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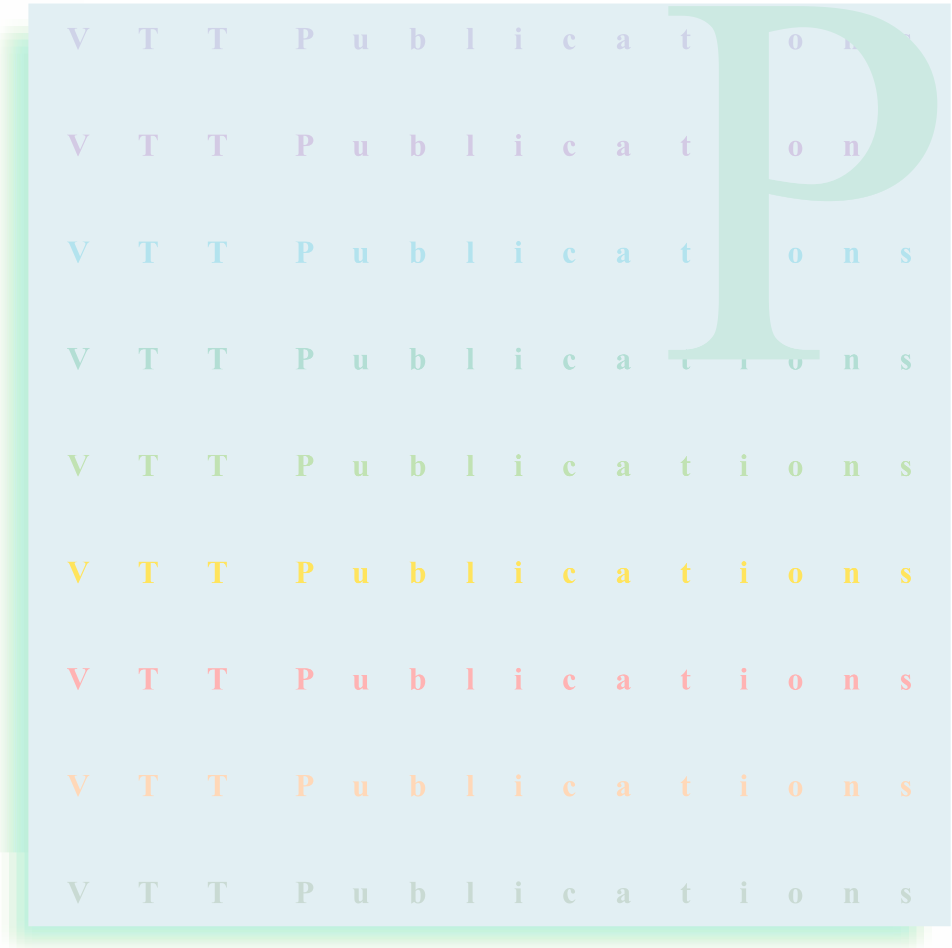
Anja Oasmaa & Cordner Peacocke

A guide to physical property characterisation of biomass-derived fast pyrolysis liquids



TECHNICAL RESEARCH CENTRE OF FINLAND ESPOO 2001

VTT PUBLICATIONS 450

A guide to physical property characterisation of biomass-derived fast pyrolysis liquids

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TECHNICAL RESEARCH CENTRE OF FINLAND
ESPOO 2001

ISBN 951–38–5878–2 (soft back ed.)
ISSN 1235–0621 (soft back ed.)

ISBN 951–38–6365–4 (URL:http://www.vtt.fi/inf/pdf)
ISSN 1455–0849 (URL:http://www.vtt.fi/inf/pdf)

JULKAISIJA – UTGIVARE – PUBLISHER

Valtion teknillinen tutkimuskeskus (VTT), Vuorimiehentie 5, PL 2000, 02044 VTT
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Technical editing Maini Manninen
Text preparing Tarja Haapalainen

Otamedia Oy, Espoo 2001

Oasmaa, Anja & Peacocke, Cordner. A guide to physical property characterisation of biomass-derived fast pyrolysis liquids. Espoo 2001. Technical Research Centre of Finland, VTT Publications 450. 65 p. + app. 34 p.

Keywords pyrolysis liquid, biomass, fast pyrolysis, physical properties, fuel oil properties, test methods, characterization, homogeneity, sampling, specifications

Abstract

This publication is a revised and updated version of VTT Publication 306: Physical characterisation of biomass-based pyrolysis liquids, issued in 1997. The main purpose of the on-going study is to test the applicability of standard fuel oil methods developed for petroleum-based fuels to biomass-derived fast pyrolysis liquids. New methods have also been tested and further developed to extend the range of properties that may be accurately determined. The methods were tested for pyrolysis liquids derived from hardwood, softwood, forest residue and straw. Recommendations on transport, liquid handling and analyses are presented. In general, most of the standard methods for fuel oils can be used as such, but the accuracy of the analyses can be improved by minor modifications. Homogeneity of the liquids is a critical factor in the accurate analyses, and hence procedures for its verification are presented.

Preface

VTT (Finland) has had a central role in analysing both liquid and solid fuels for the Finnish industry for over two decades. Considering these experiences, the standard fuel oil analyses developed for petroleum-based fuels were applied to pyrolysis liquids. This original study was published as VTT Publication 306 (http://www.inf.vtt.fi/pdf/publications/1997/P306.pdf) on physical characterisation of biomass-based pyrolysis liquids, issued in 1997. In this publication, the former study has been expanded to include more feedstocks, analyses and developments in test methods from other sources to encompass as many properties of the liquids as possible. Additional information on health and safety are also summarised. At Aston University, special analyses, e.g. specific heat capacity and conductivity, have been carried out by C. Peacocke, who presently works in a consulting company Conversion And Resource Evaluation Ltd. (CARE). This company is a small to medium size enterprise operating since 1996 in the thermal conversion of biomass and wastes for energy, chemicals and speciality derived products. The focus of CARE's work has been on small-scale gasification, fast pyrolysis, and the techno-economic assessment of such systems for fuels and chemicals. In this revised report, the test results are summarised and instructions for liquid handling are suggested.

