	1.11	2.49	1.62	1.30
3. Glucose	0.55	0.99	0.64	0.41
4. Fructose	1.34	2.27	1.51	1.32
5. Glyoxal	1.42	2.47	1.75	2.18
6. Methylglyoxal	2.52	3.96	2.84	0.65
7. Levoglucosan				3.04
8. 1,6-Anhydroglucofuranose	-	-	-	2.43
9. Hydroxyacetaldehyde	6.47	7.67	7.55	10.03
10. Formic acid	5.40	7.15	6.35	3.09
11. Formaldehyde	-	-	-	1.16
12. Acetic acid	6.30	3.86	5.81	5.43
13. Ethylene glycol	0.87	0.89	0.63	1.05
14. Acetol	1.70	1.24	1.15	1.40
15. Acetaldehyde	-	-	-	0.02
Water-solubles - total above	27.7	33	29.9	34.2
Pyrolytic lignin	24.8	20.6	20.9	16.2
Amount not accounted for (losses, water soluble phenols, furans, etc.)	10.5	12.9	17.1	11.91
by G. C.				
Methanol	0.63	1.11	0.77	0.12
Furfural	0.46	0.30	-	-
Methylfurfural	0.18	0.05	0.42	-

The water-insoluble fraction was called "pyrolytic lignin". It separated as a dark brown viscous liquid which solidified during drying into a hard, black, easily powdered material. It was found to represent nearly 80 % of the original content of wood lignin. The water-insoluble fraction was analysed by ^{13}C NMR.

When using peat as feed *Piskorz and Scott* [1988] separated the tar into two fractions: THF-methanol mixed solvent washing and aqueous liquor. The water-soluble fraction was analysed by HPLC. The water-insoluble fraction was further extracted with hexane followed by a further extraction with toluene. A typical balance for the solvent fractionation used is shown in Figure 12. The hexane- and toluene-soluble fractions were analysed by GC/MS. The hexane-soluble fraction showed the presence of a series of long-chain olefinic or carbonyl compounds related to waxes, while the toluene-soluble fraction contained furans, phenols and other lower-molecular-weight aromatics.

Vasalos et al. [1994] determined the amount of pyrolytic lignin as the undissolved amount of bio-oil after the addition of water in 1/3 (bio-oil/water) weight ratio.

Sharma and Bakhshi [1993a, 1993b] have recently studied the upgrading of the Ensyn whole bio-oil (WBO) and, in addition, the pyrolytic lignin (PL) fraction of the WBO and the residual oil (RO) fraction of the WBO. The WBO was in the form of emulsion containing 21 wt% water, and its viscosity at 25 °C was 8×10^{-2} Pa·s. The PL fraction was separated by adding water to the bio-oil in 1 : 1 weight ratio. The mixture separated into two layers. The top layer comprised the water phase and the bottom layer the heavy organic phase (PL). The upper layer contained the water-soluble components, whereas the bottom layer was a viscous, dark brown liquid. The yield of pyrolytic lignin was 39.5 wt% of WBO, and its water content was 1.5 wt%.

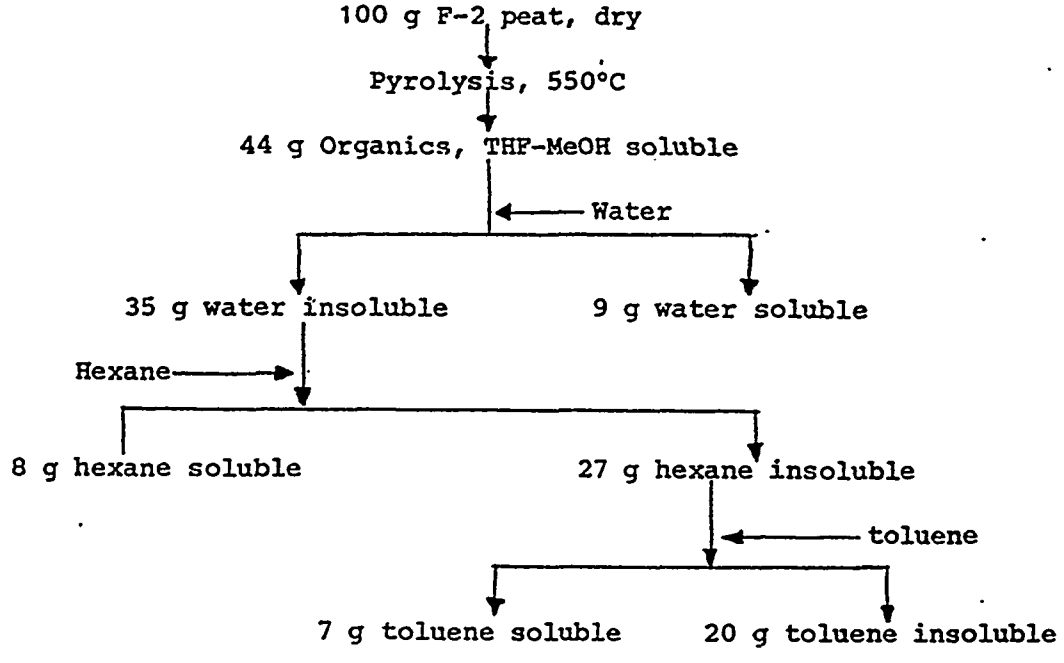

Figure 12. Solvent fractionation of peat-based pyrolysis oil [Piskorz & Scott 1988].

The RO fraction was the fraction that remained after the recovery of phenolic components (P/N fraction) from the bio-oil according to the method described by *Chum* [1989]. WBO was dissolved in EA on a 1:1.5 weight basis. The mixture was separated into two phases - an EA-soluble phase and an EA-insoluble phase. The EA-insoluble phase containing the non-phenolic compounds was carefully separated and was termed as "resid oil" (RO). The yield of this residual oil was 42 wt% of WBO, and it contained most of the water of the bio-oil. The water content of RO was thus 50 wt%.

Samples of WBO, PL and RO were distilled at 200 °C under a vacuum pressure of 172 Pa in order to determine the amounts of distillate and non-volatile residue (pitch). WBO contained 34 wt% of pitch, and about 60 wt% of WBO was low-boiling (below 220 °C at atmospheric pressure). About 55 wt% of the PL fraction consisted of pitch, non-volatile compounds. The amount of pitch in the RO fraction was small (5.5 wt%).

In the Vacuum Pyrolysis Process Development Unit of the University of Laval developed by Pakdel et al. [*Pakdel & Roy* 1988, 1990, *Pakdel et al.* 1988, 1989], the liquid products (oil and water) were fractionated directly at the outlet of the reactor by collecting them in two different condensation units (Figure 13). The oil phase was collected in the Primary Condensing Unit (PCU), which consisted of six heat exchangers installed parallel in the six reactor outlets (H-I to H-VI respectively from top to bottom of the reactor). The aqueous phase was collected in a series of cooling traps called Secondary Condensing Unit (SCU). The fractions were further fractionated by solvent extraction [*Pakdel et al.* 1988] or by liquid solid chromatography [*Pakdel & Roy* 1988, *Pakdel et al.* 1988, 1989]. In the separation of polycyclic aromatic and aliphatic hydrocarbons from pyrolysis oils a combination of liquid-liquid and liquid-solid chromatography was used [*Pakdel et al.* 1988, *Pakdel & Roy* 1990]. Six oil samples from the PCU and three aqueous samples from the SCU were fractionated according to Figure 14. Preliminary characterisation of the hydrocarbons was performed by GC/MS. FT-NMR and FT-IR spectroscopic analyses of the aromatic fractions showed a complex mixture of highly branched aromatic hydrocarbons.

4.4 ADSORPTION CHROMATOGRAPHY

Methods based on adsorption chromatography, developed from the techniques used for fossil oils, have been widely used in the fractionation of pyrolysis oils. Separation of different hydrocarbons from fossil oils is of standardised technique. Liquid chromatographic (LC) separation of coal-based tars and pitches has also been studied for a long time. In the 1980s, these techniques have been modified and developed for biomass-based oils.

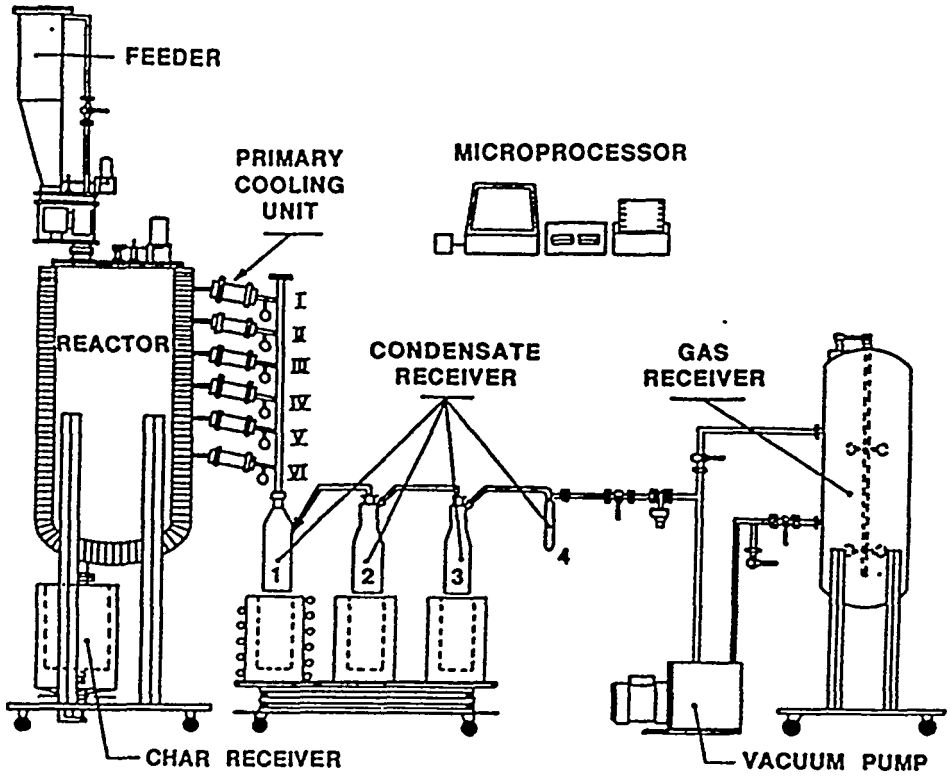

Figure 13. Process Development Unit of vacuum pyrolysis [Pakdel & Roy 1988].

For coal-based oils, many separation methods based on alumina, silica gel or on their combinations have been used. The oil samples have been divided into different hydrocarbons (saturated and unsaturated hydrocarbons, monoaromatics, diaromatics and polyaromatics) and into groups with rising polarity (neutral heteroaromatics, monophenolics, basic N-compounds and very polar substances). For bio-oils, the technique has often been based on a method developed for coal liquids [*Whitehurst et al.* 1980]. This method uses silica gel as the separating phase. The adsorption properties of silica gel are good for polar and acidic substances.

In adsorption chromatography technique the sample is divided into several characteristic fractions in a chromatography column. The methods can be grouped into three types: sequential elution with solvents chromatography (SESC), gradient elution chromatography (GEC) and extrographic technique (EX). In SESC technique the eluent and its composition are changed stronger during the run with discrete changes, in GEC technique the gradient and composition of the solvent is changed continually, steplessly and smoothly, and in EX technique the sample is eluated with one solvent at a time.

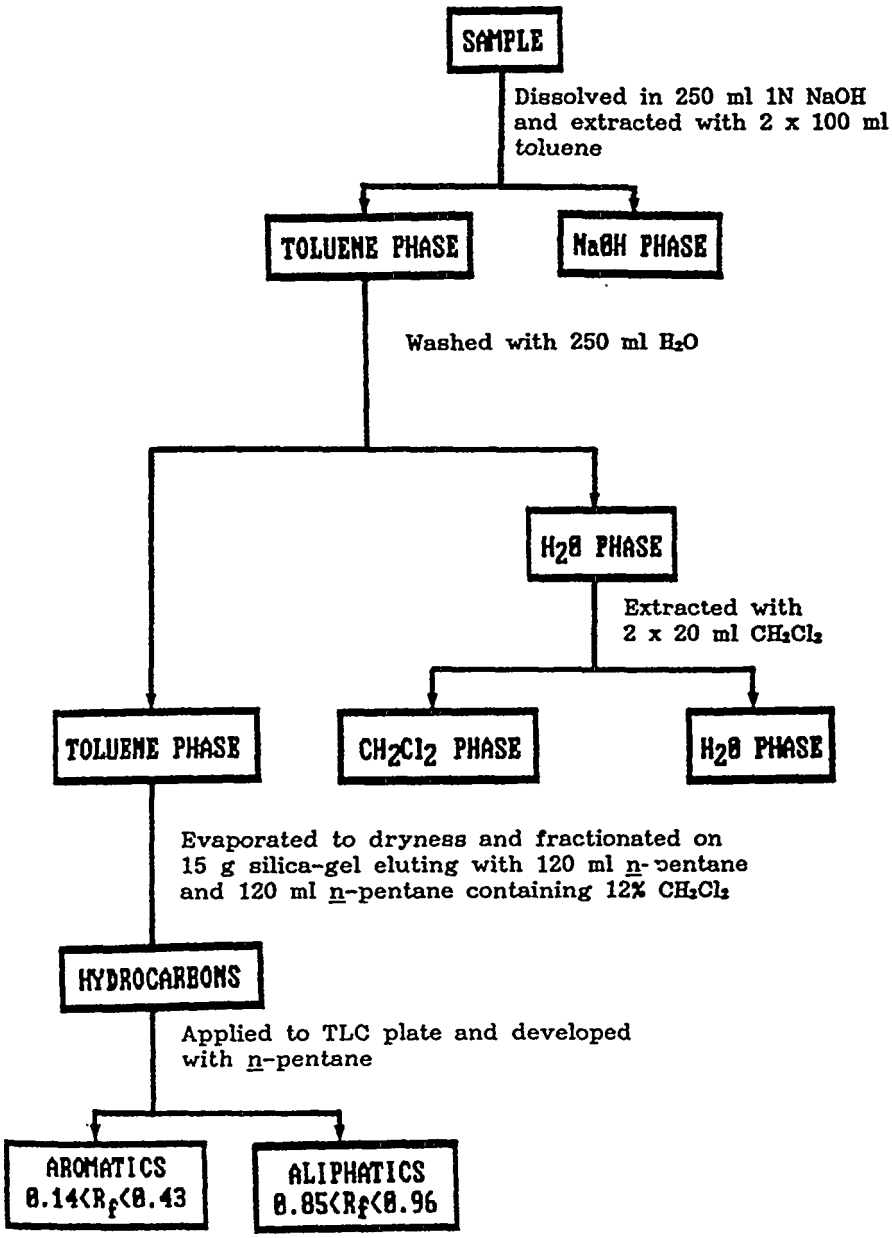

Figure 14. Fractionation scheme for separation of polycyclic aromatic and aliphatic hydrocarbons from wood pyrolysis and gasification products [Pakdel et al. 1988].

Adsorption chromatography technique has been mainly used in fractionation of bio-oils by the research groups of University of Louvain [*Churin et al.* 1988, 1989], CPERI [*Achladas* 1991], University of Laval [*Pakdel & Roy* 1987, 1990, *Pakdel et al.* 1988, 1989, 1994a, 1994b], University of Paris [*Desbene et al.* 1991a, 1991b] and NREL [*Johnson & Chum* 1988], and by the Centralised Analysis Project [*McKinley* 1989]. The SESC method has been the most commonly applied technique, and silica gel the most frequently used adsorbent.

Davis et al. [*Davis* 1985, *Chornet & Overend* 1985, *Schaleger & Davis* 1982] have described the solvent sequence used to fractionate the proto-oil from direct liquefaction of Douglas fir. The SESC sequential elution technique was found to be particularly helpful in separating product oils into chemically distinguishable fractions. Silica gel was used as the adsorbent, the ratio of sample to adsorbent being 1:40. The sample was preadsorbed onto silica gel by rotary evaporation of wood oil solution in CH_2Cl_2; the resulting semisolid was then quantitatively transferred to the top of a column packed with the aid of hexane. After elution of each fraction, the solvent was removed by rotary evaporation at water pump pressure and 50 - 60 °C, and the weight of the residue was determined. Typical recoveries were in the range of 100 - 115 %, probably owing to the impossibility of completely removing solvent. The SESC solvents are presented in Table 8. Fractions 1 - 5 were liquid while 6, 8 and 9 were solid. Fraction 7 was usually solid. The fractions were analysed by GC/MS, IR and GPC techniques. Polar aromatics and phenolic derivatives were found to constitute the majority of the oil.

Table 8. Sequential elution solvent chromatography applied to proto-oil from biomass liquefaction [Davis 1985].

Sequential solvents	Predominant molecular species	Average weight fractions of proto-oil	Average O, %	Mn [a)]	Mw [b)]
1. Hexane	Saturated hydrocarbons	0 - 6	-	143	158
2. 15 % benzene-hexane	Aromatic hydrocarbons	1 - 10	11	172	210
3. Chloroform	Polar aromatics	5 - 30	16	173	211
4. 4 % ether-chloroform	Monophenols	35 - 55	21	210	286
5. 3 % ethanol-ether	Highly functionalised	10 - 25	23	350	604
6. Methanol	phenols	1 - 3	46	181	195
7. 3 % ethanol-chloroform	Polyphenols	5 - 20	n.a.	687	892
8. 3 % ethanol-tetrahydrofuran	Unidentified	0 - 10	n.a.	n.a.	n.a.
9. Acetic acid (or pyridine)	Unidentified	-	-	-	-
10. Non-eluted	Unidentified				

[a] *Number - average molecular weight*
[b] *Weight - average molecular weight*

In the Centralised Analysis Project [*McKinley* 1989] and in the studies of *Johnson and Chum* [1988] SESC technique was performed on several biomass oils. The elution schemes were based on the work of Schlager and Davis [*Chornet & Overend* 1985, *Schaleger & Davis* 1982], though somewhat modified. *McKinley* [1989] separated the following fractions: 1 - hexane, 2 - hexane:benzene (85:15), 3 - chloroform, 4 - chloroform:ether (9:1), 5 - ether:ethanol (97:3), 6 - methanol and 7 - acetic acid. The total weight of recovered oil was often more than 100 %, because

silica gel is slightly soluble in methanol and acetic acid. The adsorbent used was Merck Silica Gel 60, 70 - 230 mesh. The pyrolysis oils were found to be fairly polar and oxygenated products as most of the materials eluted in fractions 5 and 6. According to McKinley the technique is more valuable as a means of separating the product into different groups of chemicals for further investigation, although the distribution pattern of the SESC scheme correlates with the polarity of the biomass oil. The fractions obtained were analysed with different analytical methods.

Churin et al. [1988, 1989] used preparative liquid chromatography when characterising an oil produced by pyrolysis from wastes of the olive oil industry in a demonstration unit located in Raiano, Italy. Analysis was made on silica gel (Kieselgel 60 from Merck) in an open column at atmospheric pressure. The oil was fractionated with different solvents into five fractions, which differed mainly in their chemical functions. Fraction 1 was found to be constituted of paraffinic, olefinic and aromatic hydrocarbons by thin-layer chromatography (TLC) and GC/MS. Fraction 2 comprised only monophenols. This method, although it provided very good results, was abandoned in the later studies of *Maggi et al.* [1992, 1994b], because it was long and expensive. Other fractions were not analysed.

Fagernäs and Lappi [1990] modified the SESC fractionation method developed for coal liquids [*Whitehurst et al.* 1980] to be applicable for peat-based oils (tar and its waxy and bituminous fractions) from the WFPP process. The sample was divided into seven characteristic fractions according to Table 9. The suitable solvent scheme was confirmed with TLC chromatographic tests.

Karlsson and Björnbom [1985] used GEC for fractionating peat and biomass liquids. GEC was performed on a preparative scale with alumina as stationary phase. The solvents were hexane, dichloromethane, THF and methanol. Four fractions were detected by a variable UV/Vis detector and collected by a fraction collector. The fractions were analysed by UV and IR spectroscopy, GC, GC/MS, elementary analysis and a micro distillation apparatus. The first fraction consisted mainly of hydrocarbons, the second one was highly aromatic and the third and fourth fractions were phenolic or resinous in their characters. The yield of the first fraction varied between 5 and 20 wt% of the liquefaction product, the second fraction ranged 5 - 35 wt%, the third 10 - 45 wt%, and the fourth fraction 2 - 20 wt%. The yield of the non-eluted fraction was in the range of 5 - 65 wt%, depending on the reaction conditions and the raw material. Four fractions were assumed to give adequate information in the characterisation of the liquids.

Achladas [1991] separated biomass (fir wood) pyrolysis liquids by silica gel open-column chromatography. A modified method was applied for separating the phenolic fraction from the liquids. A phenol-rich fraction was isolated and subjected to alkaline extraction. The scheme for separation of liquids is shown in Figure 15. A slurry column packed with 20 g of silica gel (70 - 140 mesh) in *n*-hexane-toluene (96:4) was prepared. The silica-to-oils ratio was 20:0.1. A procedure of

Table 9. Fractionation scheme of peat-derived oils [Fagernäs & Lappi 1990].

Eluent	Compound group
1. n-hexane	- Aliphatic hydrocarbons
2. 8 % CH_2Cl_2/hexane	- Aromatic hydrocarbons
3. $CHCl_3$	- Aliphatic esters - Low-polar, O-substituted aromatics - Non-basic heterocyclics
4. 10 % diethyl ether/$CHCl_3$	- Monophenols - Furfural derivatives - Aromatic aldehydes and ketones
5. 3 % ethanol/diethyl ether	- Alcohols - Aliphatic carboxylic acids - Aromatic poly-OH-compounds (phenols) - Basic N-heterocyclics
6. Methanol	- O-substituted and aromatic carboxylic acids - High-molecular-mass compounds with a lot of N- and O-heteroatoms - Condensed phenols
7. 3 % ethanol/THF and 20 % methanol/CH_3COOH	- High-molecular-mass uncharacterised substance

successive elutions with solvents of increasing polarity was applied. The first fraction was extracted with 10 ml of 8 % sodium hydroxide solution. After phase separation and solvent removal a yellow residue remained and was defined as "hydrocarbons". The other three fractions were combined and extracted three times with 10 ml of 8 % sodium hydroxide solution. This procedure was followed by acidification with concentrated hydrochloric acid. Extraction with diethyl ether gave a brown liquid "phenolic fraction". The recovery of phenols was over 95 %. Analysis and characterisation of the phenolic fraction were performed by TLC, GC, IR, ^1H and ^{13}C NMR spectroscopy and GC/MS. 12 - 17 wt% of the pyrolysis liquid products consisted of phenol and other substituted phenols.