Special thanks are due to Stefan Czernik (NREL, USA) for the review of the publication and valuable comments. The authors wish to acknowledge Dietrich Meier (IWC, Germany), Tony Bridgwater (Aston University, UK) and other members of the Pyrolysis Network for Europe (PyNe) for their valuable conribution and comments during the work. The valuable discussions with Steven Gust (Fortum, Finland) are greatly acknowledged. The VTT project was funded by the National Technology Agency (Tekes). Analytical work at VTT was carried out by Eija Tapola, Raili Silvasti, Jaana Korhonen, Eeva Kuoppala, Päivi Koponen, Paula Käyhkö, Sirkka-Liisa Huru, and Kaisa Lanttola. Maija Korhonen's contribution is warmly acknowledged for editing the report.

Espoo, December 2001

Authors

Contents

1. Introduction

Biomass pyrolysis liquids differ significantly from petroleum-based fuels in both physical properties and chemical composition. These liquids are typically high in water and solids, acidic, have a heating value of about half of that of mineral oils, and are unstable when heated, especially in air. Pyrolysis liquids are highly polar containing about 50 wt% oxygen (~ 40 wt% of dry matter), while mineral oils contain oxygen in ppm levels. Pyrolysis liquids are therefore highly oxygenated and are unlike conventional mineral oils. The unusual properties of the liquids must therefore be taken into careful consideration in the determination of fuel oil qualities and chemical applications for the liquids. For fuel applications, the present consensus from end users on significant liquid properties for combustion applications are stability, homogeneity, water lower heating value, viscosity, liquid density, solids content and to a limited extent chemical composition. Depending on the physical property values, the suitability of the liquid for use in a boiler, engine or turbine application can be assessed. For non-fuel applications, other properties may of interest [number of phases, pH, detailed chemical composition]. Due to these differences, the standard fuel oil methods developed for mineral oils are not always suitable as such for pyrolysis liquids. Elliott [1983] and McKinley et al. [1994] have previously addressed the importance of the reliability of the analytical methods. The typical properties of pyrolysis liquids from different feedstocks are given in Table 1. [Agblevor et al. 1996, Sipilä et al. 1998, Radovanovic et al. 2000].

Research on analysing physical properties of pyrolysis liquids has been carried out since the 1980s at PNL, USA [Elliott 1983], NREL (formerly SERI), USA [Chum & McKinley 1988, Milne et al. 1990, Czernik et al. 1994], and at the former B.C.Research, Canada [McKinley 1989, McKinley et al. 1994]. Rick and Vix [1991] published one of the few reviews on product standards for pyrolysis liquids. Fagernäs [1995], Oasmaa et al. [1997], Meier et al. [1997] and Oasmaa & Meier [Brigdwater et al. 1999 and 2001] have published up-to-date data on physical properties of pyrolysis liquids. Elliott [1983] and Diebold et al. [1997] have proposed fuel oil specifications for pyrolysis liquids.

Several round robins have been carried out in order to assess the relevant analytical procedures for pyrolysis liquids's analyses. The first IEA (International Energy Agency) thermochemical round robin was organised in 1988 as part of the IEA Voluntary Standards Activity led by B.C. Research [McKinley et al. 1994]. Two separate round robins were initiated in 1997: one within EU PyNe (Pyrolysis Network) and the other within IEA PYRA (Pyrolysis Activity). The objective of the EU PyNe round robin was to compare existing analytical methods without any restrictions. The main objective of the IEA PYRA round robin was to determine the interlaboratory precision and methods applied for elemental composition, water, pyrolytic lignin and main compounds. The latest round robin was carried out by 12 laboratories during January - March 2000. The aim was to compare the analyses, not the pyrolysis liquids. Instructions for analyses were given. [Bridgwater et al. 2001]

Based on these round robins following conclusions were drawn: liquid sample handling plays a very important role, the precision of carbon and hydrogen is very good, oxygen by difference is variable and oxygen by direct determination is poor, water by Karl-Fischer titration is accurate but should be calibrated by water addition method, accuracy of density is good, high variations were obtained for nitrogen, viscosity, pH, and solids, the methods for the determination of pyrolytic lignin and measuring stability of the liquid should be improved, [Bridgwater et al. 2001]

This publication is an updated version of a study on testing and modifying standard fuel oil analyses [Oasmaa et al. 1997]. Additional data has been included to address the wide spectrum of properties that may be required in different applications and to assist in the design of process equipment and power generation systems.

Table 1. Pyrolysis liquids properties from different feedstocks.

	Source					
Physical property	Ensyn	NREL (hot-gas filtered)	NREL	VTT	VTT	VTT
Feedstock	Mixed hardwood	Poplar	Switch grass	Pine	Straw	Forest residue*
Water, wt%	22.0	18.9	n.d.	16.6	19.9	24.1
pH	2.5	2.8	n.d.	2.6	3.7	2.9
Density (at 15°C), kg/dm^3	1.18	1.20	n.d	1.24	1.19	1.22
Elementals (dry), wt%						
- C	56.4	57.3	55.8	55.8	55.3	56.6
- H	6.2	6.3	6.9	5.8	6.6	6.2
- O (by diff.)	37.1	36.2	36.3	38.2	37.7	36.9
- N	0.2	0.18	0.79	0.1	0.4	0.1
- S	<0.01	0.02	0.03	0.02	0.05	0.03
- Ash	0.01	<0.01	n.d.	0.03	0.14	0.08
- K+Na, ppm	460	10	128	20	2	60
- Cl, ppm	3	8	1 900	30	330	<100
HHV, MJ/kg	17.0	18.7		19.1	18.5	17.4
HHV (dry), MJ/kg	23.1	22.3	23.8	22.9	23.1	23.0
Viscosity, cSt						
- 20°C	n.d.	128	n.d.	n.d.	55	152
- 50°C	50	13.5	n.d.	31	11	29 (40°C)
Flash point, °C	55	64	n.d.	n.d.	56	42
Pour point, °C	-25	-36	n.d.	-19	-36	-12
Solubility, wt% insolubles in						
- ethanol	0.045	0.045	n.d.	0.30	0.3	0.10
- methanol-dichloro-methane	n.d.	n.d.	n.d.	n.d.	n.d.	0.02

*Bottom phase (90 wt% of total liquid)

n.d. = not determined

Recent data on analytical development, stability, transport, storage, handling and health and safety issues are included. The aim of this publication is to provide guidelines for pyrolysis liquid producers and end-users in determining the fuel oil quality of pyrolysis liquids. A further objective is to provide a baseline for standardising the most important analytical methods of pyrolysis liquids.