Desbene et al. [1991a, 1991b] combined two liquid-phase chromatographic separation techniques; the improved API 60 method and the steric exclusion method combined with coupled GC/MS for the oils obtained from slow and fast pyrolysis of different woods. The oils were submitted first to a functional sorting according to a technique derived from the API 60 procedure. This method uses the differences in interactions in an organic medium between a solute and ion-exchange resins (styrene-divinylbenzene copolymers, bonded to sulphonates and ammonium moieties in cation and anion exchangers, respectively). The sample is deposited on the resin surface by means of a solvent. Bonds of different strenghts are formed

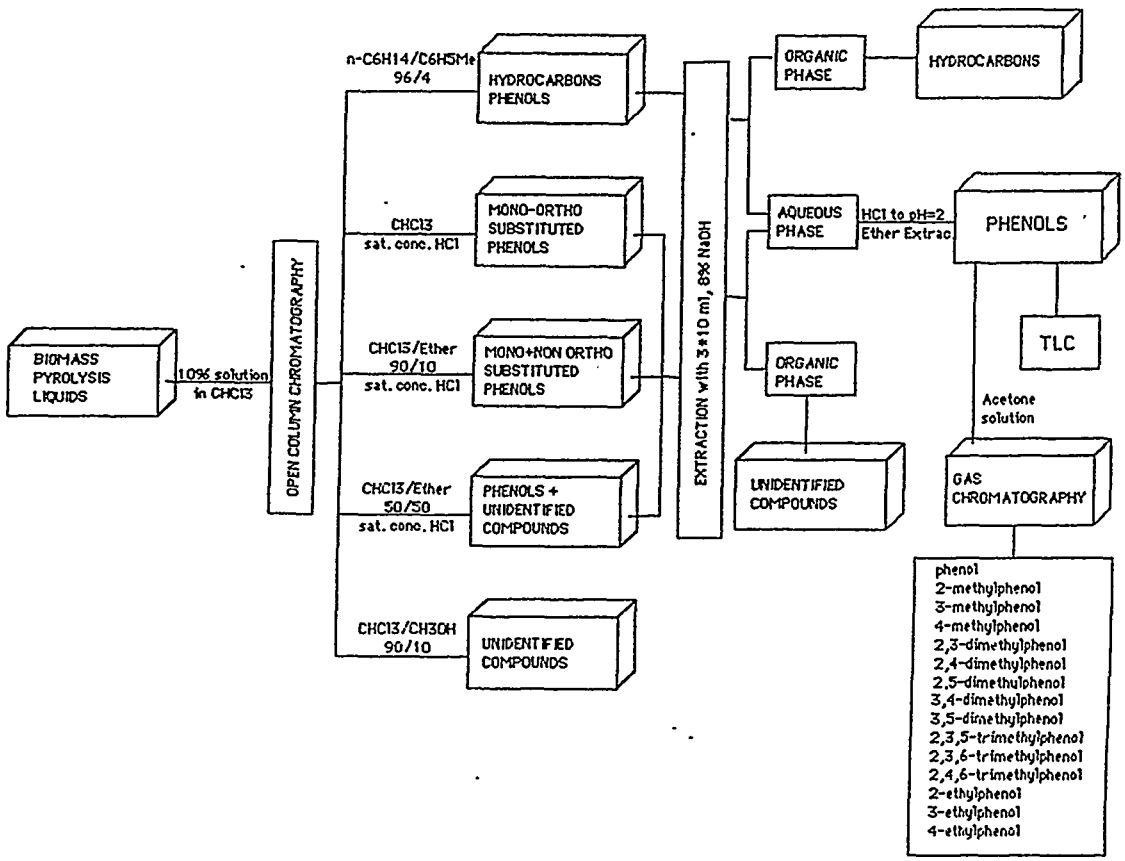

Figure 15. Scheme for separation of phenols from biomass pyrolysis liquids [Achladas 1991].

and are then progressively destroyed by thorough elution using mobile phases of increasing polarity. Hence the components are eluted according to their increasing acid-base characteristics. Originally this technique was long and tedious. *Desbène et al.* [1991b] improved it by their own device. A complete acid-base separation can now be performed in seven hours compared with more than eight days using the original method, obtaining nine fractions with different acid-base characteristics. The elution sequence used to analyse pyrolysis oils and the acid-base characteristics of the fractions collected are reported in Table 10. The acid-base balances obtained after analysis of various species are presented in Table 11. After this first separation, another preparative chromatographic separation was used for the acid-base fractions collected. This second step was based on size-exclusion chromatography (SEC). The fractions were sorted as a function of molecular size. Each of the acid-base fractions was resolved into three subfractions with different molecular weights. After this second preparative separation, 27 fractions were obtained for each of the pyrolysis oils analysed. The combination of ion-exchange chromatography and SEC with GC/MS appeared to be suitable for the analysis of pyrolysis oils.

Table 10. The elution sequence and acid-base characteristics of the fractions collected from pyrolysis oils [Desbene et al. 1991b].

Ion exchanger	Eluent	Acid-base characteristic of the fraction collected
A25 + IRA 904 (coupled)	Benzene-cyclohexane (75:25)	Neutral
IRA 904	Benzene	Weak acids
	Benzene-acetonitrile	Medium acids
	Acetonitrile	Strong acids
	Methanol	Very strong acids
A15	Benzene	Weak bases
	Benzene-THF	Medium bases
	THF	Strong bases
	Methanol	Very strong bases

Table 11. The acid-base balances obtained for pyrolysis oils [Desbene et al. 1991b].

Wood species	Acid-base characteristic of fractions collected			
	Neutral, %	Acidic, %	Basic, %	Total yield, % [a]
Hornbeam [b]	37	33.5	28	98.5
Pine [b]	65	16.5	13.5	95
Poplar [b]	35	29	27	91
Hornbeam [c]	54	22	18.5	94.5

[a] *Calculated with respect to the dry tar mass injected before dissolution.*
[b] *Slow pyrolysis*
[c] *Fast pyrolysis*

When analysing the pyrolysis oils from the vacuum pyrolysis unit of the University of Laval, *Pakdel and Roy* [1988] and *Pakdel et al.* [1989] used, in addition to solvent extraction, an adsorption chromatography method for the fractions from PCU and SCU condensing units (units described in Chapter 4.3.3) of the reactor. The pyrolysis oils obtained in the condensing units were subjected to SESC technique. 1 g of the oil sample was fractionated on 12.5 g silica gel (60 - 120 mesh) into fourteen fractions with different solvents of increasing polarity: petroleum ether, dichloromethane/petroleum ether mixtures, ether, water and formic acid in methanol (Table 12). The fractions were studied separately. Fractions 1 to 12 of all condensers were liquids with some differences in their colours and odours. Fractions 13 and 14 were found to be very viscous and nearly solid. Fractions 1 and 2 were found to contain mainly hydrocarbons followed by elution of moderately polar compounds in fractions 3 to 11. Fraction 12 contained a mixture of relatively polar compounds compared to fractions 3 - 11. Fraction 13 contained mainly high polar compounds including sugars and acids. Fraction 14 was found to contain mainly polymeric and highly polar compounds.

Table 12. Yields of various classes of compounds obtained by adsorption chromatography from pyrolytic oils (HI to HVI) from the primary condensing unit of the reactor, wt%, as received oil basis [Pakdel & Roy 1988].

Pyrolysis oil samples from	Fraction 1	Fraction 2	Fraction 3-11	Fraction 12	Fraction 13	Fraction 14	Total
H-I	0.11	0.04	26.83	31.06	27.16	1.67	86.87
H-II	0.64	0.23	26.37	32.52	26.28	1.65	87.69
H-III	0.85	0.21	22.99	36.80	26.93	2.34	90.12
H-IV	0.33	0.16	22.32	35.60	30.70	2.24	91.35
H-V	0.45	0.10	24.24	35.35	29.48	2.79	92.41
H-VI	1.44	0.12	33.18	29.09	28.26	3.28	95.37

Fraction I: *128 ml with petroleum ether.*
Fraction 2-11: *128 ml each with CH_2Cl_2/petroleum ether mixture, from 10 to 100 % CH_2Cl_2 (10 % increments) for F2 to F11, respectively.*
Fraction 12: *128 ml with ether.*
Fraction 13: *128 ml with water.*
Fraction 14: *60 ml with 10 % formic acid in methanol.*

In addition to a method development on a small column with 1 g capacity, a large column with 100 g capacity and 80 ml/min flow rate was designed [*Pakdel et al.* 1989]. The oil (~20 % H_2O content) was fractionated on 1 500 g silica gel into six major classes eluting subsequently with 10 % CH_2Cl_2 in petroleum ether, 40 % and 70 % CH_2Cl_2 in petroleum ether, 100 % CH_2Cl_2, ethyl acetate and 10 % formic acid in methanol. All the fractions were then vacuum-distilled to recover the solvents. Satisfactory mass balance (≥95 %) and separation reproducibility were obtained. Groups 2 - 4, identified as the most valuable mixtures, contributed to about 40 % of the dry oil basis. The large column fractionation was designed as a cleanup step for preparative separation of pure compounds on an HPLC system which will be installed on line with LC and pyrolysis system.

According to *Pakdel et al.* [1989] HPLC technology has recently reached a revolutionary stage, particularly in the pharmaceutical industry for large-scale preparative separations. Therefore, liquid solid chromatography was found to be a method of choice for preliminary fractionation and characterisation of vacuum pyrolysis oils at the first stage, to be followed by preparative large-scale separation of rare chemicals, as an example, which are in increasing demand.

Pakdel et al. [1988] and *Pakdel and Roy* [1990] have developed a separation method to analyse the aromatic and aliphatic hydrocarbon content of both wood vacuum pyrolysis oil and aqueous phases. The separation scheme is shown in Figure 14. A 10 g portion of the sample was dissolved in a diluted alkali solution. Toluene (100 ml) was added to the mixture and stirred for 20 min. The toluene phase was then separated from the aqueous phase, which was further extracted with another 100 ml of toluene. The toluene phases were mixed and evaporated to dryness under vacuum in a rotary evaporator. Acidic compounds, e.g., carboxylic

acids and phenols, were separated. The remaining hydrophilics were next removed by further extraction with distilled water. The polar compounds were removed by adsorbing on 15 g of silica gel packed in a glass column in *n*-pentane. The eluate was evaporated to dryness. A 40 mg portion of the extract was applied on a 20 x 20 cm prewashed and oven dried (at 120 °C for 1 h) TLC plate coated with 2 - 2.5 µm silica gel. The plate was developed with *n*-pentane. The polycyclic aromatic and aliphatic hydrocarbons were recovered and analysed by GC, GC/MS, FT-IR and FT-NMR. The aliphatic hydrocarbon content ranged between 0.08 and 0.44 % in the pyrolysis oils and 0.01 and 0.02 % in the pyrolytic aqueous phase. Aromatic hydrocarbons contributed between 0.06 and 0.24 % of the pyrolysis organic phase and only a trace quantity in the aqueous phase.

Williams and Besler [1994] and *Williams and Taylor* [1994] studied polycyclic aromatic hydrocarbons in waste-derived pyrolytic oils. The waste material derived from wood waste, municipal solid waste, rice husks and tyre waste. The pyrolysis oils were fractionated into chemical classes using mini-column liquid chromatography. The column packed with silica was sequently eluted under vacuum with pentane, benzene, ethyl acetate and methanol to produce aliphatic, aromatic, ester and polar fractions, respectively. *Williams and Horne* [1994] recently fractionated and characterised wood waste-based pyrolysis oils before and after catalysis with zeolite ZMS-5 catalyst in the temperature range of 400 - 550 °C.

The pyrolysis oil obtained from lignin derived from steam explosion of wood was fractionated by *Pakdel et al.* [1992] into eight fractions, slightly modifying the methodology presented earlier. The characteristics and relative proportion of the solvents used and the yields of the collected fractions are presented in Table 13. The fractions were analysed by GC/MS. Fractions 1 and 2 were mainly hydrocarbons and accounted for 3.4 % of the anhydrous oil. Fractions 3 to 7 were mainly mono- and diphenols and represented 41.6 % of the anhydrous oil. Fraction 8 had a very low GC/MS response due to its low volatility and/or high polarity.

Table 13. Yields of various fractions obtained by liquid chromatographic separation of lignin pyrolysis oil [Pakdel et al. 1992].

Fraction #	Eluent	Yield*, wt%
1	100 % petroleum ether	2.8
2	20 % dichloromethane in petroleum ether	0.6
3	40 % dichloromethane in petroleum ether	5.5
4	60 % dichloromethane in petroleum ether	3.4
5	80 % dichlormethane in petroleum ether	7.5
6	100 % dichloromethane	4.8
7	100 % diethyl ether	20.4
8	10 % methanol in ethyl acetate	55.0

** Based on anhydrous pyrolysis oil.*

Petroleum ether, dichloromethane, diethyl ether, water and 10 % formic acid in methanol separated hydrocarbons, phenols, polyphenols/aldehydes/ketones, sugars /high polar compounds and acid/high polar compounds (the most polar fraction), respectively. This method of separation was suggested by *Pakdel and Roy* [1992] to be considered as a standard method to evaluate different pyrolysis oils in terms of various classes of compounds and yields.

Pakdel et al. [1994b] recently analysed the polar fractions after fractionating the pyrolysis oil into 14 fractions. New compounds in the polar fractions were analysed using GC, MS, FT-IR and FT-NMR with particular attention to the characterisation of high-molecular-weight fatty acids, resin acids and steroid-type compounds. Oils pyrolysed from various waste wood species, including primary sludges from spruce wood debarking stage, spruce bark, aspen poplar wood and a mixture of spruce wood and aspen bark, were recovered and derivatised by diazomethane to methyl esters [*Pakdel et al.* 1992]. The oils were then fractionated on a silica gel column into three fractions (petroleum ether, dichloromethane and methanol). High-molecular-weight carboxylic acid methyl esters and resin acid methyl esters were recovered in the second fraction.

4.5 GEL PERMEATION CHROMATOGRAPHY

Liquid chromatography (LC) using gel permeation chromatography (GPC) can also be treated as a fractionation technique for bio-oils prior to analysis of the fractions. Otherwise GPC has been widely used in the analysis of the bio-oils. It separates the oils according to their molecular size. GPC has earlier been found to be usable in separating coal liquids, petroleum crude and its refining products into fractions based on "linear molecular size".

Sheu et al. [1984] and *Arpiainen and Lappi* [1989] have fractionated pyrolysis oils by GPC. Sheu et al. separated pyrolytic tar, obtained from pine barks and wastes by the Tech-Air pyrolysis process, and its hydrogenation products into fractions, which were composed of the following types of chemical compound: heavy nonvolatiles, light nonvolatiles and alkanes, phenols and aromatics (Figure 16, Table 14). GPC separations were performed on a Model ALC/GPC liquid chromatograph (Waters Associates) equipped with a spectrometer (Model R 401). Four 10-nm μ Styragel columns in series and THF as a solvent resulted in reasonably clean separations. The fractions were analysed by GC/MS.

Arpiainen and Lappi [1989] separated flash-pyrolysis oils obtained from peat and bark. In the GPC analysis, a Waters M-45 2-reciprocating pump, an Erma ERC-7510 differential refractometer and two Shimadzu Gel columns HSG-15 50 cm x 7.9 mm i.d. in series were used. The fractions were collected using a LKB Wallac-Superrac 2211 device. THF (1 ml/min) was used as the eluent. The molecular weight axis was calibrated with a mixture of pure reference compounds selected on the basis of a GC analysis of a typical sample. The calibration curve was close

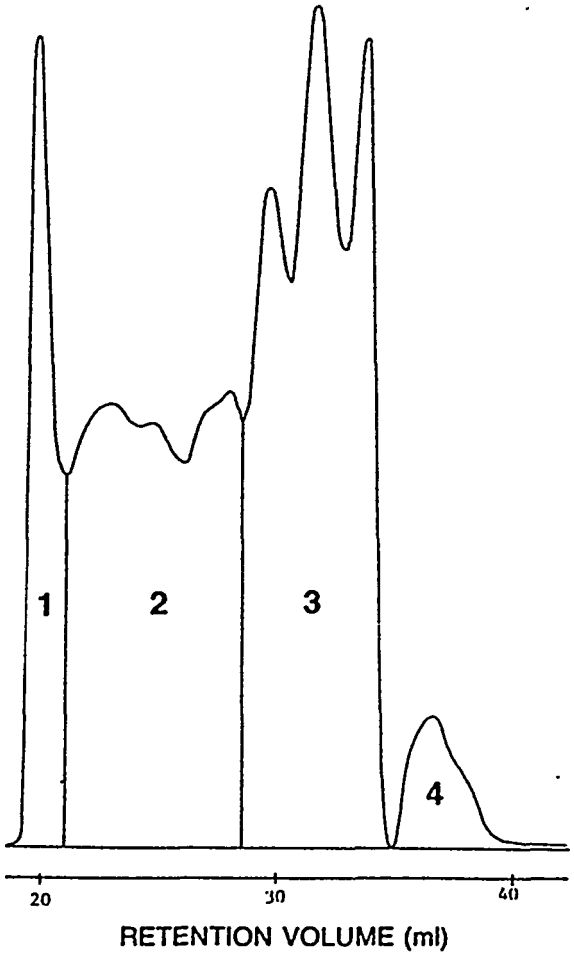

Figure 16. GPC analysis of pyrolytic tar. Fractions: 1 - heavy nonvolatiles + colloidal carbons, 2 - esters + light nonvolatiles, 3 - phenolics, 4 - aromatics [Sheu et al. 1984].

Table 14. Average weight percent and volatiles of pyrolytic tar [Sheu et al. 1984].

Fraction number	Average weight percent (GPC)	Percent volatiles in fraction (GC)	Percent nonvolatiles in fraction	Percent volatiles in sample
1	11.10	0.0	100.0	0.0
2	38.12	2.67	97.33	1.04
3	42.82	28.76	71.24	12.32
4	7.86	18.60	81.40	1.46
	99.90			14.82

to that obtained with commercial polystyrene standards. For the GPC analysis the tar samples were first concentrated by evaporation and then redissolved in THF. The GPC eluate of the peat tar formed at 600 °C was divided into the cuts shown in Figure 17. The cuts were then analysed by IR and GC methods.

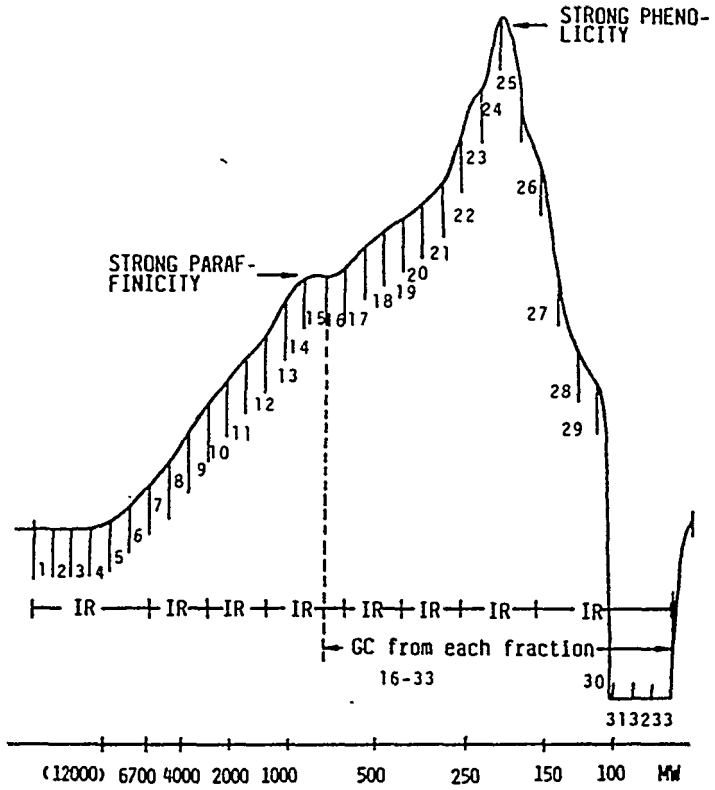

Figure 17. GPC molecular-weight distribution curve of peat tar and the cuts taken for analysis [Arpiainen & Lappi 1989].

4.6 SUMMARY OF FRACTIONATION OF OILS

The main fractionation methods for biomass-based pyrolysis oils have been solvent extraction and adsorption chromatography. Distillation of the oils has not been found to be particularly successful, and GPC has only in some cases been used for fractionation of bio-oils. Thermal instability of the oil limits the amount of volatiles recovered by distillation.

Solvent extraction fractionates the oils generally into aqueous, acidic, basic, non-polar hydrocarbon and phenolic fractions. The dominant fractions have been the acidic and separatively phenolic fractions. The basic and hydrocarbon fractions have been quite small. The emphasis and interest have focused to a great extent on the phenolic part of the oils. On the other hand, the pyrolysis oils have to be further processed to obtain hydrocarbon fuels. The aqueous fractions have contained acids, esters, ethers and alcohols, and the acidic fractions phenols and methoxy derivatives. The dominant acids have been formic and acetic acids. The phenols have contained phenol, quaiacol and syringol derivatives. In addition to the fractionation of the oils with organic solvents, it has also been general to separate the

oils into water-soluble and water-insoluble fractions. The insoluble fraction is called pyrolytic lignin and it can be fractionated further with organic solvents prior to analysis.

In adsorption chromatography, the oils have been fractionated into different hydrocarbon and polar fractions. SESC technique with silica gel as the separating phase have been the system mainly applied. The solvents most widely used have been hexane, chloroform, diethyl ether, ethyl acetate, methanol and THF. The technique has been very popular among the researchers.

Lumping of series of constituents with similar functional groups has been useful [*Sheu et al.* 1984]. In practice, however, extraction techniques have proved to be of limited utility [*Davis* 1985]. They are time-consuming and irreproducible owing to the opacity of the two phases, difficulties with emulsions and incompleteness of extractability of high-molecular-weight phenolics into aqueous caustic. The yield of extraction highly depends on the solvent volume and the extraction repetition number. According to *Elliott* [1994b] the real value of the procedure is in fractionating the oil to facilitate analysis of the separate portions.

5 CHARACTERISATION OF FRACTIONS

5.1 ANALYTICAL METHODS

5.1.1 General

Fractions obtained from the fractionation of bio-oils have been analysed with various chromatographic and spectroscopic methods. Fractionation and subsequent characterisation of the fractions give generally significantly more information than the same analysis of the whole oils.

The first methods of analysing pyrolysis oils were gas chromatography and thermogravimetric analysis [*Soltes* 1988]. However, high-performance equipment is required due to the complexity of pyrolysis oils, and new most sophisticated analysis techniques, like proton and carbon nuclear magnetic resonance spectroscopies (^{1}H and ^{13}C NMR), free-jet molecular beam mass spectrometry (MBMS) and diffuse reflectance Fourier transform infrared spectrometry (FT-IR) as well as procedures such as computerised multivariate analysis methods have been applied for the oils. Almost all available alternative analytical techniques have been evaluated.

5.1.2 Gas chromatography

Gas chromatography (GC) with open tubular columns (capillary columns) has a higher resolution than packed or column chromatography. The glass or flexible fused silica capillary columns have been widely used, for example, in the analysis of air and smoke, physiological fluids, lipids, food and beverages, pesticides, saccharides, perfume oils and diesel oil, because of the complexity of volatiles derived from them [*Jennings* 1978]. As a detector, the flame ionisation detector (FID) is used in most applications [*Hamilton & Rossel* 1987]. FID response is dependent on the carbon mass flow to the detector. When set at the optimum for a given analytical system, the FID exhibits excellent sensitivity and a wide range of linear response.

GC is still used extensively, especially in capillary mode, for pyrolysis oils [*Soltes* 1988]. Much of the pyrolysis oil is non-volatile, which causes additional problems for capillary columns. The non-volatiles can cause column deterioration of the stationary phase. Column deterioration can be minimised by periodic cleaning or rejuvenation of the column, or by occasionally removing the first centimetres of the column at the injection end containing the non-volatiles. In the prior separations of the oils into volatile or functional fractions, more suitable fractions for capillary GC work can be obtained.

For the determination of unknown compounds in pyrolysis oils, the most suitable detector has been a mass selective detector. The combination of a gas chromatograph with a mass spectrometer provides one of the most specific and sensitive means of analysing and identifying the pyrolysis products for example for lignin [*Meier & Faix* 1994]. The mass spectrometer records the mass spectrum of each compound eluting from a GC column. MS enables the direct measurement of the mass to charge ratio (m/e) of the ions, whether molecular or fragment [*Hamilton & Rossell* 1987]. When the compounds separated by GC can be directly led into the ion source of the mass spectrometer, then the mass spectra of all the constituents can be obtained.

Materials whose volatilities are too low for gas chromatographic analysis can be subjected to thermal degradation [pyrolysis (Py)] to produce volatile products whose analysis may provide information about the original sample. When the pyrolysis system is separated from the analytical instrument, the pyrolysis and analysis being performed in two steps, the approach is termed "off-line". In the "on-line" approach, the pyrolysis unit and the analytical instrument are directly coupled [*Meier & Faix* 1994]. Pyrolysis may be combined with a monitoring instrument, preferably a mass or FT-IR spectrometer (Py-MS, Py-FT-IR). Alternatively, pyrolysis may be combined with GC using a detection system based on FID, MS, or FT-IR. Analytical pyrolysis combined with high-resolution capillary GC and/or MS has been used, e.g., for polymer and lignin analysis.

5.1.3 Liquid chromatography

In addition to fractionation technique, liquid chromatography (LC), in forms of high-performance liquid chromatography (HPLC), high-performance size exclusion chromatography (HPSEC), gel permeation chromatography (GPC) and capillary electrophoresis (CE), is used for analysing fractions of pyrolysis oil.

HPLC has a number of advantages over other chromatographic systems. It is able to handle compounds which cannot be separated by GC because they are decomposed by high temperatures or active sites. HPLC is able to separate mixtures of high-molecular-mass, polar and thermally labile compounds. In addition, the separated components can be collected at the end of the column and further identified, e.g., by spectroscopic techniques. In an HPLC unit a solvent is pumped at high pressure (up to 140 bar) to a column packed with micro-particulate beads. The solvent sweeps up a sample and carries it to the column, which separates it into its different components and these components flow on over the detector. Several detection systems are presently available in HPLC. The ultra-violet (UV) detector and the differential refractometer are probably the most popular ones.

Gel permeation chromatography (GPC) is a technique, which separates sample components on the basis of the molecular sizes. The name of size-exclusion chromatography (SEC) is also used. In GPC the sample solution flows through a

column (or a series of columns) packed with porous particles. Sample components are eluted in the descending order of molecular sizes. Differential refractometer is used as the general detector. It measures the difference of refractive index (RI) between the solvent and the liquid being eluted. Spectrophotometric detectors (UV, IR) are also general. The chromatograms obtained show the molecular weight (MW) distribution. The technique is commonly employed for polymers.

Capillary electrophoretic (CE) separation is also a liquid chromatographic technique. The CE system creates an electric field. Charged analytes respond to the electric field by migrating along the capillary. CE separates analytes on the basis of their different velocities as they migrate along the capillary under the influence of the electric field. The applied voltage and capillary length being the same, the factor determining the separation is the mobility of a particular analyte, in particular, the electrophoretic mobility. CE offers a possibility of investigating very small amounts of complex mixtures due to the very low injection volume in the nanoliter range. Careful filtration is needed, as the capillary can be blocked by particles.

5.1.4 Spectroscopic techniques

All parts of the spectrum of electromagnetic radiation have found some practical application in the study of organic molecules [*Roberts et al.* 1971]. The three most important types of spectral analysis are infrared (IR), electronic (ultraviolet and visible), and nuclear magnetic resonance (NMR). In each, the absorption of a photon of electromagnetic radiation produces an excited state. The methods most widely applied for pyrolysis oils have been FT-IR and proton (^{1}H) and carbon (^{13}C) FT-NMR spectroscopies.

Absorption of IR radiation causes changes in the vibrational and rotational energy levels of molecules. Recording IR spectrophotometers with excellent resolution and reproducibility are available and widely used in organic research. In NMR spectroscopy the nuclei of some kinds of atoms act like tiny magnets and become lined up when placed in a magnetic field. The energy required to change the alignment of magnetic nuclei in a magnetic field is measured. NMR involves absorption of very low-energy radio-frequency photons by atomic nuclei in an applied magnetic field. NMR has expanded rapidly over the last decade, largely as a result of the increasing power, sophistication and availability of the instrumentation, such as the wider availability of high-field superconducting magnets and the application of Fourier-Transform (FT) techniques. NMR has been used extensively in the characterisation of petroleum and coal liquefaction products as well as of lignin and carbohydrates.

5.1.5 Combined techniques

In recent years impressive advances have been made with the physical coupling of two or more chromatographic and/or spectroscopic techniques into so-called "hyphenated" methods, e.g., GC/MS, LC/MS, GC/FT-IR, GC/FT-NMR, etc. Integration of the analytical data by means of multivariate analysis methods like canonical correlation analysis has been studied for a coal-derived pyrolytic tar [*Hoesterey* 1988]. A feasibility study of the tar using a combination of chromatographic (LC), spectroscopic (MS, IR, ^{1}H and ^{13}C NMR) and chemometrics (factor and canonical correlation analysis) techniques was carried out. A consensus interpretation of the major components contained in LC eluted samples from a pyrolysis oil was attempted using the four spectroscopic techniques, and valuable information was gained by correlating these techniques.

5.2 FRACTIONS FROM DISTILLATION

The distillates, i.e., fractions obtained by fractionating bio-oils with distillation, have been mainly analysed by GC. Information about the GC technique applied is scarce.

In vacuum distillation of the proto-oils, five to seven fractions obtained by Elliott [*Chornet & Overend* 1985] were individually analysed by GC/MS. The mixture was a blend of carrier oil with derived phenolic and oxygenated cyclic components. Between 30 and 50 % of the oil could thus be routinely characterised.

The composition of the fractions collected by *Bakhshi and Adjaye* [1994] during atmospheric distillation of the Ensyn bio-oil are presented in Table 15. The compounds were analysed by GC/MS. The volatiles were composed of water and various organic compounds, organic acids and esters comprising the main components. The amount of acids and esters was 47 wt% of the volatile fraction at a cut temperature of 65 °C decreasing to a value of 9 wt% at 104 °C. Propanoic acid, 3-hydroxybutanoic acid, and dibutyl ester of ethanoic acid were the main components. The next major group of compounds was aliphatic hydrocarbons. Only small fractions of alcohols, aldehydes, amines, furans and phenols were identified.

Adjaye et al. [1992] analysed distillates obtained from vacuum distillation of the bio-oil, using a Carle GC (Series 500) fitted with a 30 m long fused silica capillary column and a FID. The temperature in the oven was programmed to operate from 45 to 210 °C at 70 °C/min. Various peaks in the chromatogram were identified by GC/MS analysis and with pure compounds. The oxygenated compounds included acids, cyclic alcohols, aliphatic alcohols, aldehydes, cyclic ketones, substituted furans, ethers and alkyl substituted and methoxyphenols. The hydrocarbons consisted of aromatic, polycyclic and long-chain unsaturated hydrocarbons. In all, 85 individual compounds were identified by GC/MS. The distillate contained 19 - 23

Table 15. The composition (wt% of volatile fraction) of various fractions collected during atmospheric distillation of the Ensyn bio-oil [Bakhshi & Adjaye 1994].

Composition	Distillation temperature range, °C				
	Fraction 5 Up to 65	Fraction 6 66 - 73	Fraction 7 74 - 81	Fraction 8 82 - 97	Fraction 9 98 - 104
Acids (and esters)	47.2	34.5	22.5	14.5	9.0
Alcohols	1.9	-	-	-	-
Aldehydes	1.0	0.9	0.7	0.6	1.0
Aliphatic hydrocarbons	8.6	2.5	2.3	1.9	2.4
Amines	0.4	-	-	0.1	0.2
Aromatic hydrocarbons	-	-	-	-	-
Ethers	-	-	-	-	-
Furans	1.7	0.5	0.2	0.6	0.6
Ketones	-	-	-	-	-
Phenols	0.1	0.9	0.4	0.3	0.9
Unidentified fraction	7.1	5.7	2.9	2.0	0.9
Water	32.0	55.0	71.0	80.0	85.0
Total	100	100	100	100	100

wt% aromatic hydrocarbons, 11 - 35 wt% phenols, 9 - 13 wt% naphthenes, 5 - 11 wt% aliphatic hydrocarbons, 7 - 14 wt% aldehydes and ketones and 3 - 10 wt% alcohols (Table 4). The concentrations of acids, ethers and furans ranged from 2 to 6 wt% in the distillate. 7 - 18 wt% of the distillate remained unidentified. The phenolics comprised mainly phenol, quaiacol, *p*-cresol, *p*-and *o*-quaiacol, isoeugenol and catechol. The acids consisted of formic acid, acetic acid and traces of propionic acid.

5.3 FRACTIONS FROM SOLVENT EXTRACTION

5.3.1 General

In the analysis of the fractions obtained from solvent extraction of pyrolysis oils, GC/MS has been used by various researchers: by *Elliott* [1983, 1985, 1988], *Maggi and Delmon* [1994b], *Vasalos et al.* [1994], Chum et al. [*Pat. U. S.* 1993] *Fahmy et al.* [1982], *Beaumont* [1985], *Pakdel and Roy* [1987, 1990], *Pakdel et al.* [1989] and *Sharma and Bakhshi* [1993a]. HPLC has been used by *Scott et al.* [1988a], *Piskorz and Scott* [1988], *Piskorz et al.* [1988b], *Chum* [1989] and *Chum et al.* [1993]; FT-IR by *Chum* [1989, 1991], Chum et al. [*Pat. U. S.* 1993], *Pakdel et al.* [1989], *Pakdel and Roy* [1990] and by *Maggi and Delmon* [1994b]; and NMR by *Radlein et al.* [1987], *Scott et al.* [1988], *Chum* [1989, 1991], Chum et al. [*Pat. U. S.* 1993], *Pakdel et al.* [1989] and *Pakdel and Roy* [1990].

5.3.2 Gas chromatographic analyses

The analytical technique most widely used for the fractions from solvent extraction has been GC/MS. In the studies of *Elliott* [1983, 1985] a detailed chemical analysis of selected biomass liquefaction products as CH_2Cl_2 extract solutions (5 mg/ml in solvent) was performed by GC/MS followed by quantitative GC with a FID. As a column a 60 x 0.25 i.d. mm DB-5 WCOT silica capillary column from J&W Scientific, Inc. was used. The column was run directly to the source of an HP 5985 GC/MS. The HP splitless injection system was used with an injector temperature of 200 °C. The temperature was programmed from 20 to 300 °C at 5 °C/min. The 70 eV electron impact spectra were recorded from 20 to 300 m/e at a scan rate of 250 amu/s. The identifications were performed using the library search and as a confirmation authentic samples of the compounds. The response of the FID was measured for representative members of each of the compound classes present.

The volatile components identified by *Elliott* [1983] for the wood-derived Sherbrooke vacuum pyrolysis oil were primarily oxygenated products including acids, alcohols, ketones and aldehydes, as well as furans. Some of the larger components were phenolic. The components of poplar oil from Waterloo flash pyrolysis were quite similar to those of the vacuum pyrolysis oil. More ketones were identified in the flash pyrolysis product and only half as much phenolic content was measured. The furan content also appeared lower in the flash pyrolysis oil. But the major distribution of chemicals in vacuum and flash pyrolysis oils was very similar, i.e., no hydrocarbons, but low amounts of phenolics and high amounts of ketones, aldehydes and acids were present. On the other hand, the main components of the peat flash pyrolysis oil were hydrocarbons, mostly straight-chain olefins. Ketones were noted in minor quantities, but no acids, alcohols or furans were identified. Phenols were also identified and some guaiacols, but no dimethoxyl components were seen.

Low volatility of the compound will interfere with the identification of the compound in a GC system. According to *Elliott* [1988], high-molecular-mass components would therefore not be identified in this system, nor would highly polar compounds. High-molecular-mass hydrocarbons, up to 276 molecular weight, were identified in his studies. Single-hydroxy, double-ring aromatic compounds (phenylphenols and naphthols) seemed to be the upper limit for high-molecular-mass polar compounds. Specific isomer identification was difficult with this type of analysis. Often no reference listing could be found for many of the alkylated aromatics and phenolics found in these tars. Therefore, identification is usually limited to functional type and molecular weight.

The fractions of slow and flash pyrolysis oil samples were analysed by *Maggi and Delmon* [1994b, 1994c] with GC/MS and FT-IR. The fractions were acidic (I), basic (II), neutral (III), hydrocarbon (IV) and aqueous (V) fractions (Figure 7). Six

oils were studied by GC. The acacia and RTP oils were then subjected to more detailed analyses of GC/MS. GC analyses were performed in a Packard 428 gas chromatograph with a FID and equipped with a DB-5 capillary column (23 m x 0.25 mm i.d.). All mass spectra were recorded in the electron impact ionisation mode at 70 eV from a GC/MS Finnigan Mat TSQ spectrometer coupled with a Varian gas chromatograph equipped with an RSL-200 capillary column (30 m x 0.25 mm i.d.). Mass spectra were interpreted using a computerised library searching program. Tables of retention times were used to identify some isomers.

The most abundant fractions of the oils were acidic fractions (I). They contained phenols and methoxy derivatives. The chromatograms of the acidic fractions of all the slow pyrolysis oils were very similar; the same compounds were usually identified but in different ratios. Marked differences between slow pyrolysis oils and RTP oil were found in the acidic fractions. The main compounds identified in the acidic fraction of the RTP oil are presented in Table 16. They constituted of phenolic structures of only one ring. Compounds with up to five oxygen atoms per ring were detected. In the slow pyrolysis acacia oil, almost exclusively methoxy and alkyl groups were present, acidic, ketonic and aldehydic functions being detected in smaller proportions. In the RTP oil, a large number of phenols were identified with acidic, ketonic and aldehydic substituents such as vanillin, vanillic acid and 3,5-dihydroxybenzoic acid, which was the most abundant compound.

The chemical composition of fractions II, III, IV and V was similar for all the oils studied. The hydrocarbon ('non-polar') fractions (IV) contained mainly aromatic and cyclic compounds of two, three or four rings, with molecular weights varying between 128 ($C_{10}H_8$) and 218 ($C_{16}H_{26}$). Some aliphatic hydrocarbons were identified their molecular weights varying between 156 ($C_{11}H_{24}$) and 422 ($C_{30}H_{62}$). The proportions of the basic fraction II were very small. These fractions were composed of N-containing aromatic compounds, such as quinoline and aminonaphthalene. The 'polar' neutral fractions (III) also represented a small proportion of the oils. Their characterisation by GC/MS was very difficult because of the high polarity of the molecules. Nevertheless, some compounds (γ-butyrolactone and other cyclic esters) were identified. The 'aqueous' fractions (V) consisted mainly of carboxylic acids and esters, ethers and alcohols.

According to *Maggi and Delmon* [1994b, 1994c] the RTP oil was a typical flash pyrolysis oil. The high oxygen content was reflected by the presence of mostly oxygenated functions such as carboxyl and carbonyl groups produced by pyrolysis of the cellulose, and phenolic and methoxy groups produced by pyrolysis of the lignin. This was confirmed by the GC/MS study that showed a large number of substituted hydroxybenzoic acids, phenylaldehydes and phenylketones. This explains the weak solubility of RTP oil in the weakly polar solvent dichloromethane and its affinity with water.

Table 16. The main compounds identified in the acidic fraction of RTP oil [Maggi & Delmon 1994b].

Molecular weight	Formula	Compound
94	C_6H_6O	Phenol
106	C_7H_6O	Benzaldehyde
108	C_7H_8O	Methyl phenol*
112	$C_5H_4O_3$	Furancarboxylic acid
	$C_6H_8O_2$	2-Methylcyclopentanedione
		2-Hydroxy-3-methyl cyclopenten-1-one
122	$C_8H_{10}O$	Dimethyl phenol*
124	$C_7H_8O_2$	Guaiacol*
126	$C_7H_{10}O_2$	2-Cyclopenten-1-one, 3-methoxy-5-methyl-1,3-cyclo-pentanedione, 2,4-dimethyl
138	$C_7H_6O_3$	Hydroxybenzoic acid*
	$C_8H_{10}O_2$	Ethoxy phenol*
		Dimethoxy phenol*
		Ethylcatechol*
140	$C_7H_8O_3$	1,3-Cyclopentanedione, 2-acetyl
152	$C_8H_{10}O_3$	2,4-Dihydroxy-6-methylbenzaldehyde
		Vanillin (3-methoxy-4-hydroxybenzaldehyde)
	$C_9H_{12}O_2$	Dimethyl methoxy phenol*
154	$C_8H_{10}O_3$	Dimethoxy phenol*
	$C_7H_6O_4$	Dihydroxybenzoic acid*
164	$C_{10}H_{12}O_2$	Benzoic acid, dimethyl, methyl ester
		Methylethylbenzoic acid
		Propenyl methoxy phenol
166	$C_9H_{10}O_3$	Acetovanillin
		Acetovanillone
	$C_{10}H_{14}O_2$	Tertbutylcatechol
168	$C_8H_8O_4$	Vanillic acid
		Benzoic acid, 1,2-dihydroxymethyl ester
	$C_9H_{12}O_3$	Trimethoxybenzene*
180	$C_{10}H_{12}O_3$	3,4-Dimethoxyphenylacetophenone
182	$C_9H_{10}O_4$	2,6-Dihydroxy-4-methoxyphenylacetophenone
		3,5-Dimethoxy-4-hydroxybenzaldehyde
194	$C_{11}H_{14}O_3$	Dimethyldimethoxybenzaldehyde*
		2,6-Dimethoxy-4-propylenephenol
	$C_{10}H_{10}O_4$	4-Hydroxy-3-methoxycinnamic acid
196	$C_{10}H_{12}O_4$	4-Hydroxy-3-methoxybenzoic acid
		Ethyl ester
		4-Hydroxy-3,5-dimethoxyacetophenone
198	$C_9H_{10}O_5$	4-Hydroxy-3,5-dimethoxybenzoic acid
210	$C_{10}H_{10}O_5$	Dihydroxymethoxyacetylbenzaldehyde*
212	$C_{10}H_{12}O_5$	4-Hydroxy-3,5-dimethoxybenzoic acid, methyl ester

** Several possible isomers*

Fahmy et al. [1982] used GC for analysis of the pyrolytic tar obtained from cotton stalks by rapid continuous pyrolysis. After fractionating the tars (ether extractives) into phenols, acids and neutral components, the phenols being the largest fraction, the fractions were separated by GC (Table 6). The separation was done in a Varian 2868 gas chromatograph. The amounts of identified phenols are presented in Table 17. The phenols represented a relatively heterogeneous mixture. At 400 °C the syringol was the main component and it constituted 35 % of the identified phenols. With its derivatives the syringol constituted about 60 % of the identified phenols, followed by guaiacol. At 600 °C the main component was phenol comprising about 20 % of all the identified phenols.

Table 17. The amounts of identified phenols in the phenolic fraction of the ether extractives of the oil obtained at 400 °C and 600 °C pyrolysis temperatures, mg [Fahmy et al. 1982].