As pyrolysis liquids will be pumped, shipped, atomised and combusted, as wide a range of measured properties, mainly from VTT, but other sources have been included to allow this publication to be used as a guide to test methods, a reference for measured values for comparison and as a guide to the determination of properties primarily for fuel applications.

A brief summary of technology developers and providers is given (chapter 2) providing details up to August 2001. Chapter 3 allows the user to assess the hazard posed by the liquids for transport, storage and handling and their toxicity with some indications of precautions to be taken in use. Chapter 4 then addresses how samples may be assessed for homogeneity, prior to use. Chapter 5 summarises the methods for determination of basic liquid properties [water content, solids and particle size, elemental composition, ash and metals content] to determine initial suitability for fuel use. Once the basic properties of the liquid have been determined, principal fuel properties are reviewed [density, viscosity, heating value, flash point, pour point and Conradson carbon residue]. Other useful properties for process design are included [thermal conductivity, specific heat capacity and electrical conductivity and lubricity]. The more unusual properties of pyrolysis liquids are summarised in Chapter 7 and proposed fuel oil specifications for different qualities of pyrolysis liquids are in Chapter 8. Conclusions and recommendations on the fuel oil test methods and values for pyrolysis liquids are presented in Chapter 9. More specific information on test methods and reproducibility are presented in Appendices A–H.

All comments from oil end-users or producers concerning the significance of some specific methods or suggestions for further developments are highly appreciated (Anja.Oasmaa@vtt.fi).

2. Pyrolysis liquids production

Pyrolysis liquids can be produced with a range of processes, each with their own particular features. Our aim is not to review each type of process available, but to give some indication of the degree of development of the technology.

A wide variety of configurations has been tested (Table 1), showing considerable diversity and innovation in meeting the basic requirements of fast pyrolysis, and these have been extensively reviewed [Bridgwater & Peacocke 2000]. Most fast pyrolysis processes give 65–75% liquids based on dry wood input.

The essential features of a fast pyrolysis reactor are very high biomass heating and heat transfer rates; moderate and carefully controlled vapour temperature; and rapid cooling or quenching of the pyrolysis vapours [Bridgwater 1995, Diebold & Bridgwater 1997]. Commercial operation is currently only been achieved from a transport or circulating fluid-bed system, and only for food and flavouring products. Fluid-beds have also been studied extensively, are an ideal R&D tool and have been scaled up to a pilot plant size with plans in hand for demonstration processes in several locations within the EU.

Most pyrolysis systems employ cyclones to remove char and ash from hot product gases and vapours. Some fine char is inevitably carried over from cyclones. Unless removed by a hot vapour filter, which is still under development, char will collect in the liquid and may be removed by liquid filtration employing, for example, cartridge or rotary filters. Almost all of the biomass ash is retained in the char, and hence, successful char removal generally involves successful ash removal. Char separation, however, is difficult and may not be necessary in all applications, i.e., chemical applications.

Char contributes to secondary cracking by catalysing secondary cracking in the vapour phase. Rapid and complete char separation is therefore desirable. Even char in the cooled collected liquid product contributes to instability problems, accelerating slow polymerisation processes, which are manifested as increasing viscosity.

The time and temperature profile between the formation of pyrolysis vapours and their quenching to liquid affects the composition and quality of the liquid product. High temperatures continue to crack the vapours and the longer the vapours are at higher temperatures, the greater the extent of cracking. Although secondary reactions become slow below around 350°C, some secondary reactions continue down to room temperature in the liquids, which contributes to the instability of the pyrolysis liquid. Char also contributes to vapour cracking as described above. A vapour residence time of a few hundred milliseconds is apparently necessary for optimum yields of certain chemicals, while fuels can tolerate a vapour residence time of up to around 2 seconds at 400 °C. A longer residence time results in significant reductions in organics yields from cracking reactions.

The collection of liquids has long been a major difficulty in the operation of fast pyrolysis processes due to the nature of the liquid product that is mostly in the form of aerosols rather than a true vapour. Quenching, i.e., the contact with a cooled liquid is effective, but careful design and temperature control are needed to avoid blockage from differential condensation. High-volatility components are important in reducing liquid viscosity and therefore need to be recovered. Electrostatic precipitation has been shown to be very effective in recovering aerosols. In fluid-bed type systems, the vapour/aerosol concentration can be very low, further increasing the difficulty of product separation due to the low vapour pressure, significantly increasing the size of product recovery equipment. The pyrolysis processes in operation, commissioning or under design (June 2001), are listed with capacities and applications in Table 2.

Table 2. Pyrolysis liquids production processes, 2001 [> 10 kg/h].

Host organization	Country	Technology	kg/h	Applications	Status
BTG	Netherlands	Rotating cone	2000	Fuel and chemicals	Planned 2002
BTG/KARA	Netherlands	Rotating cone	250	Fuel and chemicals	Operational
Dynamotive	Canada	Fluid bed	400	Fuel and chemicals	Operational
Dynamotive	Canada	Fluid bed	80	Fuel and chemicals	Operational
ENEL/Ensyn	Italy	Transported bed	625	Fuel and chemicals	Operational
Fortum	Finland	Own	500–600	Fuel	Construction
Pyrovac	Canada	Vacuum moving bed	3500	Fuel and chemicals	Operational
Red Arrow/Ensyn	USA	Circulating transported bed	1250	Fuel and chemicals	Operational
Red Arrow/Ensyn	Canada	Circulating transported bed	125	Fuel and chemicals	Operational
RTI	Canada	Circulating transported bed	20	Fuel and chemicals	Operational
University of Hamburg	Germany	Fluid bed	50	Waste disposal	Operational
		Circulating transported bed	50	Fuel and chemicals	Operational
University of Laval	Canada	Fluid bed	20	Fuel	Operational
VTT / Ensyn	Finland	Circulating transported bed	20	Fuel	Operational
Wellman Proc. Eng Ltd	UK	Fluid bed	250	Fuel	Commissioning

3. Health, safety and transport

3.1 Toxicity of pyrolysis liquids and their derivatives

In general, all toxicity testing methods can be divided into two categories. The first category consists of tests that are designed to evaluate the overall effects of compounds on experimental animals. The individual tests in this category differ from each other concerning the duration of the test and the extent to which the animals are evaluated critically for general toxicity. The tests are defined as acute, prolonged and chronic toxicity tests.