Particle size	Less than 0.5 mm		More than 0.5 mm	
Experiment No.	1	2	3	4
Pyrolysis temperature, °C	400	600	400	600
Phenol	7.11	28.52	7.42	34.76
o-Cresol	15.86	19.83	20.33	21.92
p-Cresol	5.99	25.03	7.62	28.24
Ethyl phenol	1.85	10.37	2.26	11.65
Propyl phenol	1.76	3.57	1.90	5.49
Guaiacol	24.53	4.22	28.19	0.0
Methyl guaiacol	11.32	3.22	16.04	2.17
Ethyl guaiacol	5.77	1.53	8.77	2.07
Propyl guaiacol	4.33	2.79	6.40	1.30
Syringol	64.74	14.59	97.41	19.98
Methyl syringol	24.17	4.52	50.42	3.41
Ethyl syringol	8.95	4.62	15.20	8.13
Propyl syringol	8.71	2.74	12.60	2.07
Dihydroconiferyl alcohol	3.44	4.27	13.77	5.48
Sum	188.53	129.82	288.33	146.04

Input in all experiments was 25 grams air dry cotton stalks with 8 % moisture content.

Acid and neutral fractions from beech wood pyrolysis oil and the whole oil after chemical derivations were analysed by *Beaumont* [1985] with different gas chromatographic systems. The analyses were performed on a Girdel 3000 chromatograph equipped with a double flame detector and a catharometer. The analytical parameters and the columns varied in the different analyses (Table 18). MS identifications were achieved by coupling the same columns to a Varian CH7 spectrometer. The phenol compounds required a capillary column coupled to a Ribert quadrupolar spectrometer. Quantitative analysis was carried out by GC with internal standard.

Table 18. Conditions and columns used for gas chromatographic analysis of pyrolytic oils [Beaumont 1985].

	Column number				
	1	2	3	4	5
Fraction analysed	Light fraction	Acid fraction Neutral fraction Total pyrolytic oils Ketones from Girard's extraction	Tar fraction (T.M.S. derivatives)	Neutral fraction	Benzyl esters of carboxylic acids
Internal standard	Ethyl acetate	2,4-dimethoxy-acetophenone	D-mannose T.M.S.		Benzyl-butyrate
Stationery phase	Porapak Q 50 - 80 mesh	20 % Carbowax 20 M-TPA	5 % SE 52	SE 52	10 % butane diol succinate
Support		Chromosorb WAW 80 - 100 mesh	Chromosorb WAW 80 - 100 mesh		Chromosorb WAW 80 -100 mesh
Length, m	2	3	3	40	3
Tubing, in. inox	1/8	1/8	1/8	Capillar column	1/8
Detector	Thermal conductivity - 150 mA	FID 250 V	FID 250 V	RIBERT quadrupolar spectrometer	FID 250 V
Carrier gas, ml/min	Helium, 40	Nitrogen, 20	Nitrogen, 30	Helium	Nitrogen, 30
Injector temperature, °C	150	120	120		150
Reactor temperaturee, °C	250	250	250		200
Temperature programming, °C	110 - 230	100 - 230	120 - 200	80 - 250	130 - 170
Programming speed, °C/min	5	5	4	5	2

Girard's reactives were used for the extraction of ketones [*Beaumont* 1985]. Four ketones were isolated and identified. The carboxylic acids were isolated as benzyl esters and analysed by GC. The carbohydrates were analysed after evaporation of the tarry fraction at 105 °C and silylation. The analysis of silylated carbohydrates was then carried out by GC. Comparison of retention volumes was sufficient for identification of the lightest compounds. Spectra of middle-weight compounds of the neutral fraction and acids were interpreted by comparison with literature data. Spectra of phenolics were not available in literature; they were identified with the help of studies on fragmentation of lignin model compounds. The main compounds found in the beech-derived pyrolysis oil were acetic acid (10.1 % of dry

wood), ethylenic acids, 1-hydroxypropan-2-one (4.3 %), methanol (2.5 %), 1-hydroxybutan-2-one (2.1 %) and 2-furaldehyde (1.3 %). Three cyclic oxygenated chemicals were obtained with more than 1 % yield: furfurylic alcohol, 2-hydroxy-3-methyl-2-cyclopenten-1-one, and α-angelicalactone. Phenolics accounted for 7 % with predominance of the more substituted. Levoglucosan (1,6-anhydrogluco-β-D-pyranose, 1.2 %) was the only carbohydrate that was identified in the oil.

The fractions obtained by *Vasalos et al.* [1994] with liquid-liquid extraction from the eucalyptus oil of Union Fenosa (Figure 9) were analysed by GC/MS. The analysis of each fraction was performed using an HP5989 MS Engine with an HP Ultra 1 capillary column. The phenolic fraction contained mainly phenolic compounds and, in addition, various aldehydes and ketones. The main compounds of acidic fraction were found to be aldehydic and ketonic substituted furans and cyclopentans, alcohols, cyclo- and benzene-diols, benzaldehydes and acids. The neutral fraction contained mainly aldehydic and ketonic substituted furans, pyrans, indans and cyclopentans, cyclo-pentanols and diols.

The phenolics and neutrals fraction P/N separated from the pyrolysis oil by Chum et al. [*Pat. U. S.* 1993] was analysed with various techniques, i.a. by GC/MS. An HP 5970 B GC/MS unit and an Ultra 2 capillary column (25 m x 0.20 mm i.d.) were employed. Verification of peak assignments was based on the library of spectra and was verified, where possible, by injection of pure samples, and by acetylation of the P/N oil to increase, as much as possible, the amounts of volatile materials eluted from the column. Regardless of the method used, the GC method detected less than about 15 % of the total compounds. 21 compounds were identified and identification of additional 15 compounds was suggested. The former calibrated compounds represented those that had been verified and calibrated by injection of pure compounds in known amounts. The latter uncalibrated compounds were not verified and their assignments were tentative. In particular, the absolute position of substituents is the most uncertain feature of these data.

Radlein et al. [1987] analysed the low-MW phenolic portion of WFPP pyrolysis oil derived from a whole-tree hybrid poplar. The high-MW fraction of the pyrolytic lignin was precipitated by diluting the oil with three parts of cold water. After filtration the dark-brown aqueous phase was clarified by adsorption on activated carbon, which was filtered off and extracted with acetone. After evaporation of the bulk of acetone the viscous red-brown residue was examined by GC/MS. The column used was an HP fused silica capillary (12 m x 0.20 mm) column, split ratio 1:9, and the temperature programme 60 °C for 5 min, 10 °C/min to 150 °C. An HP 5970 mass selective detector was used as the detector. The compounds identified comprised hydroxyacetaldehyde, acetic acid, acetol, phenol, guaiacol, pyrocatechol and syringol.

Sharma and Bakhshi [1993a] analysed upgraded products obtained from the pyrolytic lignin (PL) and resid oil (RO) fractions of whole bio-oil (WBO) (Chapter

4.3.3). The upgraded liquid product was in the form of two layers: an organic layer and a water layer. The organic layer was distilled for 30 min at 200 °C under a vacuum pressure of 172 Pa to separate the "organic distillate" from the "residue". The organic distillate was later analysed by GC (Carle GC 500) using a 30 m long capillary column and FID. The identity of the peaks was confirmed by GC/MS analysis of the sample and by using pure compounds. The organic distillates contained aromatic and aliphatic hydrocarbons, phenols, ketones and alcohols. The aromatic yield, which was the most desired group, was at maximum 11 wt% of wood from the WBO, 6.5 wt% from the PL, and <5 wt% from the RO.

Preliminary characterisation of the aliphatic and aromatic hydrocarbons, obtained by *Pakdel and Roy* [1990] in the fractionation of aspen poplar-derived vacuum pyrolysis oil, was performed by GC/MS (Figures 13 and 14). Gas chromatographic analyses were performed on a 6000 Varian gas chromatograph with FID and on-column injector. The capillary column was J&W fused silica, DB-1701 (15m x 0.32 mm i.d.). The oven temperature was maintained at 50 °C for 2 min, then programmed to 90 °C at 30 °C/min and finally to 280 °C at 4 °C/min. In addition, an HP-5890 gas chromatograph with split injector (1:40 split ratio at 290 °C) was used with J&W fused silica capillary column DB-5 (30 m x 0.25 mm i.d., film thickness 0.25 μm). The oven temperature was programmed from 50 to 100 °C at a rate of 30 °C/min and then to 290 °C at a rate of 4 °C/min. An HP-5970 mass-selective detector was used as the detector. Typical MS operation conditions were as follows: transfer line 270 °C, ion source 280 °C, electron energy 70 eV. Data acquisition was done with HP-UX Chemstation software using an HP-UNIX computer and NBS library data base.

Aliphatic hydrocarbons represented 0.08 to 0.44 % of the oil phase (PCU) and 0.01 to 0.02 % of the aqueous phase (SCU) (Chapter 4.3.3) [*Pakdel & Roy* 1990]. Both the oil and the aqueous phase mainly contained cracked alkanes with some alkenes. Most aliphatic hydrocarbons were produced near the top of the pyrolysis reactor (Figure 13). The aliphatic hydrocarbon fraction of the H-VI oil at the bottom section of the reactor was dominated by n-alkanes in the range of n-C_{19} to n-C_{26}. Aromatic hydrocarbons contributed between 0.06 to 0.24 % of the oil phase and were detected only in trace amounts in the aqueous phase. The aromatic hydrocarbon fraction of the H-VI oil was less complex compared with H-I to H-V oils.

Vacuum pyrolysis produced a high yield of carboxylic acids, which consisted mainly of formic and acetic acids [*Pakdel et al.* 1989]. The quantitative GC analysis method of the low-molecular-weight carboxylic acids had earlier been developed by *Pakdel and Roy* [1987]. The C_1 to C_7 carboxylic acids of the wood pyrolysis oils were analysed by GC following their conversion into benzyl esters via tetrabutylammonium salts and purification by solvent extraction and silica gel elution chromatography. With this method it was possible to measure the acids directly in both the oil and aqueous phases [*Pakdel et al.* 1989]. The acid yield was

about 9 wt% of wood, on a dry ash-free basis. The benzylation technique was considered a reliable method for the C_1 - C_7 carboxylic acids [*Pakdel & Roy* 1987]. The chemical reaction is mild and eliminates the possibility of any side reactions during derivatisation. The purification technique eliminates any coelution interferences with compounds other than acids and makes the life of the gas chromatographic column longer. In the analyses, the same capillary gas chromatograph (Varian 6000) and the same capillary column, coated with DB5, as in the analysis of hydrocarbons were used. The system was in split injection mode (100:1). The column temperature was maintained at 50 °C for 4 min, then programmed to 210 °C, and then to 290 °C, at heating rates of 10 and 30 °C/min, respectively.

5.3.3 Liquid chromatographic analyses

HPLC technique has been used only for fractions from solvent extraction of pyrolysis oils by *Scott et al.* [1988], *Piskorz and Scott* [1988], *Piskorz et al.* [1988b], *Chum* [1989], Chum et al. [*Pat. U. S.* 1993] and *Vasalos et al.* [1994].

WFPP oil was separated into water-soluble and water-insoluble fractions by *Scott et al.* [1988] by adding water to the oil. The water-soluble fraction was analysed by HPLC and the water-insoluble fraction by ^{13}C NMR. In HPLC analyses, the column used was Aminex HPX-87H (300 x 7.8 mm), a high-performance cation exchange resin in hydrogen form. The eluent was 0.007 N H_3PO_4 and the eluent flow rate 0.80 ml/min.The temperature was 65 °C. The detector was R 401 differential refractometer from Waters. *n*-Propanol was used as an internal standard.

The HPLC analysis was applied for oils derived from different woods [*Scott et al.* 1988, *Vasalos et al.* 1994], peat [*Piskorz & Scott* 1988] and cellulose [*Piskorz et al. 1988b*]. The water-soluble fractions were found to contain sugars and anhydrosugars, carbonyl and hydroxycarbonyl compounds and acids. The acids consisted of formic and acetic acids. The fraction was considered to originate from carbohydrate. Quantitative data obtained for different woods and celluloses are presented in Tables 7 and 19. Results for different woods show that 81 % to 92 % of the content of the pyrolysis oils were quantitatively identified.

To obtain relative response factors and retention times, the pure compounds were fed and then eluted. Some of them, such as cellobiosan and 1,6-anhydro-β-D-glucofuranose, had to be synthesised. Confirmation of compound identification was obtained by GC/MS by using an HP 5970 mass selective detector coupled to a 5890 gas chromatograph. Prior to GC/MS analysis, sugars and anhydrosugars were trimethylsilylated to the corresponding ethers. Small amounts of simple phenols and of furanoid compounds were also detected by GC/MS. These components were not quantified by HPLC.

Table 19. The yields and composition of WFPP oils obtained from different celluloses [Piskorz et al. 1988b].

Source	Commercial SS 144	Treated SS 144*	Avicel pH-102	Treated Avicel*	Sherbrooke
Temperature, °C	500	502	500	503	500
Yields, % mf of feed					
Organic liquid	72.5	83.5	87.1	86.3	78.0
Water	10.8	6.1	3.1	?	5.2
Char	5.4	1.3	2.5	0.7	4.8
Gas	7.8	3.9	8.9	3.3	7.1
Hydroxyacetaldehyde	15.3	6.2	8.6	0.43	15.2
Levoglucosan	7.0	31.8	26.9	38.41	9.3
Cellobiosan	4.0	11.5	10.1	5.6	5.1
Glucose	1.0	1.8	2.1	2.0	1.4
Fructose	2.0	3.0	4.7	2.7	0.0
Glyoxal	3.5	5.5	6.5	2.1	2.9
Methylglyoxal	0.8	1.3	0.23	0.30	0.9
Formic acid	5.5	1.9	3.8	1.5	7.7
Acetic acid	4.9	0.1	1.4	0.03	4.8
Ethyleneglycol	1.7	0.02	0.56	0.00	2.5
Formaldehyde	1.2	0.94	0.72	0.24	1.0
Acetol	2.2	0.12	0.04	0.02	1.1
Anhydroglucofuranose		5.5		7.0	
Oligosaccharides		5.3		5.7	
Ash	0.062	0.00	<0.01	0.00	0.40
DP	164	186	227	222	258

** Pretreated with 5 % sulphuric acid at 90°C for 5.5 hours.*

The phenolics and neutrals fraction P/N separated from the pyrolysis oil [*Chum* 1989, Chum et al. *Pat. U. S.* 1993] was analysed by HPSEC. The analysis was performed using an HP 1090 high performance chromatograph with an ultraviolet diode-array detector (HP1040) and a refractive index detector (HP1037). An HPSEC column (PolymerLabs, PL Gel, 300 x 7.5 mm) of polystyrene-divinylbenzene copolymer particles (5μm diameter) with a mean pore diameter of 50 Ångström was used; the solvent employed was THF. Calibrations were made with polystyrenes and Igepals standards of known MW. The weights of the P/N products are relative to these standards and are called apparent molecular weights. The P/N products had approximately 42 % of components in the range of 0 - 250 apparent MW, 25 % in the 250 - 450 range, and 25 % from 450 to several thousand. As a basis of HPSEC analyses the P/N product had a higher amount of low-MW materials compared with those eluted from the gas chromatograph. This is due to the fact that not all these materials are volatile; they contain more polar groups than simple phenolic compounds, and are, therefore, more difficult to chromatograph under the conditions employed. From the HPSEC, e.g., monomeric, dimeric, trimeric, tetrameric and pentameric phenolic substances were present in

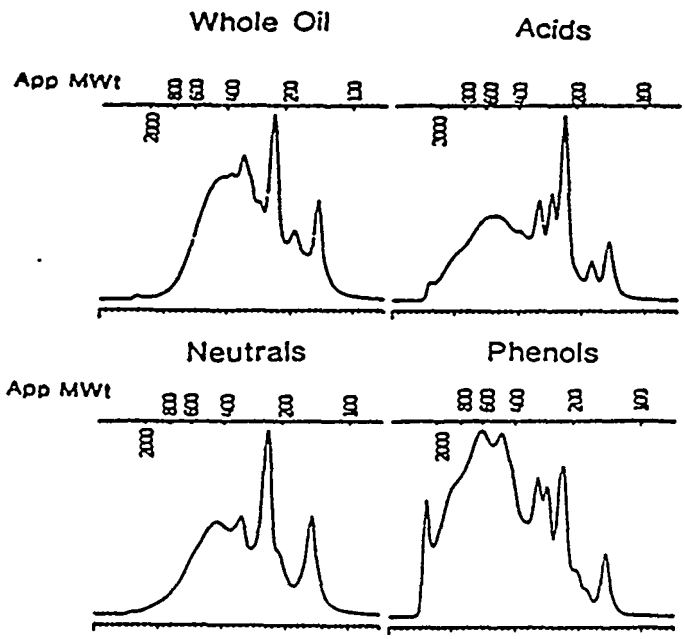

Figure 18. High-performance size exclusion chromatograms of pine sawdust pyrolysis oils and fractions of acids, neutrals and phenols contained in the ethyl acetate soluble oil [Chum 1989].

the P/N product. The products are mixtures of compounds, and the GC/MS detects only volatile monomers and a few dimeric species under the conditions presented above. The acids and neutrals fractions exhibited lower-MW components as determined by HPSEC than the P/N product. The apparent MW distributions of selected fractions of isolated oil components are shown in Figure 18. The phenols fraction contained the highest apparent MW components, and their absorption spectra in the UV region resembled that of low-MW lignins.

5.3.4 Spectroscopic analyses

Spectroscopic methods, such as IR and NMR, have been used for fractions obtained from solvent extraction of pyrolysis oils. IR has been applied by *Chum* [1989], Chum et al. [*Pat. U. S.* 1993], *Pakdel and Roy* [1990], *Pakdel et al.* [1989] and *Maggi and Delmon* [1994b]; and NMR by *Radlein et al.* [1987a], *Scott et al.* [1988], *Chum* [1989], Chum et al. *[Pat. U. S.* 1993], *Pakdel and Roy* [1990] and *Pakdel et al.* [1989]. In addition, *Chum* [1989, 1991] and Chum et al. [*Pat. U. S.* 1993] have used molecular-beam mass-spectrometry (MBMS) for the fractions.

FT-IR is a powerful technique for characterising complex substances, such as lignocellulosic biomass, its components, and derivatives therefrom. According to

Chum et al. [*Pat. U. S.* 1993] FT-IR is a very powerful fingerprint method for the P/N product, its feedstock, the method of preparation, and the thermal history of the P/N sample.

The P/N fractions obtained by *Chum* [1989] and Chum et al. [*Pat. U. S.* 1993] were analysed for their total and phenolic hydroxyl content. The total phenolic content of lignin was determined by conductimetric titrations. Spectroscopic determinations were carried out using the Nicolet 5SXC FT-IR spectrometer and the JEOL FX-900 FT-NMR spectrometer. In addition, the solid state CP/MAS ^{13}C NMR spectra were obtained. The MBMS analyses were carried out on equipment described by *Evans and Milne* [1987a]. Pyrolysis of the oils (or fractions) was performed under controlled conditions and followed in real time by a free-jet MBMS. Pyrolysis products and fragmentation ions were detected.

The assignment of FT-IR bands was carried out by comparison with the spectra of known lignins, model compounds and related substances. Only a few of these frequencies correspond to unequivocally assigned modes, but many result from combinations of modes. The FT-IR spectrum contained a complete set of structural information on the P/N product. There were similarities between the FT-IR of the P/N product and the FT-IR of the corresponding wood lignins.

The typical whole oil contained about 6.2 % and 0.4 % phenolic hydroxy and carboxylic acid, respectively. The P/N fraction contained 6.6 % phenolic hydroxy and no carboxylic acid, whereas the acids fraction contained 9.2 % and 0.9 % of phenolic hydroxy and carboxylic acid, respectively.

From MBMS of the pyrolysis products of the P/N fractions, a number of phenolic compounds were detected: guaiacol, catechols, isomers of substituted 2-methoxyphenols with alkyl groups. Carbonyl groups were also present and gave rise to vanillin, coniferyl aldehyde and acetovanillone. In addition, a few carbohydrate-derived components were present, such as furfuryl alcohol and other furfural derivatives.

From the proton NMR of the P/N fraction, of the total proton intensity, the aromatic protons (6.5 to 10 ppm) constituted 52 %, the aliphatic (1.5 to 3.5 ppm) about 20 %, and the methoxy region (3.0 to 4.2 ppm) 30 %, which was in agreement with the proposed compounds obtained from the MBMS pyrolysis experiment. The ^{13}C-NMR spectra of the P/N fraction also indicated mixtures of compounds with aromatic carbons in the 110 to 148 ppm region, a very pronounced methoxy peak at 55.6 ppm, and aliphatic carbons.

Fractions of 'slow' and flash pyrolysis oils have been analysed by FT-IR by *Maggi and Delmon* [1994b]. The IR analyses were performed on a Bruker IFS 88 FT-IR spectrometer. Liquid samples were introduced as a liquid film between NaCl plates. Published spectra of standard products were used to assign bands to structures. In the spectra of the acidic, basic, 'polar' neutral and hydrocarbon fractions

from RTP oil, signals related with typical functions were detected: OH stretching and C=O stretching in the acidic fraction; NH stretching and aliphatic C-N in the basic fraction; and the different C-H stretchings in hydrocarbons. The spectra of the basic, neutral and hydrocarbon fractions of all the oils were similar to each other. On the other hand, important differences were noted between RTP and BASA acidic fractions. These results were along the same lines as those obtained for these oils by GC (Chapter 5.3.2).