The second category of tests consists of those tests that are designed to evaluate in detail specific types of toxicity. The prolonged and chronic tests do not detect all forms of toxicity but they may reveal some of the specific toxicities and indicate the need for more detailed studies. The second category of tests has been developed to meet these needs. Examples of specific toxicity tests are:

Teratogenic	effects on the foetus
Reproduction tests	effects on reproduction
Mutagenic tests	effects on the genetic code system
Tumourigenicity	ability of agents to produce tumours [also known as carcinogenicity test]
Neurotoxicity	effects on various behaviour patterns [also known as behavioural tests]
Immunotoxicity	effects on the immune system

Other tests include skin and eye tests which are important for personal safety in transport, storage and handling. There is no data on the carcinogenicity, teratoxicology or mutagenicity of pyrolysis liquids. This will become an area where information will be required for the transportation of the liquids and assessing the allowable exposure limits for those working with the liquids, whether at research scale or commercial production scale.

The health risks posed by fast pyrolysis liquids have not been clearly elucidated so far, although recent reports [Diebold 1999] would suggest that there is a limited degree of mutagenicity and teratogenicity from the liquids, depending on source, chemical composition and dosage.

Analogous work on liquid smoke [Putnam et al. 1999] suggests that depending on the type of pyrolysis product, some cytotoxic and mutagenic effects may be observed. Other studies suggest that aerosols of wood smoke are mutagenic [Lewis et al. 1988]. Exposure to the aerosols is to be avoided. Skin contact is also to be prevented by the use of protective gloves, clothing and safety glasses.

3.2 Material and Safety Data Sheets (MSDS)

During the testing and utilisation of pyrolysis liquids, the liquids must be handled, stored, transferred and sampled. Material and Safety Data Sheets are essential for the safe use, handling, storage and transportation of fast pyrolysis liquids. So far, there is no accepted standard, due to the high variability in properties and limited developments in commercial systems. Large pyrolysis liquid producers (Ensyn, Dynamotive, BTG, Fortum) have their own MSDS for pyrolysis liquids. Czernik (Bridgwater et al. 1999) prepared with IEA Bioenergy Pyrolysis Activity Group 1999 a MSDS based on all available data. A MSDS prepared at Aston University (UK) which is suitable for inclusion with samples for shipment is presented in Appendix A. All use of pyrolysis liquids requires the use of adequate safety equipment and facilities [protective clothing, chemical resistant gloves, safety glasses or goggles and a well ventilated environment].

3.3 Transport, storage and handling

As the demand for fast pyrolysis liquids increases, it is important that they are transported in a safe and environmentally secure manner [Peacocke & Bridgwater 2001]. The appropriate national and international regulations need to be met and it is likely that the fast pyrolysis liquids will be classified as "dangerous" or "hazardous" substances in transportation. Pyrolysis liquids are not listed on the UN approved carriage list [Anon 2000], and therefore its own classification has been determined for them. The classification derived is:

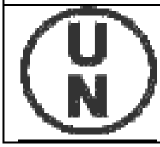
UN 1993 Flammable Liquid, N.O.S., (Fast Pyrolysis Liquid), 3, 1º(a), 2º(a), 1

This code is valid for pyrolysis liquids containing less than 10 wt% acetic acid. A separate classification is required for liquids with an acetic acid content higher than this, although up to date no fast pyrolysis liquids with a content higher than approximately 5wt% have been reported.

Label requirements for fast pyrolysis liquids

All packages of any size should be clearly marked with the information given in Table 3, both on the sample and on the relevant transportation documents. A set of Material Safety Data Sheets (MSDS) must also accompany any samples (Appendix A).

Table 3. Label information for packages.

UN symbol:	Substance ID No.	Name of substance	Hazard identification No.	Label model Nos.	Class and item numbers
	1993	Flammable liquid [Fast pyrolysis liquid]	33	3 6.1 11	3 1°(a), 2°(a), 2°(b), 3°(b), 5°(c)

Class 3 Flammable liquid
Label 3

Class 6 Toxic substances
Label 6.1

Store this way up
Label 11

Figure 1. Packaging labels for fast pyrolysis liquids. All should be used on all shipments nationally and internationally.

Table 4. Label sizes for shipments.

Capacity of package	Dimensions of label
Not exceeding 3 litres	At least 52 x 74 mm
Exceeding 3 litres but not exceeding 50 litres	At least 74 000 x 105 000 mm
Exceeding 50 litres but not 500 litres	At least 105 x 148 mm
Exceeding 500 litres	At least 148 x 210 mm
Exceeding 3000 litres	At least 250 x 250 mm

If the size of the package requires, the dimensions of the label may be reduced, provided they remain clearly visible. IBCs [intermediate bulk containers] are not suitable for pyrolysis liquids transport, due to the potentially hazardous nature of the liquids. In addition, for tankers, or other large bulk transport, placards typical of road and rail transports are used. The placard dimensions are typically at least 30 cm high and 40 cm wide, numerals to be at least 10 cm high. The requisite codes for a placard are:

Substance Identification No. [lower part]	Name of substance	Hazard Identification No. [upper part]
1993	Flammable Liquid [Fast Pyrolysis Liquid]	33X

A placard for large quantities [> 500 l] with the correct transportation codes is shown in Figure 2.

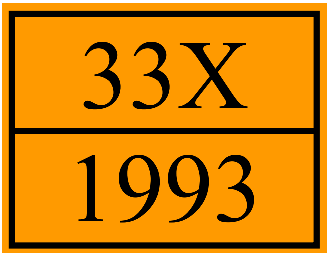


Figure 2. Placard for transportation in containers and bulk carriage.