The water-insoluble fraction (pyrolytic lignin) of the WFPP oil studied by Scott et al. [*Radlein et al.* 1987, *Scott et al.* 1988] was analysed by ^{13}C NMR-spectroscopy. The NMR spectra were recorded using a 9 % solution of pyrolytic lignin in DMSO-d_6 at 62.9 Mz and 50 °C with broad-band proton decoupling. Delay time between pulses was 10 seconds. The NMR analyses were carried out for the pyrolytic fractions of the oil and also of the oil pretreated with mild hydrolysis. The ^{13}C NMR spectrum of the pyrolytic lignin from pyrolysis of poplar wood is shown in Figure 19. Its structure appeared to be very similar to that of steam exploded lignin. The broad features did confirm that the material isolated did in fact originate from lignin although it had clearly suffered extensive degradation. Thus the two main groups of peaks characteristic of wood lignin were present. These are

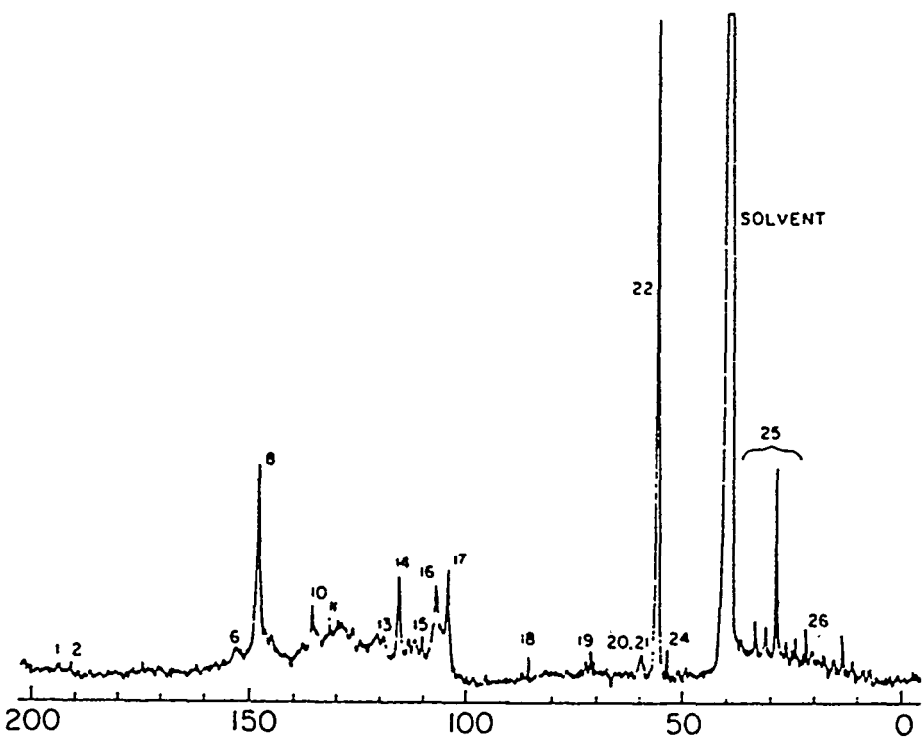

Figure 19. ^{13}C NMR spectrum of pyrolytic lignin from fast pyrolysis of poplar wood, peak numbers refer to Table 20 [Radlein et al. 1987].

Table 20. Assignments for the most important peaks in the ^{13}C NMR spectrum of pyrolytic lignin [Radlein et al. 1987].

Peak No.	Chemical shift	Assignment*
1	~193	α-CHO
2	~191	γ-CHO in cinnamaldehyde
6	~152	C_3/C_5 in S (etherified)
8	148.3	C_3/C_5 in S (non-etherified)
		C_3 in G
10	135.4	C_1 in G (etherified)
11	131.7	[C_β in cinnamaldehyde]
12	~119	[C_6 in G (etherified)]
14	115.5	C_5 in G (non etherified)
		C_3/C_5 in *p*-hydroxyphenyl
15	~111	[C_2 in G (etherified)]
16	107.2	[C_2/C_6 in S with α-CHO
17	104.3	C_2/C_6 in S
18	~ 86	C_β in β-O-4
19	~ 72	C_α in β-O-4
20, 21	~ 60 - 62	[C_γ in β-0-4 and phenylcoumaran]
22, 23	56.3	Methoxyl in S and G, respectively
24	~ 54	C_β in phenylcoumaran units
25, 26	15 - 45	Saturated aliphatic side chain

** G denotes a guaiacyl and S a syringyl unit. The term 'etherified' refers only to the link at C4 and not to methoxyls. On account of the somewhat unsatisfactory signal-to-noise ratio the bracketed assignments should be regarded as tentative. The others seem well established by the works of Nimz and Marchessault.*

from 20 - 90 ppm, characteristic of aliphatic side chains, and 105 - 160 ppm, characteristic of olefinic side chain and aromatic carbons. Methoxy content was relatively high, and syringyl units appeared to predominate over guaiacyl units.This was consistent with the observations obtained from the GC/MS results of the low-molecular-weight phenolic portion of a similar pyrolytic oil and presented in chapter 5.3.2 [*Radlein et al.* 1987]. The pyrolytic lignin appeared to be somewhat more degraded than steam exploded lignin and was probably lower in molecular weight. Assignments for the more important peaks are given in Table 20.

In the characterisation of the aliphatic and aromatic hydrocarbons, obtained in the fractionation of aspen poplar-derived vacuum pyrolysis oil by *Pakdel and Roy* [1990], in addition to GC/MS analyses, FT-NMR and FT-IR spectroscopic techniques were used. FT- ^1H NMR spectra of 20 % solution in deuterochloroform ($CDCl_3$) were recorded on a XL200 Varian instrument. FT-IR spectra were recorded on a Digilab FTS-60 spectrometer. Assignment of absorption bands was based on information in the literature. FT-NMR spectroscopy enabled the hydrogen type distribution of the aromatic hydrocarbon fractions to be determined. Aliphatic side chain hydrogens of the aromatic fractions contributed approximately

between 47 and 58 % of the totalhydrogens, indicating their long and highly branched nature and possibly their low mutagenic activity. Highly branched chain hydrocarbon nature of the aromatic fractions were confirmed by FT-IR spectroscopic analysis.

5.4 FRACTIONS FROM ADSORPTION CHROMATOGRAPHY

5.4.1 General

Fractions obtained from adsorption chromatography fractionation have been analysed with chromatographic methods by *Davis* [1985], *Johnson and Chum* [1988], *Karlsson and Björnbom* [1985], *Churin et al.* [1988], P*akdel and Roy* [1988], *Pakdel et al.* [1992], *Pakdel et al.* [1994], *Achladas* [1991] and *Desbene et al.* [1991a, 1991b]; and with spectroscopic techniques with IR by *Davis* [1985], *Karlsson and Björnbom* [1985], *Pakdel et al.* [1989] and *Achladas* [1991], with NMR by *Pakdel and Roy* [1988], *Pakdel et al.* [1989] and *Achladas* [1991]; and with UV by *Karlsson and Björnbom* [1985].

5.4.2 Chromatographic analyses

The most dominant analytical method for the fractions from adsorption chromatography has been GC/MS.

The fractions obtained from fractionation of several biomass-derived oil samples with the SESC technique by *Davis* [1985] were subjected to GC/MS, GPC and IR analysis, elemental analysis and solubility classification. MW distributions of fractions were obtained by GPC. GPC employed two columns in series packed with 200 - 400 mesh styrene divinylbenzene copolymer beads with 8 % and 12 % cross-linkage. The solvent was THF. MW calibration curves were constructed using a series of 12 polystyrene and phenolic standards. The high-MW exclusion limit was 700 - 800 daltons. The calibration was checked frequently with nordihydroguaiaretic acid or phenolphthalein. The solvent was pumped 1.2 ml/min with UV detection at 254 or 280 nm. Generally little or no elutable material having molecular weights above the exclusion limit of the system was observed. The average ranges of percentages found in each fraction of the oils, the average percentage of oxygen in the fraction, molecular weights and the predominant molecular species were presented in Table 8. In the IR spectra the predominant band in most fractions was that due to hydroxyl stretching. Other bands were the carbonyl stretching band and those characteristic of the aromatic ring. As a basis of GC/MS analyses, fractions 1 and 2 (Table 8) contained aromatic hydrocarbons, and fraction 3 polar aromatics. Anisole, cycloalkanones, a butyrophenone, and a hindered phenol were found in the fraction 3. Fraction 4 consisted largely of monophenols. Fractions 5 and 6 were also phenolic, as evidenced by solubility in aqueous caustic, IR and elemental analyses. Fraction 6 was involatile, highly polar and

phenolic. Methanol marked the approximate line between asphaltenes (benzene-soluble pentane insolubles) and preasphaltenes in SESC.

The wood-oil fractions obtained by SESC by *Johnson and Chum* [1988] were analysed by HPSEC with the same method as *Chum* [1989] analysed the P/N fractions presented in Chapter 5.3.3. The HPSEC showed a general trend to higher apparent molecular weight, as the polarity of the solvent was increased up to that of methanol. The fractions obtained for tyre waste-derived pyrolysis oils by *Williams and Taylor* [1994] were also analysed by the SEC system.

The bio-oil produced by the pyrolysis of wastes of the olive oil industry in Raiano in Italy was separated into five fractions by preparative liquid chromatography by *Churin et al.* [1988]. Fraction 1 was constituted of paraffinic, olefinic and aromatic hydrocarbons as determined by TLC and GC/MS. The paraffins and olefins were long-chain hydrocarbons, representing series of C_nH_{2n+2}, C_nH_{2n} and C_nH_{2n-2} and comprising about 5 % of the whole oil (Figure 20). The hydrocarbons contained C_{10}-C_{30} carbon numbered compounds. The maximum concentrations corresponded to C_{10} and C_{14} members. For the olefin series, the chains comprised between 12 and 26 carbon atoms. The C_nH_{2n-2} series was constituted of only three

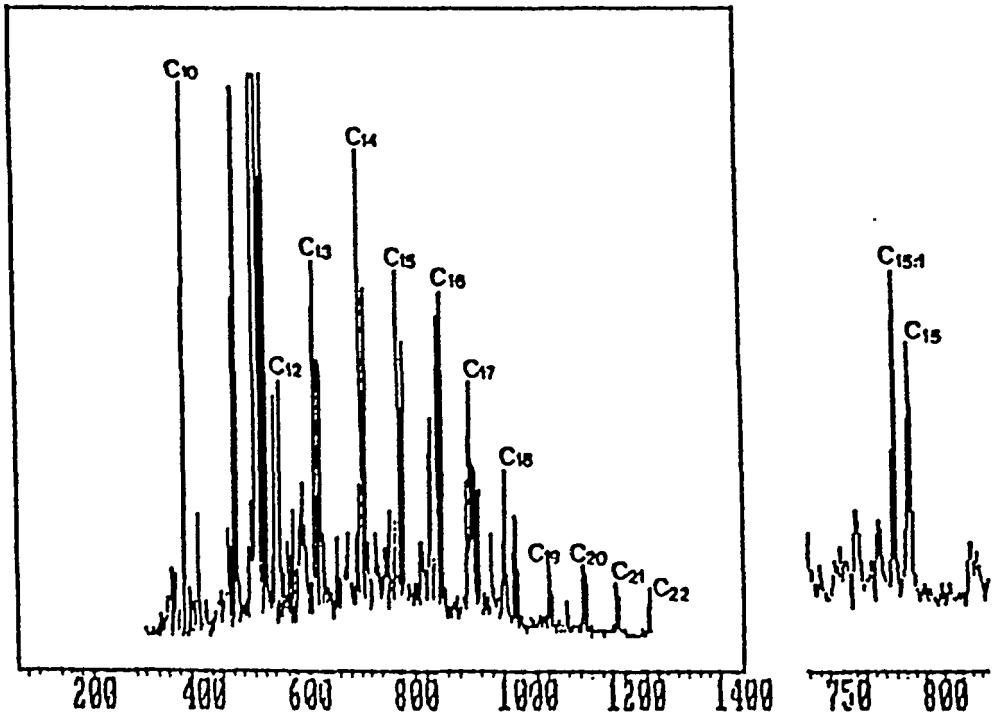

Figure 20. Total ion current signal from the GC/MS analysis for paraffinic and olefinic hydrocarbons of the bio-oil [Churin et al. 1988].

compounds of 16, 17 and 18 carbon atoms with two isomers for C_{16}. Of the aromatics, trimethylbenzene, naphthalene, tetralin, fluorene, phenanthrene or anthracene, and pyrene were detected. Fraction 2 comprised monophenols only, the most abundant compounds being phenol and *o*-cresol. A very interesting compound existed in a rather high concentration: 2,6-di-tert-butyl 4-methylphenol, which is one of the most important additives used as antioxidant in gasolines.

Pakdel and Roy [1988] analysed the 14 fractions obtained from wood pyrolysis oils derived from the vacuum pyrolysis unit of University of Laval (Table 12) by GC/MS, IR and NMR techniques. GC analyses were performed on a 6000 Varian apparatus with FID with on-column and split injectors. The capillary columns were J & W fused silica DB5 (30 m x 0.25 mm i.d.) and DB1 (30 m x 0.32 mm i.d.). The oven temperature was maintained at 50 °C for 2 min, then programmed to 150 °C and 290 °C at rates of 4 and 10 °C/min, respectively. Various standard mixtures were prepared with the available compounds. Their relative response factors to benzophenone were measured. Silica gel eluates were added with an accurate quantity of benzophenone as internal standard. Their gas chromatograms were compared with the standard mixtures for peaks identification and followed by integrations for their quantifications. The low molecular weight carboxylic acids were characterised with the method presented above (Chapter 5.3.2). The results for the 14 fractions are presented in Chapter 5.4.3.

Pakdel et al. [1992] also fractionated the pyrolysis oil from lignin derived from steam explosion of wood into eight fractions (Table 13). The fractions were analysed by GC and GC/MS. The column used was an HP5 capillary column (50 m x 0.2 mm i.d.). GC/MS analyses were performed by BC Research on a bench type Quadrupole HP 5890 GC equipped with a 30 m x 0.32 mm i.d. and 0.25 µm film of DB5 capillary column. Fractions 1 to 7 were analysed by GC [*Pakdel et al.* 1992]. Due to their high polarity or high molecular weights, the compounds present in fraction 8 could not be analysed by GC. Fractions 1 and 2 were mainly saturated and aromatic hydrocarbon mixtures, respectively. Fractions 3 to 7 represented 42 % of the anhydrous oil. All the peaks in these fractions were sufficiently separated and resolved and could be characterised with less ambiguity. They were mainly composed of phenolic, aldehydic, ketonic and alcoholic compounds with increasing polarity from low-polar methoxybenzene to high-polar diphenolic and aldehydic compounds. A detailed GC/MS analysis of fractions 3 to 7 is presented in Table 21. There were only a few standards available and therefore only major peaks were quantified. The methanol soluble fraction 8, which accounted for 55 % of the oil, possibly contained several high-value oxygenated chemicals such as polyphenols, hydroxyphenols, sugars and acids. LC/MS analysis was suggested to be possibly an appropriate technique for characterisation of that particular fraction.

Pakdel et al. [1994b] have recently analysed the polar fractions after fractionating the pyrolysis oil derived from wood and bark into 14 fractions. New compounds in the polar fractions were analysed using GC, MS, FT-IR and FT-NMR.

Fractions 1 - 3 were composed of hydrocarbons. Fractions 4 - 12 were analysed by GC/MS. An HP model 5890 was used with a DB1 fused silica capillary column from J & W (30 m x 0.25 mm, i.d., film thickness 0.25 μm). The end of the column was directly led into the ion source of an HP model 5970 series MSD operated with electron impact ionisation mode. The mass range m/z 30 - 600 Dalton was scanned every 0.8 s. Quantitative analysis of fractions 4 - 12 were made using

Table 21. Major compounds found in various fractions of the lignin pyrolysis oils [Pakdel et al. 1992].

Fraction	GC peak	Compound identified by GC-MS	Yield*
3	1	3,4,5-Trimethyl-2-cyclopentene-1-one	0.6
	2	2-Methoxy-4-methylphenol (creosol)	0.2
		4-Ethyl-2-methoxyphenol	
	3	Isoeugenol	0.1
		Methyl-16-methyl-heptadecanoate	
4	4	Phenol	0.8
		2-Methylphenol (*o*-cresol)	
		4-Methylphenol (*p*-cresol)	
		2,3,4-Trimethyl-2-cyclopentene-1-one	
		3,4- or 2,4-Dimethylphenol	
		3,5-Dimethylphenol	
	5	2-Methoxy-4-methylphenol	0.2
		4-Ethyl-2-methoxyphenol	
		2,6-Dimethoxyphenol (syringol)	
		3-Methoxy-1,2-benzenediol	
5		2,6-Dimethoxyphenol (syringol)	
	6	2,6-Dimethoxy-4-(2-propenyl)phenol	2.3
6		2-Methyl-2-butenal	
	7	3-Methoxy-1,2-benzenediol	1.2
		or 2-Methoxy-1,3-benzenediol	
		3-Methyl-1,2-benzenediol	
		3,4-Dimethoxyphenol	
		1-(4-Hydroxy-3-methoxyphenyl)ethanone	
		1-(4-Hydroxy-3-methoxyphenyl)-2-propanone	
7		3-Methyl-2-cyclopentene-1-one	
		2-Hydroxy-3-methyl-2-cyclopentene-1-one	
		1,3-Benzenediol (catechol)	
	8	3-Methoxy-1,2-benzenediol	1.2
		3-Methyl-1,2-benzenediol	
		4-Ethyl-1,2-benzenediol	
		2,6-Di-*tert*-butyl-4-methylphenol	
		Syringaldehyde	
	9	1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanone	0.4
		1-(2,4,6-Trihydroxy-3-methylphenyl)-1-butanone	

* *Wt% of total lignin pyrolysis condensates (condensates included: water, water soluble organics and water insoluble organics)*

fluoranthene as an internal standard. Response factors were premeasured using similar standard compounds to those identified in fractions 4 - 12 and included 2-furaldehyde, furfuryl alcohol, α-angelicalactone, phenol, 2-octanone, methylcyclopentenone, methyl-2-methylbenzoate, vanillin, resorcinol, and benzophenone.

The results of the GC/MS analyses are presented in Appendix 1. Over 80 % by weight of the components of fractions 4 - 11 were quantified. The majority of components in fraction 12 were identified and about 50 % were quantified. No quantitative analysis was performed on fraction 13. Fractions 12 and 13 were highly polar and may contain high-MW compounds. Due to its high polarity and/or low volatility, fraction 14 could not be characterised. It was however expected to contain also high-MW fatty acids and heterocyclic compounds.

High-MW fatty and resin acids have been characterised by GC/MS after the diazomethane methylation of the total pyrolysis oils and concentration of the methyl esters on silica gel liquid column chromatography. The oils used for analysis were derived from wood, barks and primary sludges [*Pakdel et al.* 1994a, 1994b]. 1 g of the methylated oil was fractionated on 15 g of prewashed silica gel. The column was eluted sequentially with 100 ml of distilled petroleum ether, dichloromethane and methanol. The dichloromethane fraction was analysed in detail by GC/MS. Fatty acids and resin acids response factors were measured with respect to anthracene which was used as an internal standard for quantitative analysis. The compounds consisted of fatty acids, resin acids, sterols and alkaloids. Depending on the raw materials and the thermal decomposition conditions used, pyrolysis oils from softwood contained 2 - 2.5 % C_{12} - C_{26} fatty acids and 1 - 2 % resin acids [*Pakdel et al.* 1994b]. High total amounts of fatty acids (C_4 - C_{28}) and resin acids were recently reported [*Pakdel et al.* 1994a]. The oils from spruce bark, from primary sludges derived from spruce, and from spruce wood contained 10.6 %, 9.6 % and 3.9 % fatty and resin acids, respectively, corresponding to about 3.7 %, 3.0 % and 3.2 % of source materials.

The phenolic fraction separated from the fir wood pyrolysis liquids by *Achladas* [1991] was analysed by GC-FID, GC/MS, TLC, IR and ^{1}H and ^{13}C NMR spectroscopies. GC was carried out on an HP Model 5710A gas chromatograph equipped with a FID. GC/MS was performed on a QMD 1000 GC/MS system (Carlo Erba) equipped with a J&W DB-WAX fused-silica capillary column (60 m x 0.32 mm i.d., film thickness 0.5 μm). GC/MS was also performed on an ion trap detector (ITD) system of Finnigan MAT, equipped with a 25 m SE-54 capillary column directly coupled to the ITD.

GC analysis was carried out using anisole and eugenol as internal standards. Identification and determination of phenolic components was based on matching relative response factors of pure phenol standards. The separation appears in Figure 21. The total proportion of light alkylphenols was calculated to be 9 wt% of the phenolic fraction. The phenolic fractions were also subjected to GC/MS. Peak identification was performed partly by GC/MS and partly by the use of appropriate

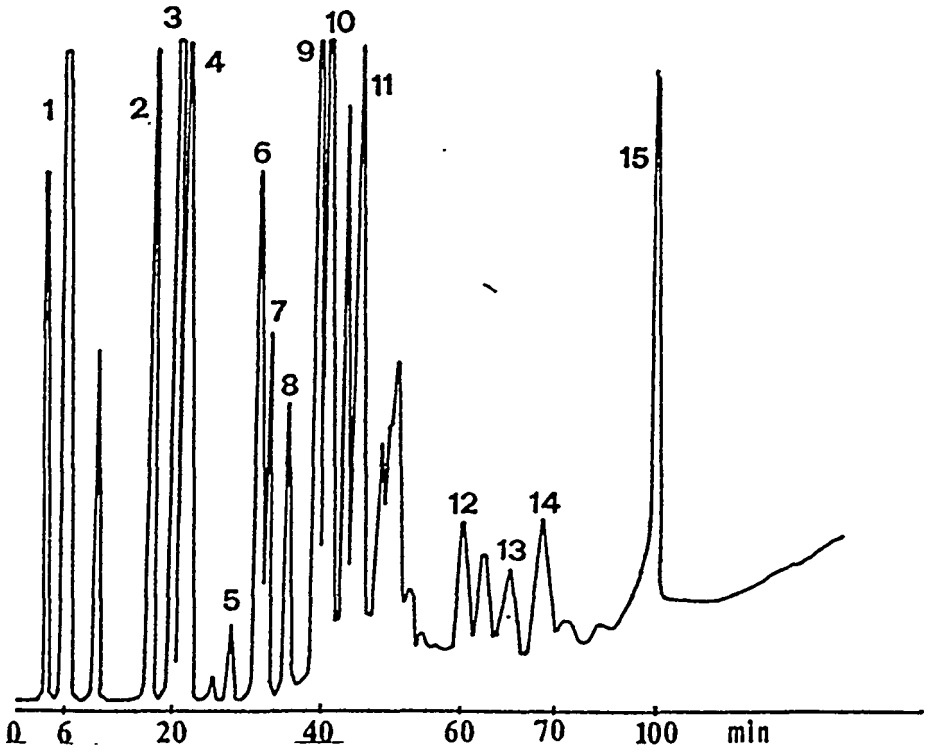

Figure 21. GC separation of phenols from the phenolic fraction of a pyrolysis liquid [Achladas 1991]. Peak identifications: 1: phenol, 2: 2-methylphenol, 3: 3-methylphenol, 4: 4-methylphenol, 5: 2-ethylphenol, 6: 3-ethylphenol, 7: 4-ethylphenol, 8: 2,6-dimethylphenol, 9: 2,4- and 2,5-dimethylphenol, 10: 2,3- and 3,5-dimethylphenol, 11: 3,4-dimethylphenol, 12: 2,4,6-trimethylphenol, 13: 2,3,6-trimethylphenol, 14: 2,3,5-trimethylphenol, 15: eugenol (internal standard).