4. Homogeneity and sampling

4.1 Homogeneity of pyrolysis liquids

Pyrolysis liquids contain compounds with different chemical functionalities. The homogeneity of the liquids is connected with the complex solubility and reactivity of these various chemical compounds in the liquid. Typically, pyrolysis liquids are single-phase liquids (Appendix B/3) containing varying amounts of solids due to feedstock, process, and product recovery (see Chapter 2.1). The heavy phase, containing entrained solids of the pyrolysis liquid, gradually settle on the bottom of the container forming a sludge. The degree of sedimentation depends on the density difference of the liquid and the particle size [Särkilahti 1996]. If the water content of pyrolysis liquid exceeds a certain limit (typically 30 wt%), the liquid separates into two phases (Appendix B/4). This type of phase separation happens typically when the moisture content of the feedstock has been too high (>15wt%).

Due to the inherent properties of some feedstocks, the liquid products may on collection, exhibit two or more phases. Typical feedstocks that can give multiple phases on pyrolysis, are forest residue, barks, pine [thin scum layer due to terpenes in biomass], some straws [e.g. wheat and rape straw], tropical hardwood species [mahogany], eucalyptus and rape meal. These biomass types with either high levels of hydrocarbon-soluble extractives or alkali metals are more prone to give multiple phases. These phases cannot typically be mixed together and they should be analysed separately.

Forest residue yields a pyrolysis liquid with a 10–20 wt% extractive-rich top phase of low in polarity. The bottom phase, its amount being 80–90 wt%, is similar to white wood liquids. The amount of top phase depends on the feedstock composition (extractives), process, and product collection conditions. The top phase is, compared to bottom phase, low in water and density (see 6.1, Figure 4), and high in heating value (see 6.6, Figure 7) and solids content (Appendix D/6). In addition, it is slightly a non-Newtonian liquid (Figure 5). Some extractives (e.g. C_{18}-C_{26} fatty acids) appear as crystals in the liquid.

4.2 Homogenisation and sampling

Mixing and sampling methods depend on the type and size of the pyrolysis liquid container (Appendix B). Attention should be paid to proper mixing of the liquid. Small samples can be homogenised in routinely used laboratory mixers.

The pyrolysis liquid in barrels or in large totes can be homogenised by propeller mixers. In case of a fresh single-phase low-to-medium viscous pyrolysis liquid the liquid stays, under proposed storage conditions, homogenous for 6 to 12 months without any mixing. Only solids in the liquid settle gradually to the bottom. Circulation pumping or propeller mixing homogenizes the solids content in the liquid [Oasmaa et al. 1997]. Round pumping can be employed if taken care that the whole liquid is in movement. Heating of the liquid to > 50°C for longer periods should be avoided to prevent evaporation of volatiles and/or viscosity increase due to the chemical instability of the liquid.

In case of aged or poor-quality liquids, continuous stirring, emulsion stirring (with a top-mounted slow revolving propeller stirrer) must be used during storing to avoid stratification/separation. Ordinary stirring methods, such as round pumping (with heating), are not sufficient for inhomogeneous pyrolysis liquids for creating storage circulation. Channelling, separation of light compounds, or heavy (sediment) material concentrating in the round pumped stream can appear. Handling, storage, and pumping may all affect liquids in different ways.

An aged phase-separated pyrolysis liquid can only be homogenised by adding polar solvents, like alcohols (Appendix B/5). Acids, like acetic acid, also homogenise the liquid, but decrease the pH.

The homogeneity of the liquid after mixing can be verified by microscopic determination and/or by sampling from different depths and analysing the moisture content (Appendix B). The sampling device should be wide-mouthed for obtaining a homogenous sample.

5. Composition

5.1 Water

Water is regulated in petroleum fuels, because it forms a separate phase, which can cause corrosion, trouble in burners, or emulsion formation. Typically, water is dissolved in pyrolysis liquids. The dissolved water in the fuel can increase the efficiency of the boiler at levels of up to 15% and efficiency losses are not significant, until levels of 20% or higher are reached (Diebold et al. 1997).

The water content of pyrolysis liquids has been typically analysed by Karl Fischer (KF) titration. Pyrolysis liquids contain low-boiling (below 100°C) water-soluble compounds, and hence conventional drying methods cannot be used. The amount of volatile water-soluble compounds in the pyrolysis liquid is high, and hence xylene distillation [ASTM D 95] in which the water is distilled away with a co-solvent, cannot be used.

Earlier [Oasmaa et al. 1997] two standard methods, ASTM D 1744 and ASTM E 203, with several variables have been tested for hardwood, softwood, and straw pyrolysis liquids. It was concluded that both KF titration methods can be used for determination of water for pyrolysis liquid. The most important factor is good dissolution of the sample. In 2000 the D 1744 has been removed from ASTM standards without a replacement. The referred standard therefore is: Test Method E 203-96: Standard Test Method to Water Using Volumetric KF Titration.

In order to determine the water content by Karl Fischer volumetric or coulometric titrations are used. The coulometric titration is developed for analysing trace amounts of water. By proper choice of the sample size, KF reagent concentration and apparatus, the volumetric titration is suitable for measurement of water over a wide concentration range, that is, parts per million to pure water.

In volumetric KF titration the method is calibrated by determining the water equivalent. It is usually quoted in mg of water per ml of KF solution:

$$\text{Titre } t = (\text{mg of water})/(\text{ml of KF solution}) \qquad (1)$$

In the titration the sample is dissolved in a suitable solvent (e.g. chloroform:methanol = 0..3:1) and titrated by a KF reagent. The reagent (e.g. 2-methoxy ethanol) contains the reactive components: anion of the alkyl sulfurous acid, iodine, and base (e.g. imadazol, pyridine). In the titration the anion of the alkyl sulfurous acid reacts with the alcohol and forms ester. The ester is neutralized by the base (2):

$$ROH + SO_2 + RN \rightarrow [RNH]SO_3CH_3 \qquad (2)$$

The anion of the alkyl sulfurous acid oxidizes to alkyl sulphate by iodine (3). This reaction consumes water. For staying in optimum pH range (5-7) imadazol is used.

$$H_2O + I_2 + [RNH]SO_3CH_3 + 2\ RN \rightarrow [RNH]SO_4CH_3 + 2[RNH]I \qquad (3)$$

ROH	An alcohol for instance, methanol, ethanol, ethylene-glycol-mono-ethyl-ether
RN	A caustic solution, for instance imadazol or pyridine

As the use of chlorinated solvents is not recommended, methanol may be considered as a solvent when the dissolution of the sample is not a problem. Various solvent combinations were tested for forest residue liquid (Appendix C/3): Chloroform:Methanol in ratios of 3:1, 1:1, 1:3, and pure Methanol. There was no difference in water contents. However, the titration end-point was easier to detect when chloroform was present. Hence, the sample solvent for KF titration [ASTM E 203] is recommended to be a mixture (3:1) of methanol and chloroform. It must be noted that also new KF reagents, including those containing no pyridine, are on the market. In order to verify the use of another sample solvent or reagent the use of water addition method (C/1) for calibration is recommended.