GC standards. Twenty compounds were identified in the phenolic fraction. Good agreement of the two separate GC/MS analyses was observed. The phenol content in pyrolysis liquids was found to be 12 - 17 wt%. 2,6-Bis(1,1-dimethyl-ethyl)-4-methylphenol was identified in the phenolic fraction.

The fractions obtained by *Williams and Besler* [1994] and by *Williams and Horne* [1994] for waste-derived pyrolytic oils were analysed by capillary GC/MS, together with retention indices, to identify the polynuclear aromatic hydrocarbons. The system was a Carlo-Erba Vega HRGC with cold on-column injection, coupled with a Finnigan Mat ITD via a heated transfer line. The capillary column was a DB5 column. The oils were found to contain substantial concentrations of hydrocarbons, consisting mainly of naphthalene, fluorene and phenanthrene, and their alkylated substituents. Low-MW aromatic and polycyclic aromatic species up to phenanthrene were in the pentane fraction, whilst higher-MW species were found in the benzene fraction. The compounds are presented in more detail in Chapter 6.5. The concentrations of aromatic and PAH species increased after with increasing the catalyst temperature [*Williams & Horne* 1994]. Before catalysis, the

oxygenated species were mainly carboxylic acids, phenols and benzene-diols and their alkylated homologues.

The fractions obtained from the API 60 acid-base separation and subsequent preparative SEC of wood pyrolysis oils from different species by *Desbene et al.* [1991a, 1991b] were analysed by GC/MS. The apparatus used for the SEC comprised a Model 6000 A dual-piston pump, a U6K universal injector, a model M 440 UV-visible detector and a R 401 differential refractometric detector, all from Waters Assoc. The separations were performed on two columns, a 5-μm μ Spherogel 50 Å coupled with a 7-μm μ Styragel 100 Å. The mobile phase was THF. GC analyses were performed using an HP Model 5880 A gas chromatograph fitted with a 25-m fused-silica column coated with CP Sil 5 and a FID. In GC/MS analyses, a model R 10-10 quadrupole spectrometer fitted with the same column as above was used. Spectra were interpreted by matching the results with library spectra and with known standard compounds.

After the first separation, the organic matrix was fairly simplified, but the complexity of the nine fractions remained too great and impeded the identification of the components by GC/MS. In the second preparative separation obtained 27 fractions were analysed by GC/MS. Every fraction was studied using two ionisation modes: electron impact at 70 eV and chemical ionisation by ammonia and methane. These two modes were complementary; the former allowed the fragmentation of molecules and gave important structural information and the latter was used to obtain molecular weights.

The neutral and acid fractions of pyrolysis oils from slow pyrolysis of wood contained mainly saturated hydrocarbons and aromatics (in neutral fraction), ethers (abundant in neutral fraction), esters (in neutral and weak acid fractions), aldehydes and ketones (in neutral fraction and weak, medium and strong acid fractions), phenols (monophenols essentially in the weak and medium acid fractions and naphthols and diphenols only in the most polar fractions; medium, strong and very strong acid fractions) and some organic acids in strong and very strong acid fractions. Of these groups numerous components were isolated. In addition, alcohols and lactones were present, but only some of their components were found in pyrolysis oils [*Desbene et al.* 1991a, 1991b].

The combination of ion-exchange chromatography and SEC with GC/MS appeared to be suitable for the analysis of pyrolysis oils. It allowed an appreciable improvement compared with chromatography: 60 % of the original material could be analysed by capillary GC after fractionating pyrolysis oils into 27 subfractions. The compounds were separated regardless of their volatility and polarity. The approach of mapping as a function of polarity (acid-base characteristic) was an innovation in this field of applied organic analysis. The strategy was, however, inadequate for the characterisation of nitrogenous bases contained in the tars from wood pyrolysis. Analyses of the subfractions by means of techniques that are

complementary to capillary GC and better adapted to low-volatility compounds are underway in the University of Paris. For example, the capillary supercritical fluid chromatography has a higher performance than LC and is relatively well adapted to medium-polarity compounds.

5.4.3 Spectroscopic analyses

The spectroscopic techniques IR, NMR and UV have been used for the fractions from adsorption chromatography.

Karlsson and Björnbom [1985]fractionated peat and biomass liquids into four fractions (Chapter 4.4). The fractions were analysed with different techniques (UV, IR, GC, GC/MS, elementary analysis and a micro distillation apparatus). The first fraction consisted mainly of hydrocarbons. IR and UV data indicated that the main type of components were branched saturated hydrocarbons. Approximately 2/3 of the first fraction distilled under 370 °C. The distillate only consisted of highly branched and cyclic saturates. More than 100 isomers of C_{10} - C_{22} saturates occurred. The molecules containing heteroatoms and aromatics were concentrated in the distillation residue. The nitrogen occurred as amines and the oxygen as ethers according to IR spectra. The second fraction was highly aromatic according to IR, UV and elementary analysis. The oxygen occurred mostly as ketone or ester groups and the nitrogen as amines and pyridines. Distillation data indicated that 2/3 of the second fraction was distillable up to 370 °C. The third and fourth fractions were phenolic or resinous according to IR and UV spectra. Very little of the fourth fraction was distillable under 370 °C. The non-eluted material was found to consist of asphaltenes, preasphaltenes and inorganic material.

Pakdel and Roy [1988] analysed 14 fractions from the wood pyrolysis oils obtained from the vacuum pyrolysis unit of University of Laval with GC/MS (Chapter 5.4.2), IR and NMR techniques. ^{1}H FT-NMR spectra of 5 % solution in DMSO were recorded on XL 200 Varian instrument. Fraction 1 contained hydrocarbons. ^{1}H NMR spectra showed long alkyl and alkenyl side chains on benzene rings. Fraction 2 had also an aromatic nature but with a slightly high polarity. Many of the compounds in fractions 3 - 11 were characterised by GC, consisting of mainly monophenolic types and oxygenated heterocyclic compounds. Of the low-MW carboxylic acids formic and acetic acids were the major constituents of pyrolysis oils. Hydrogen distribution of fraction 12 obtained by ^{1}H NMR spectrum showed a higher hydroxyl group than that in the initial oil. Fraction 13 contained the highest percentage of the high-polar compounds, oligosaccharides in particular. Fraction 14 had presumably a polymeric structure.

Pakdel et al. [1994b] recently characterised the fractions of vacuum pyrolysis oils with FT-IR and FT-NMR. These analyses were both useful for the characterisation of the high-polar fraction and revealed its acidic and polyalcoholic nature. FT-NMR and FT-IR analyses were performed for fraction 13, for which no

quantitative analysis had not been made. The spectra revealed the oxygenated aliphatic and cyclic nature of fraction 13. It was concluded that the acidic and alcoholic compounds including sugars were the main constituent of fraction 13. FT-IR exhibited a strong absorption band of O-H stretching in polyalcohols (3 400 cm^{-1}), a moderate aliphatic C-H stretching absorption (2 700 - 2 960 cm^{-1}), C=O and C-O stretching absorptions (1 718 and 1 603 cm^{-1}, respectively), C-H deformation bands of CH_3COO-, CH_2CO-, -$COOCH_3$ and -CH_2-CO- (1 380 - 1 440 cm^{-1}) and C-O-stretching absorptions of -C-O-H (1 100 - 1 260 cm^{-1}) and C-O-stretching absorptions of aliphatic ethers and alcohols. ^{1}H NMR spectrum showed two major proton resonance ranges: bands at about 1 - 3 ppm were due to the aliphatic protons and 3.5 - 4.5 ppm were due to the aliphatic hydroxyl protons. A resonance band at 8.5 ppm was due to the carboxylic proton. ^{13}C NMR spectrum demonstrated a series of resonance bands at 20 - 60 ppm due to the aliphatic carbon nuclear, 60 - 80 and 110 ppm due to (R_2)CH-OH, RCH_2OH, and RCH_2-O-CH_2R', and 160 - 180 ppm due to R-COOH.

The phenolic fraction separated from the fir wood pyrolysis liquids by *Achladas* [1991] was, in addition to GC/MS analyses, analysed by TLC, IR, ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR spectra were recorded on a Varian T-60 NMR spectrometer in $CDCl_3$-tetramethylsilane (TMS) as internal standard, and ^{13}C NMR spectra were obtained on a Bruker WP-80 NMR spectrometer in $CDCl_3$-TMS. IR spectra were recorded on a Beckman IR 18-A spectrophotometer in $CDCl_3$ and THF. IR spectra (KBr) of the phenolic fraction were measured on a Model 1430 ratio recording IR spectrometer.

The main bands of the IR spectra for the phenolic fraction are presented in Table 22. Integration of the peaks in the ^{13}C NMR spectra showed carbons attached to the phenolic hydroxyls. The phenol content in biomass pyrolysis liquids was 12 - 17 wt%. The phenolic fraction consisted mainly (85 - 95 wt%) of light and heavy non-ortho- and ortho-substituted alkylphenols. The light alkylphenol content was calculated to be about 9 wt% of the phenolic fraction.

Table 22. Main bands of the IR spectra in the phenolic fraction [Achladas 1991].

Wawe number, cm^{-1}	Origin
3 600 - 3 200	O-H stretching vibration
2 920 - 2 940	C-H substituted on aromatic ring stretching vibration
1 710	Carbonyl stretching, unconjugated
1 595 - 1 497	Common benzene skeletal vibration
1 359	O-H bending vibration
1 220	Characteristic C-OH stretching vibration of phenolics

5.5 FRACTIONS FROM GEL PERMEATION CHROMATOGRAPHY

Fractions obtained from pyrolysis oils by GPC have been analysed mainly by GC [*Sheu et al.* 1984, *Arpiainen & Lappi* 1989]. Combined use of GPC and GC enables characterisation of complex mixtures such as pyrolytic oils.

The fractions (Table 14) separated from biomass pyrolytic tars by *Sheu et al.* [1984] were analysed by high-resolution GC/MS. The oil was derived from southern pine and bark. Less than 20 % of the oil was eluted by GC. The fractions from GPC separation were concentrated without removing THF completely in order to detect some low-boiling-point components, such as toluene and xylene, although their analysis was not quantitative. Prior to GC analysis, 1-decene was added as an internal standard. The GC analyses were performed using a Model 560 GC system (Tracor) and a FID. The GC/MS analyses were performed by a Model HP 5985A system. A DB-5 fused silica capillary column with an immobilised methylsilicone phase (J&W Scientific) was used in the characterisation. A 12-ft glass column packed with 10 % SP-2100 on 100/80 Supelcoport was used to estimate the volatiles, which were defined as the total amount of components detected by FID and calculated using an internal standard method and relative response factors for different species. The response factors for fraction 2 (alkanes) and fraction 4 (aromatics) were assumed equal to one, and was 0.75 for fraction 3 (phenols).

Fraction 1 was composed of high-MW species, and the GC analysis at the oven temperature to 300 °C did not detect any volatiles. Fraction 2 contained long-chain esters most compounds being 'light' nonvolatiles. Fraction 3 contained all phenols, large aromatics and smaller nonvolatiles. Fraction 4 had a smaller linear molecular size than that of heptane and most aromatics were expected in this fraction. The fraction also contained some of the oxygenated species which did not readily hydrogen-bind with THF, mainly aldehydes, ketones and ethers. Trace aromatic components in pyrolytic tar, which contained phenols, could not be identified by GC/MS prior to the separation of the sample by GPC. The phenols had broader peaks and can mask trace aromatics.

GPC could separate the complex mixture into fractions, enriched with fewer components mostly with similar functionalities. The species, which were in low concentration, could be enriched, and components which were masked by the bulk in GC could be freed by GPC.

The fractions, i.e., the cuts obtained by GPC from peat and bark flash pyrolysis oils by *Arpiainen and Lappi* [1989] (Figure 17), were analysed with IR and GC methods. The chemical character of the cuts varied according to their position on the MW distribution curve. The peak at the light end was rich in phenolics while that in the middle range was rich in paraffins. In the cuts taken from the heaviest part of the eluate, aromaticity, phenolicity, and more generally, bonds between the aromatic ring and oxygen were prominent.

5.6 SUMMARY OF CHARACTERISATION OF DIFFERENT FRACTIONS

Compositions of the fractions obtained with different fractionation methods (distillation, solvent extraction, adsorption chromatography and GPC) have most often been analysed by GC/MS technique. Other methods applied have been LC techniques, such as HPSEC and HPLC, IR, UV and ^{1}H and ^{13}C NMR spectroscopies.

In GC analyses, different gas chromatographs (e.g. HP, Varian, Carle) have been used in the analyses. The columns used have almost solely been long (about 30 m) fused silica capillary columns. The most common column has been a DB5 column, a bonded silica of moderate polarity. The temperature range has been from 50 to 300 °C at different rates of temperature rise. Identification has often been carried out by MS with library spectra and pure compounds with known fragmentation patterns. The most common ionisation technique has been electron impact (EI) ionisation at 70 eV. Applied to lignin pyrolysis products, this mode of ionisation has been found to produce molecular and typical fragment ions in sufficient abundance to permit structure assignments to be made [*Meier & Faix* 1994].

GC/MS technique is well adaptable to pyrolysis oil fractions. The fractions are not as complicated as the whole oils. Generally, GC has a limited application and is not meant for very complex and less volatile mixtures. The pyrolysis oils are largely non-volatile. High-molecular-weight components would not be identified by this system, nor would highly polar compounds. About 40 - 60 wt% of the pyrolysis oils after different fractionations have been identified with GC/MS. The compound groups analysed are, for example, monocarboxylic acids, alcohols, aldehydes, ketones and phenolics. The remaining oils have been difficult to characterise due to their high molecular weight, high polarity or thermal lability. Other analysis techniques ought to be used for characterising them.

LC techniques are more suitable than GC techniques for pyrolysis oils. With HPSEC, a higher amount of fractions can be analysed than with GC. Higher-molecular-weight and more polar compounds have been identified with HPSEC. The HPLC method has been used successfully for water-soluble compounds, such as sugars, anhydrosugars and hydroxycarbonyl compounds.

Of spectroscopic methods, IR and NMR are the techniques most commonly used for the fractions of pyrolysis oils. Both of them are suitable for more polar and higher-molecular-weight fractions. They give further information about the composition when used in addition to other analysing techniques. IR gives structural information on the fractions. NMR is suitable for the structural analysis of highly polar, phenolic, lignin-derived substances.

6 CHARACTERISATION OF WHOLE PYROLYSIS OILS

6.1 GENERAL

Characterisation of whole oils as such, without fractionation them prior to analysis, has also been used for bio-oils, but to a lesser extent. The methods used have been GC, GC/MS, PyGC, HPSEC, GPC, CE, FT-IR, ^{13}C NMR and ^{1}H NMR, MS/MS and MBMS.

Whole oils have been characterised with GC by *Elliott* [1983, 1985], *Besler et al.* [1994], *Pakdel et al.* [1994a, 1994b], *Pakdel and Roy* [1987] and *Güell et al.* [1994], with LC by *Johnson and Chum* [1988], *Williams and Taylor* [1994], *Güell et al.* [1994] and *Desbene et al.* [1991a], and with spectroscopic methods mainly by *Elliott* [1983, 1985], *Churin* [1989], *McKinley* [1989], *McKinley and Barrass* [1988], *Evans and Milne* [1987a, 1987b, 1988], *Milne et al.* [1984] and *Moore et al.* [1988].

The analytical methods can give information on the entire sample, for example, HPSEC, FT-IR, NMR, elemental analysis and thermal analysis, or on specific portions, such as volatiles by GC, GC/MS, MS/MS and MBMS.

6.2 GAS CHROMATOGRAPHIC ANALYSES

GC techniques are very useful for the identification of individual compounds, but only a fraction of the pyrolysis oils can be analysed by these methods. Generally, GC has a limited application and is not meant to be used for very complex and less volatile mixtures. Gas chromatograms of pyrolysis oils suffer, in general, from low resolution and, consequently, the quantitative analysis is less accurate. Narrow bore and long capillary columns, however, improve the resolution. In addition, direct injection of a complex mixture into the gas chromatograph tends to deteriorate the column by building up of non-volatile matter in the column inlet leading to gradual decomposition of the column stationary phase. Only the volatile fraction (5 - 50 %) of underivatized oils can be analysed by GC, and therefore it has not been applied for whole pyrolysis oils as extensively as for fractions separated from the oils prior to the analysis.

As regards whole pyrolysis oils, GC has been applied for dichloromethane extracts by *Elliott* [1985, 1988] (Chapters 4.3.1 and 5.3.2). *Besler et al.* [1994] investigated the hydrocarbon distribution of pyrolysis oil derived from *Euphorbia rigida*, after extraction of the oil in *n*-pentane. C_5- C_{37} hydrocarbons were found in the oil. *Pakdel et Roy* [1987] determined low-molecular-weight carboxylic acids (C_1-C_7) from the wood vacuum pyrolysis oils by GC after their conversion into benzyl esters via tetrabutylammonium salts and purification by solvent extraction

and silica gel elution chromatography (chapter 5.3.2). High-molecular-weight fatty and resin acids were analysed by *Pakdel et al.* [1994a, 1994b] by GC/MS after the methylation of the total oils by diazomethane and concentration of methyl esters on silica gel liquid column chromatography (Chapter 5.4.2).

Güell et al. [1994] characterised tars from hydropyrolysis experiments carried out between 300 and 700 °C at pressures up to 70 bar in a re-designed wire-mesh pyrolysis reactor. The tars derived from pine-wood and pine-wood lignin were analysed using GC/MS, SEC and UV-fluorescence spectroscopy. GC/MS analyses were performed with a Kratos Concept S instrument. The tar samples in methanol were concentrated from about 20 ml to 0.5 ml and injected by flash vaporisation into a DB5 column (30 m x 0.32 mm i.d.) with the column oven held for 5 min at 80 °C, then heated at 5 °C min^{-1} to 300 °C. The total ion chromatograms (TIC) showed broad irregularly shaped clusters of peaks, which in terms of chemical functionalities would imply the presence of oxygen bearing groups, such as carboxylic acids, phenolic groups and possibly aliphatic hydroxyl groups (Figure 22, Table 23). The TICs also showed evidence of sharp, Gaussian-shaped peaks which in general indicate molecular species with few oxygen functional groups; typical of hydrocarbons, phenols, aromatics, ethers and esters. The high-pressure hydrogen in hydropyrolysis was seen to influence chiefly as reducing the proportion of oxygen-bearing groups and possibly generating more material to pass through the chromatographic column. As a conclusion of these studies, the mild hydropyrolysis process was presented to produce biomass pyrolysis tars which are lighter and less polar and possibly more stable under storing than the pyrolysis tars from atmospheric pressure.

6.3 LIQUID CHROMATOGRAPHIC ANALYSES

LC methods are more applicable for whole pyrolysis oils than GC methods. Analytical techniques giving a rapid, broad classification of oils are desirable for whole pyrolysis oils. HPSEC has been shown to be a useful method of characterising pyrolysis oils giving a good indication of their MW distribution. It has the advantage that the whole sample may be analysed under very mild conditions. It has been used for oils from a variety of sources, including oils derived from coal, heavy crude petroleum oils and from the pyrolysis of biomass. For pyrolysis oils from biomass and wastes SEC has been applied by *Johnson and Chum* [1988], *Güell et al.* [1994], *Williams and Taylor* [1994] and *Williams and Horne* [1994].

Several pyrolysis oils have been analysed with HPSEC by *Johnson and Chum* [1988]. The analysis was performed on HP 1084 and 1090 liquid chromatographs using HP1040A diode array and HP-1037A refractive index detectors. The columns used were purchased from Polymer Laboratories Inc. and were a PL Gel 100 Å and a PL Gel 50 Å. The solvent employed was THF. The HPSE chromatograms of the pyrolysis oils, shown in Figure 23, indicate, that HPSEC may be used to characterise pyrolysis oils obtained from different sources, and the oils can be

compared in terms of their relative apparent MW distributions as long as the analyses were carried out under the same chromatographic conditions.