If the sample has dissolved properly, the fading titration end-point may be due to a reaction of ketones and aldehydes [Riedel-de Haën 1995] with the titrant. Aldehydes and ketones may form acetals and ketals for example with methanol yielding water as reaction product. This water is then titrated yielding to too high water content. Aldehydes are more prone to this reaction than ketones. One solution for this is to use HYDRANAL K reagents [Riedel-de Haën 1995], which prevent this reaction. Other error sources include: impropriate homogenisation and/or sampling, too small sample size both for the sample and for the water equivalent, wet drying agent, wet titration solvent, air-leakage, dirt on electrode, dirty solvent, and sample deposits on the walls of the sample vessel (Appendix C/2).

The accuracy of titration for good quality white wood liquids is ±0.1 wt% [Oasmaa et al. 1997]. For extractive-rich forest residue liquids 0.5 wt% deviation of duplicates should be accepted.

Attention should be paid to proper sample homogenisation. A sample size of 0.25 g is recommended for pyrolysis liquids containing about 20 wt% water. The final water content is calculated based on the water equivalent of the titrant and the consumption of the titration reagent. For a good quality pyrolysis liquid the 0.01 mg/ml deviation in water equivalent can be accepted. A variation of 5.70–5.73 mg water/ml titrant in the water equivalent yields a variation of 28.50–28.65 wt% in the water content (0.25 g sample, 12.50 ml consumption of titration reagent).

5.2 Solids

There are varying amounts of solids in pyrolysis liquids due to feedstock, process, and product recovery (see chapter 2.1). The solids content of pyrolysis liquids affected particulate emissions observed in combustion tests in a commercial heavy fuel oil boiler at Birka Energi (former Stockholm's Energi), Sweden, [Hallgren 1996], in a commercial heavy fuel oil/light fuel oil boiler at Oilon, Finland [Oasmaa & Kytö 2000], and at Fortum [Gust 1997] and Sandia National Laboratories [Suppes et al. 1996].

Various solvents (ethanol, methanol, acetone) for solids determination have been tested previously [Oasmaa et al. 1997]. The main observations were: 1) Ethanol was a better solvent than acetone for pyrolysis liquids from hardwood (oak/maple, eucalyptus). 2) Filtration of the acetone solution was more difficult (long filtration time, sticky filter cake) than that of the ethanol solution. 3) For the straw pyrolysis liquid, a clear difference (10 wt%) in solids contents was observed when determined using ethanol and acetone. Acetone either did not dissolve the straw pyrolysis liquid properly or reacted causing precipitation. 4) The filter pore size (0.1–10 µm) did not affect the amount of solids retained except for the case of straw liquid, which contained high amounts of submicron particles. 5) The differences in solubility in ethanol and methanol were very small. Methanol was a slightly more effective solvent than ethanol for pyrolysis liquids from pine, eucalyptus, and straw. For an oak/maple liquid, no difference in methanol and ethanol insolubles was obtained.

A number of effective polar solvents, like methanol and ethanol, may be used for measuring the solids content of pyrolysis liquids. At VTT, ethanol was chosen for white wood liquids because its solubility power is high for several different pyrolysis liquids, and it is safer for use in routine measurements than methanol. However, in case of extractive-rich pyrolysis liquids like forest residue liquid, a neutral solvent is needed with a polar one. For forest residue liquids (see 4.1), a mixture of methanol and dichloromethane was effective (Appendix D). For bottom phase (low in extractives) of forest residue liquid 20 vol% dichloromethane in methanol was the most effective solvent of those tested (D/4). For top phase (high in extractives), the best solvents were (an order of preference D/6): Methoxy Propanol-Dioxane (1:1), Industol (PE2, a trade name, 88.3% ethanol, 2.7% methyl-isobutylketone, 1.8% acetone)-Dioxane (1:1), Isopropanol (IPA)-Dioxane (1:1), IPA-Dichloromethane (CH_2Cl_2) (1:1), Methanol- CH_2Cl_2 (1:1).

A 1 µm filter is used because of fine particles in the liquid. If the filtration time is long (high solids content), a 3 µm filter can be used and the filtrate filtered through a 1 µm filter. A sample size yielding 10–20 mg residue and a sample to solvent ratio of 1 : 10 with several washings is recommended (Appendix D). Maximum 10 wt% difference between duplicates can be accepted.

5.3 Particle size distribution

Two optical methods have been previously tested for determining particle size distribution for pyrolysis liquids: a particle counter and an image analyser [Oasmaa et al. 1997]. Observations as follows were made: 1) A dark colour of the pyrolysis liquid may disturb the detection. 2) Overlapping of several particles can be detected as one large particle. 3) The flow rate may have some effect on the particle size distribution.

A method for measuring particle size distribution of pyrolysis liquid is to use microscopy with the particle counter model. At VTT, Leica DM LS microscopy with Leica Qwin Lite Standard photo analysis programme is used. In the system, the particles are marked and the computer programme measures, calculates and classifies them. In Figure 3 (see also Appendix E), the particle size distribution (1 µm and above) of forest residue liquid (whole liquid, solids ~ 0.5 wt%) based on maximum length of particle is presented. The method gives particles below 1 µm as "undersize particles". The numerical amount of these submicron particles is large, but the volumetric amount small (Appendix E). The reproducibility (triplicates) of the determination is good. If the solids content is high, overlapping of particles may cause error in the results.

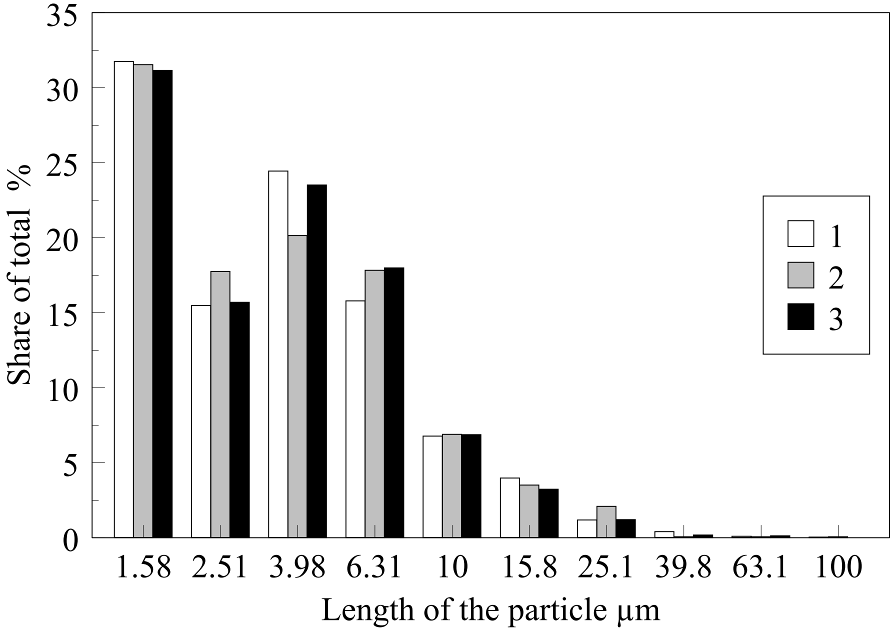


Figure 3. Particle size distribution of forest residue liquid. Solids 0.47 wt% as methanol-dichloromethane insolubles.

5.4 Elemental composition

Elemental analysis of carbon, hydrogen, and nitrogen was carried out at VTT with LECO CHN600 according to ASTM D 5291. In the method, carbon, hydrogen, and nitrogen are simultaneously determined as gaseous products (carbon dioxide, water vapour, and nitrogen).

The accuracy of carbon and hydrogen is good, but poor for nitrogen [Oasmaa et al. 1997]. This is due to low concentrations of nitrogen (≤0.1 wt%) in wood liquids and to the low nitrogen detection limit (0.1 wt%) of the method. Pyrolysis liquids from straw and forest residue contain higher (0.2–0.4 wt%) concentrations of nitrogen and hence stdevp% is lower [Oasmaa et al. 1997]. Because of the small sample size, the reproducibility of the elemental analysis is dependent on the homogeneity of pyrolysis liquids. At least triplicates are recommended, if the sample is inhomogeneous.

The sulphur content of wood pyrolysis liquids is typically very low (60–500 ppm). The straw liquid has also a low sulphur content (400–500 ppm). The detection limit for sulphur analysis by LECO SC 32 according to ASTM D 4208 is 0.1 wt%. Lower concentrations can be analysed, e.g., by ICP (Inductively Coupled Plasma). The detection limit for analysing sulphur by ICP is about 5 ppm due to wet oxidation as the pretreatment method. Low sulphur contents can be analysed by capillary electrophoresis technique after combusting the sample in an oxygen bomb according to ASTM D 4239. Simultaneously, the total chlorine is also given. The chlorine content of pyrolysis liquids from different feedstocks has been below 5 ppm for hardwood (oak maple) liquid, 75 ppm for softwood (pine) liquid, and 300–400 ppm for forest residue (high content of green material) and straw (wheat) liquid. Oxygen (dry basis) is calculated by difference.

5.5 Ash and metals

Ash or char is present in the pyrolysis liquids due to inefficiencies in char removal equipment such as cyclones leading to carryover of char into the liquid collection system. It is the inorganic part of solids presented earlier containing unburnt carbon, and metals. It may also contain sand from process heat carrier. Depending on the use of the fuel, ash content and composition has a considerable bearing on whether or not detrimental effects will occur. High ash content can cause high wear in pumps and injectors, deposits in combustion equipment, or corrosion in gas turbines due to alkali metals in ash. Large boilers and low-speed engines can tolerate more ash than more sophisticated equipment.

Ash content is measured according to DIN EN 7. In the standard method, the sample is ignited and burnt in a crucible (Pt, quartz or porcelain). Carbon containing residue is ashed at 775°C, cooled, and weighed.

A high amount of water in pyrolysis liquids can cause foaming or splashing during heating of the sample. Hence, a controlled evaporation of water is needed. A sample of 20 ml pyrolysis liquid may be let to heat in a porcelain crucible on a heating plate or in a temperature-controlled small sand bath for evaporation of water and other volatile components. Addition of isopropanol or ash-free filter paper for absorbing the water can prevent splashing.

Part of ash consists of alkali metal oxides. As the alkali content of wood pyrolysis liquids is low, possible evaporation during ashing may not be important for the total ash. In case of pyrolysis liquids from straw and grasses the situation may be different. These liquids contain much higher amounts of alkali metals. During ashing, part of alkali metals may evaporate and the rest may form oxides that can lead both to underestimation (evaporation) and overestimation (oxidation) of the ash content.

Ash contents have typically been low (0.1–0.2 wt%) for white wood pyrolysis liquids and higher (0.2–0.4 wt%) for forest residue and straw liquids. For hot-vapour filtered pyrolysis liquids (hardwood, softwood, straw), low ash contents (0.01 wt%) have been obtained due to efficient removal of char fines with alkali (Na, K, Ca, Mg) metals (below 10 ppm) [Oasmaa et al. 1997].

For alkali metal analyses, different sample pretreatment methods for ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) and AAS (Atomic Absorption Spectrometer) have been tested previously [Oasmaa et al. 1997]. The straight dissolution in isopropanol (IPA) was inaccurate due to incomplete dissolution of the sample. Dry combustion was time-consuming, because the water has to be evaporated carefully before ashing, or else the liquid would swell out from the Pt crucibles. If a hard crust forms on the surface of the sample before the end of drying, the water may suddenly vaporise and the sample is lost. Wet oxidation was the easiest and fastest method. However, large samples are difficult to handle with acids, and a sample size of 3–5 g is suggested as adequate. The same acid or acid mixture and concentrations should be used both in the sample and in the standard solutions.