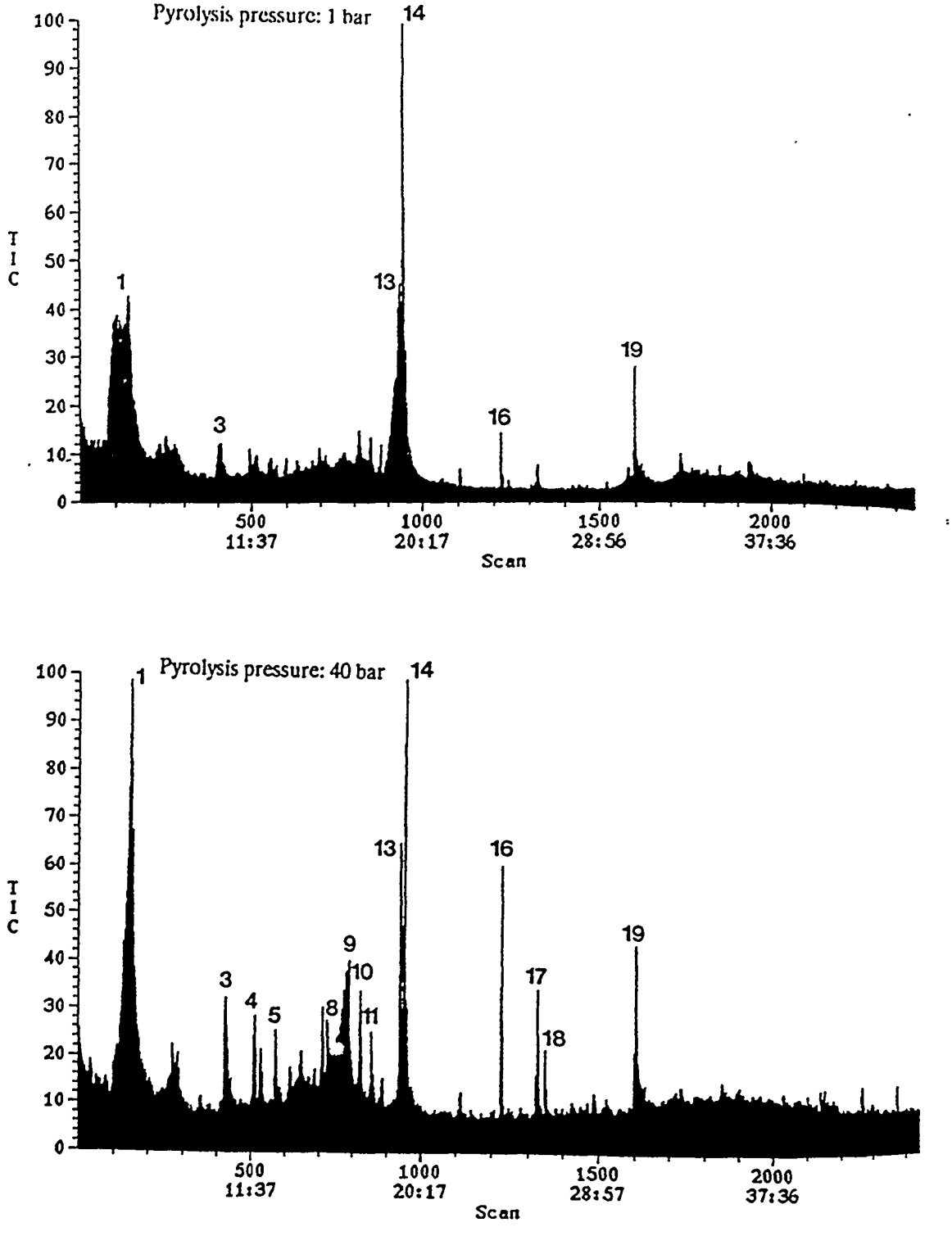

Figure 22. TICs of tars obtained from pyrolysis of pine-wood by heating at 1 000 Ks^{-1} to 400°C under H_2. Peak identification, Table 22 [Güell et al. 1994].

Table 23. Tentative identification of the peaks in TICs from wood pyrolysis oil [Güell 1994].

Peak No	Molecular ion	Decreasing order of ion intensity	Tentative identification
1	110, 126	45, 89, 58, 75	Not identified, probably catechol and cyclooctane
2	124	124, 123, 78	Not guaiacol
	150	150, 135, 107	2-Cyclohexan-1-one-3-methyl-6-isopropylidene (not phenol)
3	152	152, 151	4-Hydroxy-3- methoxybenzaldehyde (vanillin)
4	164	164, 149	2-Methoxy-4-(1-propenyl)phenol (guaiacol derivative)
5	166	151, 166, 123	4-Hydroxy-3-methoxyacetophenone
6	198	167, 152, 198	Not identified
7	180	137, 180 (60, 73)	1-(4-Hydroxy-3-ethoxy phenyl)acetone (+ alkanoic acids)
8	178	151, 178	Guaiacyl prop-3-en-1-one
	180	151, 180	Ethyl-2-butyl-cyclopent-1-enyl ketone
9	194	60, 57, 73, 98	Alkanoic acids and/or methyl glucopyranoside, methyl galactopyranoside
10	182	137, 182	4-Hydroxy-3-methoxybenzene acetic acid
11	180	137, 180, 124	4-(3-Hydroxy-1-propenyl)-2-methoxyphenol
12	194	194, 131, 163	2,6-dimethoxy-4-propenyl phenol
13	178	177	Phenanthrene
	180	137, 135, 147	Guaiacol/syringol derivative
14	180	137, 180, 124	4-(3-Hydroxyl-propenyl)-2-methoxy phenol
15	Not identified	149, 192, 223	Not phthalate ester
16	278	149, 223, 150, 205, 278	1,2-Benzenedicarboxylic acid (diisobutyl ester or dibutyl ester)
17	226	226, 225, 165	2-Methoxy-9H-xanthen-9-one
18	202	202, 101, 203	Pyrene
19	226	226, 225, 165	2-Methoxy-9H-xanthen-9-one
20	302	121, 302, 287	Not identified
21	300	285, 239, 300, 197	Phenanthrene carboxylic acid octahydro- dimethyl - isopropyl
22	302	44, 302, 259	1-Hydroxy-3,5,6-trimethoxyxanthone
23	None	149, 167, 279, 298	Phthalate + unidentified 298
24	234	234, 219	(2,4,5,7 or 3,4,5,6)-Tetramethyl phenanthrene
25	314	239, 314, 299	Podocarpa 8,11,13-trien - 15 oic acid-13-isopropyl methyl ester

With proper choice of solvent and detector systems the HPSEC, on polystyrene-divinylbenzene copolymer gels, of the whole oils can provide valuable information on their apparent MW distributions and changes that occur upon ageing or chemical fractionation. When using polystyrene-divinyl benzene polymer gel columns, THF as solvent and polystyrenes and IGEPALS™ as calibration standards a good indication of MW distribution could be obtained for oils from a variety of sources. According to *Elliott* [1994b], high-MW fractions are identified in the oils, while calibration of the technique is uncertain.

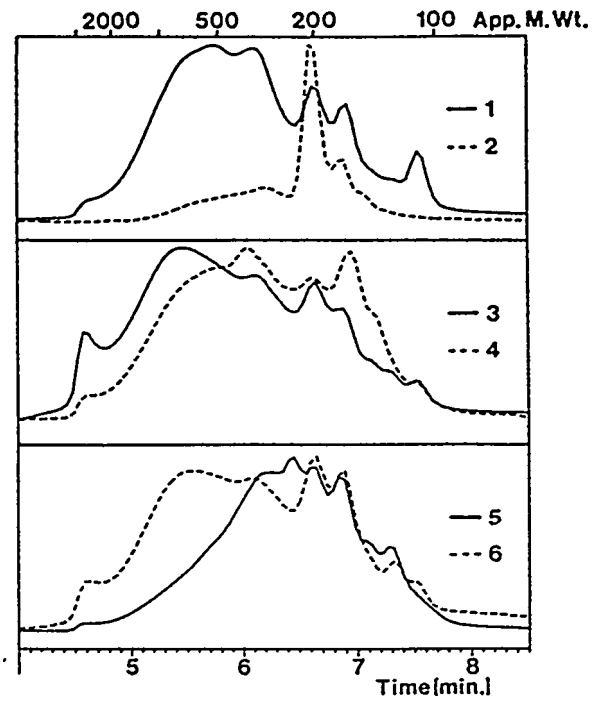

Figure 23. HPSEC of wood pyrolysis oils. The oils: 1 - flash pyrolysis oil of a poplar-aspen hybrid (University of Waterloo); 2, 3 and 6 - vacuum pyrolysis oils of Avicel, aspen-poplar hybrid and aspen, respectively (University of Sherbrooke); 4 - extract of aspen produced by supercritical acetone (B.C. Research); 5 - extract of aspen obtained with supercritical methanol (University of Laval) [Johnson & Chum 1988].

When characterising tars from hydropyrolysis *Güell et al.* [1994] used for SEC a Waters 6000 series pump and two PL-Gel columns in series. Unstabilized THF was used as the mobile phase. Molecular mass calibrations were made with PL Thermal Science polystyrene standards. The molecular mass distributions of the tars indicated that as the H_2 pressure was increased, a lighter, possibly more extensively cracked tar was recovered. These results support those obtained by GC/MS studies (Chapter 6.2).

The fuel properties of pyrolysis oils derived from different wastes (RDF, wood, rubber-tyre and crop waste) by *Williams and Taylor* [1989] were analysed by SEC using a PL Gel 10 μm, 500 Å as the column and THF as the mobile phase. The system was calibrated with polystyrene standards. The MW ranges of the oils showed a range similar to petroleum oil and a shift to higher MW was observed on storage indicating polymerisation.

The evolved pyrolysis vapours obtained from the batch pyrolysis of tyre waste at 450 °C pyrolysis temperature were passed directly to a second reactor heated to

higher temperatures (from 500 to 712 °C) [*Williams & Taylor* 1994]. The derived oil after secondary cracking was collected in a condensation trap and analysed by SEC. The SEC system with dual UV and RI detection was evaluated to determine the optimum solvent flow rate and column temperature in terms of chromatography efficiency. In addition, a measure of the aromaticity of the oils using the UV/RI single ratio was obtained. The UV detector would be sensitive to the detection of aromatic compounds and the RI detector would measure elution of all compounds. The solvent used for the mobile phase was THF. The calibration system used was based on polystyrene samples of low polydispersity in the MW range of 800 - 860 000 and benzene for low MW calibration. The optimum practical operating conditions were 0.26 ml min^{-1} flow rate and 0 °C column temperature. The MW range measured for the oils subjected to secondary cracking is shown in Figure 24. The MW range of the oils was from a nominal 50 to 1 200. The oils showed a decrease in MW and an increase in aromatic content and decrease in aliphatic content as the secondary reactor temperature was increased.

Desbene et al. [1991a] studied the analysis of pyrolysis oils and treated pyrolysis oils in a research program of the European Community concerning the upgrading of tars produced by pyrolysis of biomass. The coupling of mass spectrometry with

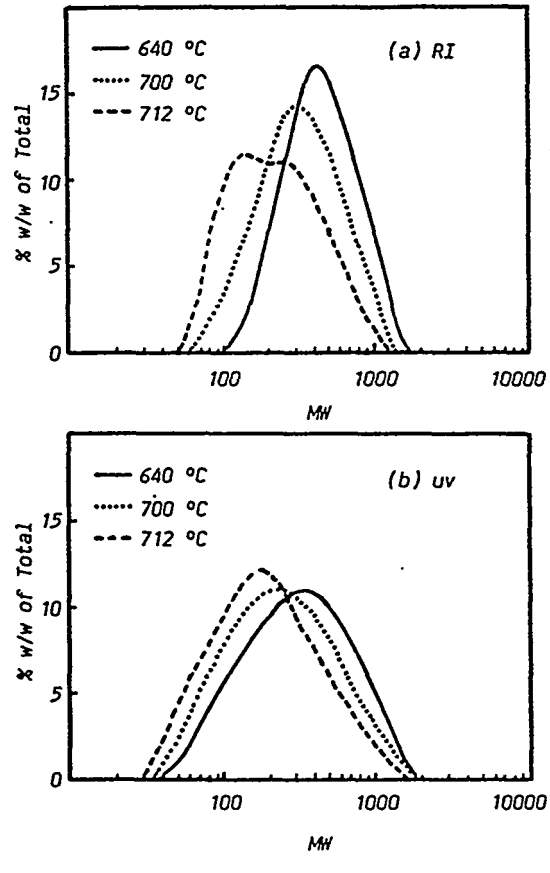

Figure 24. MW range of tyre pyrolysis oils subjected to secondary cracking at different temperatures [Williams & Taylor 1994].

different chromatographic techniques included first, on a preparative scale, the Ion Exchange Chromatography in an organic phase and the GPC, and then, on an analytical scale, the capillary GC. This coupling allows the characterisation and the identification under a double aspect (acido-basic character and molecular-weight) of an important fraction (about 60 %) of these complex mixtures. GC presents, however, a limitation in the volatility point of view. It is then necessary to work in a liquid medium. To complete the analysis, techniques such as supercritical fluid chromatography (SFC) and high performance capillary electrophoresis (HPCE) were considered. HPCE was used for the analysis of the phenolic fraction. The HPCE seemed to be an efficient technique for the analysis of pyrolysis oils. The method presents as high efficiencies as the capillary GC but allows the ability to work in a liquid medium which suppresses the volatility limit of GC. The only weakness of the method resides in the identification point of view, where the MS coupling should give a good answer. The SFC should also give good results.

6.4 SPECTROSCOPIC ANALYSES

Of spectroscopic methods, IR and ^{1}H NMR and ^{13}C NMR have been the analytical techniques most commonly applied for whole pyrolysis oils. Direct MS techniques have been used in some studies.

IR spectroscopy was employed for the pyrolysis oils by *Elliott* [1983, 1985], *Churin et al.* [1989], *Achladas* [1991], *Besler et al.* [1994] and *Williams and Taylor* [1989]. Churin et al. took IR spectra in a FT-IR spectrometer Bruker IFS 88 as a film on NaCl plates after the evaporation of the carrier solvent. Achladas recorded IR spectra on a Beckman IR 8-A spectrophotometer in $CDCl_3$ and THF.

Functional group determination of oils can be performed by IR spectroscopy. The oils have been found to be complex with carboxylic acids, alcohols, alkanes, alkenes, phenols, aromatic and polyaromatic, ketones and aldehydes being identified. The IR spectra obtained in the studies resembled significantly each other. According to *Churin et al.* [1989] the IR spectra showed signals distributed in two zones: between 3 600 cm^{-1} and 2 800 cm^{-1} and between 1 800 and 1 000 cm^{-1}. In *Elliott's* studies [1985, 1994b] IR was found to be of limited use for analysing whole oil products.

In all studies, O-H stretching vibrations were observed at 3 200 - 3 600 cm^{-1}, indicating water and free phenolic. C-H stretching vibrations were found at 2 800 - 3 200 cm^{-1} indicating alkane and alkene groups, C-H deformation vibrations at 1 350 - 1 475 cm^{-1} indicating alkene [10, 6, 83, 73, 74], C=O stretching vibrations with absorbance at 1 700 - 1 750 cm^{-1}, and C=C alkenes at 1 575 - 1 675 cm^{-1} [6, 83, 73, 74]. In addition, aromatic (1 500, 1 600, 1 680 cm^{-1}) [*Churin et al.* 1989, *Achladas* 1991], and single, polycyclic and substitute aromatic groups (675 - 900) [*Williams & Taylor* 1989] were found. FT-IR absorbance frequency, spectra

representing functional group, compositional analysis of the waste-derived oils compared with crude petroleum oil from the North Sea Brent field are shown in Figure 25.

NMR techniques have not been applied for pyrolysis oils until in the recent years. NMR is a powerful technique for the study of complex mixtures and is hence very suitable for pyrolysis oils in determining aliphatic and aromatic groups in the oils. NMR (^{1}H NMR and ^{13}C NMR) has been used for bio-oils by *McKinley* [1989], *McKinley and Barrass* [1988], *Churin et al.* [1989], *Achladas* [1991] and *Besler et al.* [1994].

McKinley [1989] studied NMR as a tool for characterisation of oils from numerous biomass liquefaction processes. The ^{1}H NMR spectra were recorded on samples dissolved in deuterated acetone with TMS as the external lock. The instrument was a Varian XL-300 spectrometer operating at 300 MHz in the Pulse Fourier Transform Mode. The ^{13}C NMR spectra were recorded on the same solutions as the ^{1}H spectra using a Varian XL-300 spectrometer at a frequency of 75 MHz with gated decoupling and without Nuclear Overhauser effect (NOE). The spectra were subdivided into broad assigned areas. The assignments for the ^{1}H and ^{13}C NMR spectra are shown in Tables 24 and 25.

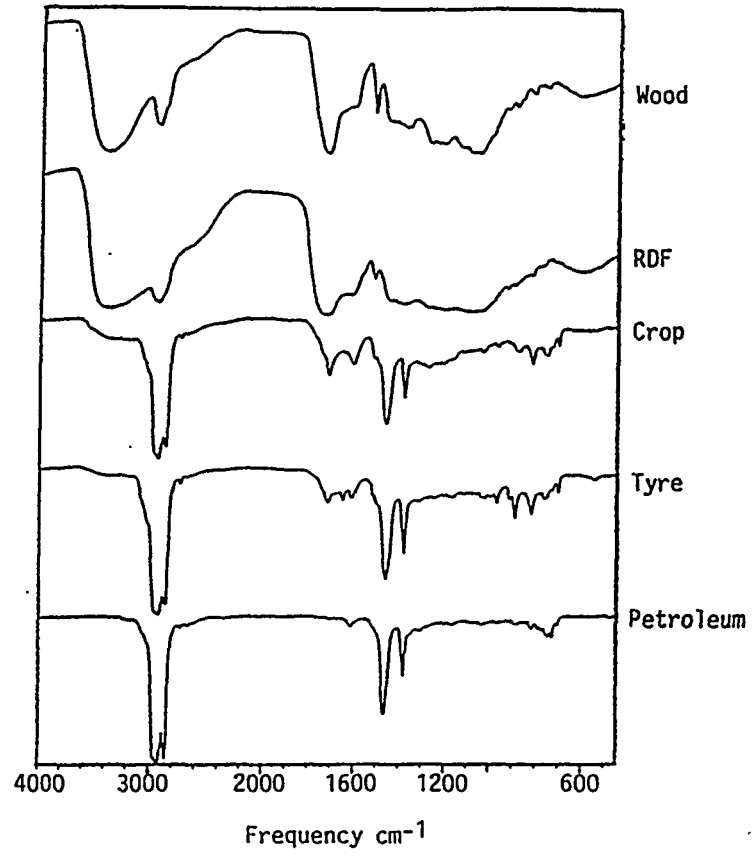

Figure 25. FT-IR spectra of pyrolytic oils [Williams & Taylor 1989].

Table 24. Approximate sub-division of spectra into proton chemical shift regions [McKinley & Barrass 1988].

Chemical shift region, ppm	Main assignments
0 - 1.6	Hydrocarbon protons
1.6 - 2.2	H-Aliphatic OH
2.2 - 3.0	H-Aromatic OH
3.0 - 4.2	H-Methoxyl
4.2 - 6.4	H_α, H_β in β -0-4, etc.
6.4 - 6.8	H-Aromatic Syringyl
6.8 - 8.0	H-Aromatic Guaiacyl
8.0 - 10.0	H-Carbonyl/Carboxyl

Table 25. Approximate sub-division of spectra into carbon-13 chemical shift regions [McKinley & Barrass 1988].

Chemical shift region, ppm	Main contributing structures
0 - 50	Alkyl
50 - 100	C-O-alkyl or C-O-aryl
100 - 163	Aromatic and vinyl
100 - 110	Syringyl
112 - 125	Guaiacyl
125 - 156	Quaternary aromatic
163 - 210	Carboxylic/Aldehydic

As the basis of these results both ^{13}C and ^{1}H NMR can be used for characterising biomass liquefaction oils. ^{13}C was found to be more useful than ^{1}H NMR because of the absence of not only a resonance from water but also the effects of water in exchange of acidic protons, which cause shifts in the observed resonances. ^{13}C NMR could be used for comparing products derived from the same process, but also for comparing samples originating from different liquefaction procedures. With ^{13}C NMR the product distribution of a bio-oil in the broad categories of alkyl, aromatics, C-O-, and carbonyl can be expressed. Later, *Churin et al.* [1989] determined the aromaticity and structure of the bio-oil. They used a Bruker spectrometer operating in the Pulse FT Mode without NOE. The spectrum obtained was divided into several regions characteristic of various carbon types. *Achladas* [1991] used for ^{1}H NMR a Varian T-60 NMR spectrometer in $CDCl_3$, tetramethylsilane as internal standard. ^{13}C NMR spectra were obtained on a Bruker WP-80 NMR spectrometer in $CDCl_3$ - TMS. The ^{1}H NMR spectra contained two major regions of signals around δ 1 - 5 ppm and δ 6 - 9 ppm, due to aromatic and aliphatic protons, indicating concentrations of methoxyl or other alkyl and aryl ethers.

Mass spectrometry has been shown to be extremely useful in the direct analysis of complex mixtures of organic compounds. Techniques such as molecular-beam

mass spectrometry (MBMS) and tandem mass spectrometry (MS/MS) give valuable information on the composition of complex samples, and thus on biomass-derived pyrolysis oils too, rapidly and efficiently. MS/MS technique has been investigated to a limited degree, and further development is required, especially for higher-MW components [*Elliott* 1994b]. Direct MS studies for biomass pyrolysis products and oils have been carried out by *Milne et al.* [1984], *Evans and Milne* [1987a, 1987b, 1988], *Moore et al.* [1988] and *Desbene et al.* [1989].

Evans and Milne [1987a] indicated that MBMS can successfully be used to obtain information on chemicals derived from wood pyrolysis. Fast pyrolysis / molecular-beam sampling / mass spectrometer were used at NREL for the study of fundamental pyrolysis processes and found to be a useful tool for analytical pyrolysis too. The schematic of the system is shown in Figure 26. They described the technique of free-jet MBMS sampling for real-time studies of pyrolysis at high temperatures and atmospheric pressure. The fundamental transformations that occur in solid-phase (primary) pyrolysis and the subsequent sequential (secondary and tertiary) gas-phase transformations as a function of reaction conditions were determined. With MBMS, a wide range of products, including low-MW products, such as methane; reactive species (coniferyl alcohol), thermally labile products

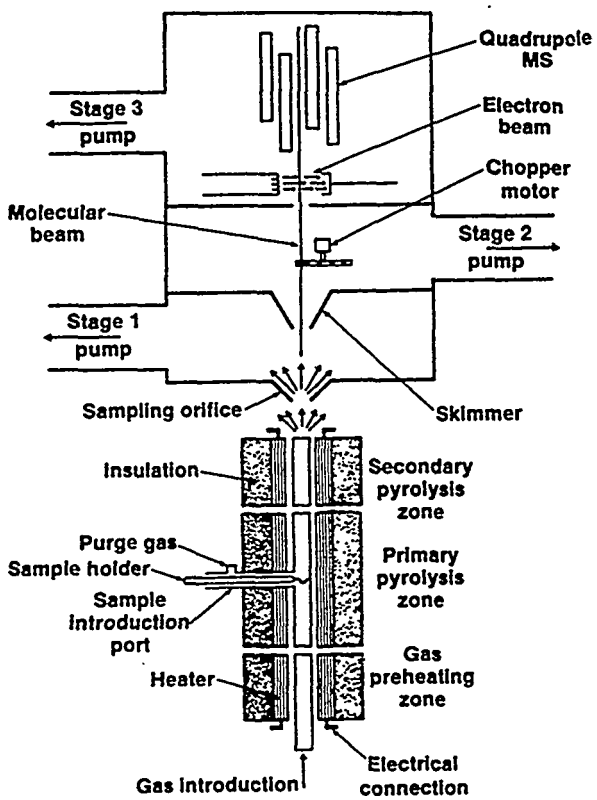

Figure 26. Schematic of pyrolysis vapor generator coupled to a molecular-beam mass spectrometer sampling system [Evans & Milne 1987a].

(levoglucosan); and high-MW products (polynuclear aromatic hydrocarbons), were detected.

The two major disadvantages of the MBMS technique are difficulty in quantitative determinations due to mass discrimination in the molecular beam and variation in ionisation sensitivities and the ambiquity in structure assignment based on only the ion mass [*Milne et al.* 1984].

Applications of MBMS for practical conversion processes were reported later by *Evans and Milne* [1987b]. The topics of the studies were wood-derived pyrolysis oil characterisation, control of primary oil composition, upgrading of oil by thermal cracking, by subsequent pyrolysis in reactive environments, and by direct catalytic conversion, and nature of gasifier condensible species and combustion products. Gas-phase pyrolysis of wood-derived vapours in methane showed that olefins were enhanced. Direct catalytic upgrading of vapours over zeolites showed complete conversion of the primary products. MBMS studies of wood vapour and model compounds over an HZSM-5 zeolite gave hydrocarbon yields of 18±4 wt% of wood, with equal amounts of light olefins and aromatics [*Evans & Milne* 1988]. To obtain yield estimates, methods of calibration were implemented. Screening of model compounds showed that the methoxyphenols, derived from lignins, gave low yields of hydrocarbons, while carbohydrate-derived ring structures, such as furfural and α- angelicalactones, were good sources of light aromatics.

A rapid and useful MS method has been developed by *Moore et al.* [1988] to analyse pyrolytic oils and to compare oils originated from different sources. The oil samples were directly introduced into the chemical ionisation source of a tandem mass spectrometer, in which they were vapourised in a plasma of isobutane using a temperature-programmed direct injection probe. The total ion current, composed mostly of parent-molecular ions, was monitored as a function of temperature by repetitively scanning the mass spectrometer. The thermograms obtained can be used to characterise and compare the oils. The individual compounds observed in the thermogram can be identified by recording the MS/MS spectra of the corresponding ions. The spectra were obtained on a Kratos MS-50 TCHM triple analyser mass spectrometer arranged in a C-shape E_1BE_2 geometry.

In the direct MS analysis of complex mixtures, the choice of suitable ionisation process and conditions is important. Two methods have frequently been used; electron ionisation (EI) using low-energy electrons, and chemical ionisation (CI) using a suitable reagent gas. CI has been found to have many advantages in the analysis of pyrolytic oils [*Moore et al.* 1988]. *Desbene et al.* [1989] have studied pyrolysis of wood and its constituents cellulose and lignin directly by MS under different ionisation conditions. They found that different ionisation techniques (NH_3, N_2, NH_3+N_2) for the MS analysis of primary products led to similar pyrograms. Another important parameter in the direct analysis is the determination of the optimum temperature at which the sample should be vapourised into the ion source of the mass spectrometer [*Moore et al.* 1988].

6.5 TOXICOLOGICAL ANALYSES

Biomass-based pyrolysis oils have been found to be complex and contain hundreds of different organic compounds. Hence, the health and safety factors of the oils are of utmost significance. It is important to determine their impacts on the environment when transporting, storing and processing them, and on the people working with them and using them.

Toxicological analyses have been performed for pyrolysis oils only by some researchers, e.g., by *Elliott* [1987] and *Gratson* [1994]. The toxicological impact of bio-oils concerns, in particular, the content of polynuclear aromatic hydrocarbons (PAH). PAH compounds have been analysed and detected in pyrolysis oils by *Elliott* [1987], *Elliott et al.* [1988], *Evans and Milne* [1987a], *Pakdel and Roy* [1990] and *Williams and Besler* [1994]. The content of PAH compounds is highly affected by pyrolysis conditions, such as temperature and residence time, and by biomass feedstock.

Elliott [1987] carried out a comparative analysis of biomass pyrolysis and gasification condensates. Of pyrolytic processes, three entrained-flow pyrolyses (Georgia Tech; SERI, primary oil; SERI, cracked oil) were included in the study. Initial biological testing, including Ames assays and mammalian-cell carcinogenity assays, was performed for the samples. Toxicological activity was found only in high-temperature tars. Mutagenic activity in the gasification/pyrolysis condensates varied depending on process conditions and correlated strongly with the concentration of high-MW PAH compounds. Low-temperature flash pyrolysis oils contained no PAH, while flash pyrolysis oils produced at high temperatures (above 700 °C) contained high concentrations of PAH. The compounds included naphthalene, phenanthrene, fluoranthene, pyrene, benzanthracenes, and benzopyrenes. When analysing pyrolysis products from fast pyrolysis of wood with MBMS, *Evans and Milne* [1987a] showed that primary pyrolysis oils contained only small concentrations of PAH, but secondary cracking reactions of the vapours at high temperatures increased the concentrations of PAH. For example, naphthalene, anthracene, phenanthrene, fluorene, pyrene, benzofluoranthenes and benzopyrenes were identified.

PAH contents of pyrolysis oils derived from wood waste, municipal solid waste and rice husks have been analysed by *Williams and Besler* [1994] (Chapter 5.4.2). The oils were found to contain substantial concentrations of PAH, comprising mainly naphthalene, fluorene and phenanthrene, and their alkylated substituents. The oils were reported to contain also some species of known carcinogenic or mutagenic activity, e.g., methylfluorenes, phenanthrene, methylphenanthrenes, chrysene and methylchrysene. According to Williams and Besler the waste-derived pyrolysis oils may hence be deemed a potential health hazard.

Gratson [1994] recently carried out a toxicological testing of two whole-wood oils produced in the Vortex Pyrolysis reactor of NREL. The tests included dermal toxicity, eye irritation, inhalation toxicity and Ames mutagenicity. The dermal and the inhalation acute toxicity test evaluates the potential of a material to cause systematic toxicity or death with skin contact and/or vapour inhalation. The Ames testing is a preliminary assessment of the potential of the test material to induce genetic toxicity. The results indicated the acute concern to workers in potential contact with biomass-derived pyrolysis oils. The results of dermal toxicity showed that the bio-oils have little potential for crossing the skin barrier. Mutagenicity was also seen. As a conclusion of these results the oils can be handled safely on a routine basis with commonly used safe work practices, including the use of readily available personal protective equipment.

6.6 SUMMARY OF CHARACTERISATION OF WHOLE OILS

Due to the complexity of pyrolysis oils, characterisation of whole oils has not been applied as widely as analysis after fractionating the oils.

For whole oils, GC methods have been applied only limitedly. LC methods have been found to be more applicable for these oils and, in particular, HPSEC has proved to be a useful method of characterising oils in terms of their molecular weight distribution, especially when studying the changes occurring in ageing and in upgrading of pyrolysis oils. In the determination, PL gel columns, solvent THF and calibration with polystyrene standards have been used. However, calibration of the method has proved to be troublesome.

Of spectroscopic methods, FT-IR, FT-NMR (^{1}H and ^{13}C) and direct mass spectroscopic techniques have been the most important ones. Functional group determination can be performed with IR. NMR has proved to be an efficient technique for the study of complex mixtures such as pyrolysis oils when determining aromatic and aliphatic groups. Direct mass spectrometric techniques, such as MBMS and MS/MS methods, are rapid, interesting and efficient tools in characterising pyrolysis primary products, in subsequent upgrading of vapours and in studying the pyrolysis process itself.

Health and safety aspects and toxicological properties have been investigated only to a limited extent. However, the interest in studying these is increasing as the pyrolysis processes are developing and the application alternatives are increasing.

7 CONCLUSIONS

The physical and chemical properties and the chemical composition of biomass-derived pyrolysis oils are important factors in terms of utilisation, behaviour, upgrading, handling and storage of the oils. The most important physico-chemical properties or fuel oil analyses for the bio-oils are water content, acidity, density, viscosity, heating value, inorganics content and stability. In their determinations, standard methods, as such or as modified, and, in addition self-developed methods have been used. The standard methods are not often suitable as such for biomass-derived pyrolysis oils. The analytical methods of bio-oils should be standardised in order to be able to compare different bio-oils.

The chemical composition of pyrolysis oils is very complicated, comprising mainly decomposition products of carbohydrates and lignin. Almost all oxygen containing chemical groups are present in the oils. The oils consist of different acids, aldehydes, anhydrosugars, alcohols, phenolic compounds, esters, and hydrocarbons. In addition, they contain a significant amount of high-molecular-mass, apparently lignin-derived substances. The oils also contain a large amount of water. The physical and chemical nature of bio-oils varies with feedstock, process conditions, and recovery techniques. Hence, the properties and composition of the bio-oils differ from those of the raw oil-based liquid fuels.

Characterisation of pyrolysis oils has been a challenge to researchers and has been studied at many universities and research institutes in North America and Europe in the 1980s and 1990s.

Fractionation of the oils prior to analysis has been found more favourable than analysis of the whole oils. Fractionation produces different fractions that are more easy to analyse, being less complicated than the whole oils. Solvent extraction and adsorption chromatography methods are the most general methods used in fractionation. The oils have often been separated in acidic, phenolic, basic, hydrocarbon and aqueous fractions or in water-soluble and water-insoluble fractions. In addition to facilitating the analysis, fractionation is useful in terms of production of chemicals or chemical groups. The various fractions have then been subjected to a variety of chromatographic and spectroscopic methods. The analytical methods can give information on the entire sample, for example, HPSEC, FT-IR, FT-NMR, or on specific portions, such as volatiles by GC and GC/MS. However, the fractions have most often been analysed with GC/MS technique, which is suitable for these fractions. However, to characterise the high-molecular-weight and highly polar fractions or constituents of the fractions, other techniques such as LC methods, and IR and NMR spectroscopic techniques, have to be used. HPSEC has proved to be useful in giving information on the molecular weight distributions of the fractions, and FT-IR and FT-NMR on functional groups and aliphatic and aromatic structures and ratios.

For whole oils, GC methods have only been used to a limited extent. Other methods, such as LC methods (for example, HPSEC), FT-IR, FT-NMR (^{1}H and ^{13}C) and direct MS techniques (MBMS, MS/MS) have been found to be more applicable for these oils, because they characterise the whole part of the oils. Direct MS techniques are rapid and interesting methods of characterising the pyrolysis primary products, and in investigating upgrading of vapours and the pyrolysis process mechanisms.

Due to the complicated nature of biomass-based pyrolysis oils and the limitations of different analysis techniques, the chemical characterisation of the oils requires the use of different spectroscopic and chromatographic methods. The physico-chemical properties and the chemical composition of the oils should be studied together and support each other when trying to understand the nature and behaviour of the biomass-based pyrolysis oils in process, applications and upgrading studies.

8 RECOMMENDATIONS

The aim was to find and select, on the basis of this review, a suitable analytical system to be tested and used at VTT Energy for rapid thermal pyrolysis oils. The oils would be used for diesel and boiler fuel applications. Standard fuel oil analyses and their modifications have already been tested for different oils, and recommendations are given elsewhere [*Oasmaa et al. 1995*].

The choice of analytical methods for pyrolysis oils is greatly affected by the aims and needs of characterisation. The aim of the chemical characterisation work at VTT is to determine the nature and the composition of the oils and the effects of different factors like raw material, process conditions and oil recovery system on these, to understand the chemical behaviour of the oils in processing, upgrading, handling and storing the oils, and to solve the problems due to, for example, acidity, reactivity and unstability of the oils.

There are a wide range of different analytical methods to be chosen. The method to start the characterisation should not be too complicated, but rather a relatively simple and fast method. There should be a possibility and readiness to change methods in the progress of the work. Prior to the experimental analytical work on the oils it is impossible to make such a straightforward and definite choice. The analysis system will be applied to all the bio-oils to be studied, but if necessary it will be tailored and modified for use for certain oils, for example, for those derived from different feedstocks or upgraded in different ways.

Due to the complicated nature of the oils, fractionation prior to analysis is recommended. The fractionation should not be too complicated and time-consuming. It is recommendable to divide the oil into four or five different fractions by solvent extraction techniques. The solvents can differentiate, for example, as to polarity and can be, for example, hexane, dichloromethane, diethyl ether, tetrahydrofuran and methanol to separate aliphatic hydrocarbons, aromatics, phenolics and more polar compound groups. The fractions obtained can then be analysed with GC/MS after and without derivation such as silylation, and with FT-IR and FT-NMR.

Another alternative is to fractionate the pyrolysis oils with water into water-soluble and water-insoluble fractions. The oil-water-ratio has to be found experimentally, because it varies in the studies reviewed. The water-soluble fraction is suggested to be analysed by GC/MS after and without derivations. The low-molecular-mass carboxylic acids can be analysed as their benzyl esters by GC and other hydrophilic compounds like carbohydrates as their per(trimethylsilylated) derivatives. The water-soluble fraction can also be analysed by applying solvent extraction. The water-insoluble fraction can, if possible, be further fractionated with different solvents (hexane, dichloromethane, diethyl ether, methanol) and the fractions analysed further with GC/MS, FT-IR and FT-NMR, too. A suitable technique based on molecular mass should be found for this insoluble fraction. It

should also be useful when comparing the oils and studying the stability properties of the oils. Furthermore, the pyrolysis GC/MS can be of help when studying the character of the insoluble fraction.

With these techniques the oils might be analysed qualitatively and at least partly quantitatively to get a picture of the nature of the oils. If an exact determination of the composition is required, the oil should be fractionated into several fractions, preferably by adsorption chromatography.

It is also important to study health and safety factors in terms of handling the oils. The toxicity tests like Ames should be carried out for whole pyrolysis oils. A detailed analysis of the PAH compounds when needed should be carried out after fractionation of the aromatic hydrocarbon fractions with adsorption chromatography.

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Chemical composition of vacuum pyrolysis oil derived from *Populus deltoïdes* (Run # C025)

Fraction*	Composition	wt.%
1-3	Hydrocarbons	0.71
4	4-Methoxyphenol; 2-Methoxy-4-methylphenol; Eugenol; 2-Methoxy-4-ethylphenol; 2-Methoxy-4-propylphenol; Methyl hexadecanoate	0.41
5	Furancarboxylic acid methyl ester; 4-Methylphenol; 3,4-Dimethylphenol; 1,2-Dimethoxybenzene; 2-Methoxy-4-methylphenol; 5-Methoxy-2,3-dimethylphenol; 2-Methoxy-4-ethylphenol; Isoeugenol; 2-Methoxy-4-propylphenol; 3-Methoxy-methylbenzoate	0.29
6	1-(2-Furanyl)ethanone; Phenol; 3-Methylphenol; Methyl 2,4-hexadienoate	0.32
7	3-Methyl-2(5H)-Furanone; 2,6-Dimethoxyphenol; 1,2,3-Trimethoxy-5-methylbenzene; 1,2,3-Trimethoxybenzene; 1-(2-Hydroxy-5-methoxyphenol)ethanone; 4-Hydroxy-3-methoxy-methylbenzoate; 1-(2,6-Dihydroxy-4-methoxyphenyl)ethanone; 2,6-Dimethoxy-4-(2-propenyl)phenol	0.33
8	2(3H)-Furanone; 3-Methyl-3-penten-2-one; 2H-Pyran-2-one; 4-Oxo-methylpentanoate; 3-Methyl-2(5H)-Furanone; 2,5-Dimethyl-2,4-dihydro-2H-pyrazol-3-one; 1-(1-cyclohexen-1-yl)ethanone; 2,3,4-Trimethyl-2-cyclopenten-1-one; Dimethyl-pentanedioate; 5-Methyl-4-hexene-3-one; 4,5-Dimethyl-2-cyclohexen-1-one; 2,6-Dimethoxyphenol; Vanilline; Trimethoxy-benzene; 1-(4-Hydroxy-3-methoxyphenyl)ethanone; 1-(3,4-Dimethoxyphenyl)ethanone; 3-Methoxy-4-hydroxy-benzenacetate; 1-(2-Hydroxy-5-methoxyphenyl)propanone; 1-(2-Hydroxy-5-methoxyphenyl)butanone; 2-6-Dimethoxy-4-(2-Propenyl)phenol; 3,4,5-Trimethoxymethylbenzoate	0.92
9	Propionic acid; Butenoic acid; 2,5-Hexanedione; 3-Methyl-2-cyclopenten-1-one; Hexanoic acid; N-methyl-2-propanamine; 3-Methyl-1,2-cyclopentanedione; 2,4,5-Trimethyl-2,4-dihydro-3H-pyrazol-3-one; Furan carboxylic acid methyl ester; Benzoic acid; 1,2-Benzendiol; 1-(2,4-Dihydroxyphenyl)ethanone; 4-Methoxybenzoic acid; 1-(4-Hydroxy-3-methoxyphenyl)ethanone; 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone; 4-Hydroxy-3,5-dimethoxybenzaldehyde; Heptadecanoic acid	1.63

Fraction*	Composition	wt.%
10	Carbonic acid, ethyl-2-propenyl ester; 3-Methyl-2-hydroxy-2-cyclopenten-1-one; 3-Methyl-2-butanone; 1,2-Benzendiol; 3-(1-Methylethyl)-2,4-pentanedione; Methyl 3-hydroxybenzoate; Ethyl-1,3-benzendiol; 3-Methoxybenzaldehyde; Methyl 2-hydroxybenzoate; Methyl 3-methoxybenzoate; 1-(4-Hydroxy-3-methoxyphenyl)ethanone; 1-(4-Hydroxy-3,5-dimethoxy-phenyl)ethanone; 3,5-Dimethoxy-4-hydroxybenzaldehyde; Methyl α-phenylbenzoate; Octadecanoic acid	0.78
11	3-Methyl-1,2-cyclopentanedione; 1,4-Cyclohexadione; 1-(2-Hydroxy-5-methoxyphenyl)ethanone; 1,2-Benzenediol; 3-(1-Methylethyl)-2,4-pentanedione; 4-Hydroxybenzaldehyde; 2-Hydroxybenzoic acid hydrazide; 7-Hydroxy-(2H)-1-benzopyran-2-one; 7-Methoxy-(2H)-1-benzopyran-2-one; 3-Methyl-1-(2,4,6-trihydroxy-3-methylphenyl)butanone; [1,1'-Biphenyl]-4,4'-diol-3,3'-dimethyl	0.53
12*	1,2-Ethanediol; 1,1'-Oxybisethene; 3-Hydroxycyclohexanone; 1,2-Cyclohexanedione; Methyl 3-hydroxybutanoate; 2,3-Butanedione monoxime; Methyl-3-oxo-butanoate; Ethenylbutanoate; 2-Propenylbutanoate; Ethyl 2-methyl-2-propenoate; 4-Methoxy-2,3-dimethylbutylaldehyde; 2,2-Dimethyl-1-butanol; 2,2-Dimethyl-1-butanol; 3-Hydroxycyclohexanone; 2,3-Dihydro-5-methyl-(5H)-1,4-dioxepin; 4-Octanone; 1,4-Benzenediol; Methyl 2-hydroxy-4-methylpentanoate; Propyl 2-methylhexanoate; Tetrahydro-2-furanmethanol; Cineole; 2,2-Dimethyl-1-octanol; 2-Propenyl hexanoate; 2-Octanone; 6-Methyl-5-(1-methylethyl)-5-hepten-3-yn-2-one; 3-Hydroxycyclohexanone; 3-Hydroxybenzoic acid; 1-Cyclopropyl-2-propanone; 3,4,5,6,7,8-Hexahydro-4,7-dimethyl-(2H)-1-benzopyran-2-one; Heptylhexylether; 4,6-Dimethoxy-3(2H)-benzofuranone; 1-(2,4,6-Trihydroxy-3-methyl)-1-butanone	22.3
13**	1,2-Ethanediol; 1,2,3-Propanetriol; 6-Oxabicyclo[3,1,0]hexan-2-one; 2-Methyl-2-butenediamide; N,N-bis(1-methylethyl)-1,2-ethanediamine; 3-Pyrolidinol; Methyl carbonate	29.1
14	Not analyzed	3.2
Water***		32.8
Acids		18.2
Total		111.52

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Title

Chemical and physical characterisation of biomass-based pyrolysis oils

Literature review

Abstract

Biomass-based pyrolysis oils are complex mixtures of mainly organic compounds and water. The determination of their physical and chemical properties and chemical composition is a challenge for researchers. Characterisation of biomass pyrolysis oils has been studied at many universities in North America and Europe in the 1980s and 1990s. The existing literature on the analytical methods used for these oils is reviewed in this report.

The physico-chemical properties, such as water content, acidity, density, viscosity, heating value and stability, are important in terms of utilisation, storage and handling of oils. In the analyses, standard methods as such or as modified and, in addition, self-developed methods have been used. Standard fuel oil analyses are not often suitable as such for biomass-based pyrolysis oils.

For characterising the chemical composition, the bio-oils have first been mainly fractionated into different classes. Solvent extraction and adsorption chromatography are the most general methods used. In solvent extraction, the oils have often been divided into acidic, phenolic, basic, hydrocarbon and aqueous fractions or water-soluble and -insoluble fractions. In adsorption chromatography, the oils have been fractionated into different hydrocarbon and polar fractions. The fractions obtained have been analysed with various chromatographic and spectroscopic methods. Gas chromatography/mass spectrometry (GC/MS) technique is the analytical method most widely used and well adaptable for the fractions. For high-molecular-mass and highly polar compounds liquid chromatographic (LC) techniques as well as infrared (FT-IR) and nuclear magnetic resonance (1H NMR and 13C NMR) spectroscopies are more suitable due to the low volatility of pyrolysis oils.

For whole pyrolysis oils, LC techniques, primarily size exclusion chromatography and FT-IR and FT-NMR spectroscopies have proved to be useful methods, giving information on molecular weight, functional groups and aliphatic and aromatic structures and ratios. Direct mass spectrometric techniques (MS), such as molecular-beam MS and MS/MS, are rapid and interesting tools for the characterisation of the oils and for the investigation of the pyrolysis process.

In-depth characterisation of the complicated organic composition of pyrolysis oils requires the use of various techniques. The oils contain organic compounds such as acids, aldehydes, anhydrosugars, alcohols, phenolic compounds, esters and hydrocarbons, and, in addition, high-molecular, apparently lignin-derived substances, depending on feedstock, process conditions and recovery techniques.

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