Similar concentrations of alkali metals (Na, K, Ca, Mg) were obtained with both dry combustion (ashing temperature 520°C for 2 hours) and wet oxidation as pretreatment method. Stdevp% was reasonably low (0–14) when using sample sizes of 3–5 g even for alkali concentrations of 10 ppm.

Metals may be analysed by ICP-AES or AAS. If all metals are to be analysed, ICP-AES is suggested as an easier (several metals from one run) and hence, cheaper method. However, AAS is more sensitive in some cases. Wet oxidation (Appendix F) is suggested as a fast and easy pretreatment method especially for analysing alkali metals and easily volatilised toxic metals like Cr, As, Pb, Hg, and Cd.

It should be pointed out that for accurate analysis of trace alkali metals the whole procedure from the recovery of the pyrolysis liquid to the sample pretreatment should be re-checked in detail. Contaminations from glass containers and from dust in air may have an influence on the results [Diebold et al. 1997]. The use of Teflon (polytetrafluoroethylene, PTFE) bombs for sample pretreatment should be considered. If traces of alkalis are to be analysed, the use of a method requiring no sample pretreatment, like neutron activation (NA) analysis, may be advantageous.

6. Fuel oil properties

6.1 Density

Specific gravity is of little significance as an indication of burning characteristics, but is used in calculating weight/volume relationships, e.g., the heating value [Diebold et al. 1997].

The density is measured according to ASTM D 4052 at 15°C by a digital density meter. A small volume (approximately 0.7 ml) of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample. An Anton Paar DMA 55 density meter was used at VTT. A viscous pyrolysis liquid with large particles may disturb the measurement and cause erroneous results. In addition, air bubbles may disturb the determination near ambient temperatures. Therefore, vigorous shaking of the sample just before the analysis should be avoided. Instead, the sample can be rotated carefully. At elevated temperature (50°C) the air bubbles are easily avoided by preheating the sample for a short period in a closed vessel.

The density of pyrolysis liquids is typically 1.2–1.3 kg/dm^3. The precision of density measurements is good (variation below ±0.1%). Densities of wood pyrolysis liquids are a function of water content [Oasmaa et al. 1997]. In Figure 4 densities of various pine and forest residue liquids (top : bottom = 1 - 2 : 8 - 9) are shown as a function of original water content. It can be seen that the bottom phase of forest residue liquid has similar density-water correlation than pine liquids. The density of the top phase diverges from that of the bottom phase, when the water content of the top phase decreases. This is due to the concentration of extractives in the top phase, while water with water-soluble compounds moves to the more polar bottom phase.

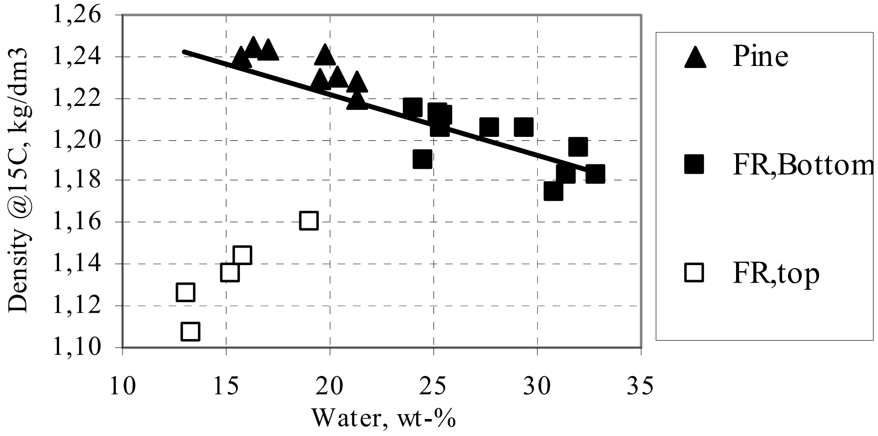


Figure 4. Density of pine and forest residue (FR, top : bottom = 1 - 2 : 8 - 9) pyrolysis liquids as a function of water content.

6.2 Viscosity

Viscosity is a measure of the resistance of the liquid to flow. The viscosity of the fuel is important, i.e., because of its effect on pumping and injecting of fuel [Dyroff 1993].

The viscosity of pyrolysis liquids can be determined as kinematic viscosity using glass capillaries or as dynamic viscosity using rotational viscometers. The correlation between the kinematic and dynamic viscosity can be presented by the following equation:

$$\eta\ [\mathrm{cSt}] = \eta\ [\mathrm{mPa} \bullet \mathrm{s}]\ /\rho\ [\mathrm{kg/dm^3}], \tag{4}$$

where

ν kinematic viscosity at temperature T
η dynamic viscosity at temperature T
ρ density of the liquid at temperature T.

The viscosity of standard fuels, which are Newtonian liquids, is typically measured as kinematic viscosity according to ASTM D 445. In the standard method, the time is measured in seconds for a fixed volume of liquid to flow under gravity through a calibrated capillary at a closely controlled temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer.

Leroy et al. [1988] have carried out an extensive study on rheological characterisation of several different pyrolysis liquids. They concluded that all pyrolysis liquids exhibited an essentially Newtonian behaviour in the range of shear rate examined (10^1 to 10^3 s^{-1}). For Newtonian liquids, the viscosity stays constant when increasing the shear rate. Additional tests were carried out by VTT at Haake Application Laboratory in Karlsruhe, Germany, using an RT 20 all-round rheometer with mechanical bearing. Haake concluded that the samples were Newtonian liquids.

Tall oil soap, which mainly consists of extractives, is a non-Newtonian material. Due to the high extractive content of forest residue liquids, its Newtonian behaviour was tested (Figure 5). The bottom phase is chemically similar to the white wood pine liquid and its Newtonian behaviour was not a surprise. The top phase containing most of the extractives showed a slight non-Newtonian behaviour at 30°C. At 45°C, the non-Newtonian behaviour was undetectable.

Kinematic viscosity can be determined by using Cannon-Fenske or Ubbelohde capillaries. The basic difference between these methods is the flow direction of the sample. For non-transparent liquids, Cannon-Fenske is easier to use near room temperature because of up-flow system and wider capillaries. In the Ubbelohde method, the sample flows downwards and the capillary bore is much smaller. This may lead to an uneven flow of viscous pyrolysis liquid in the capillary.

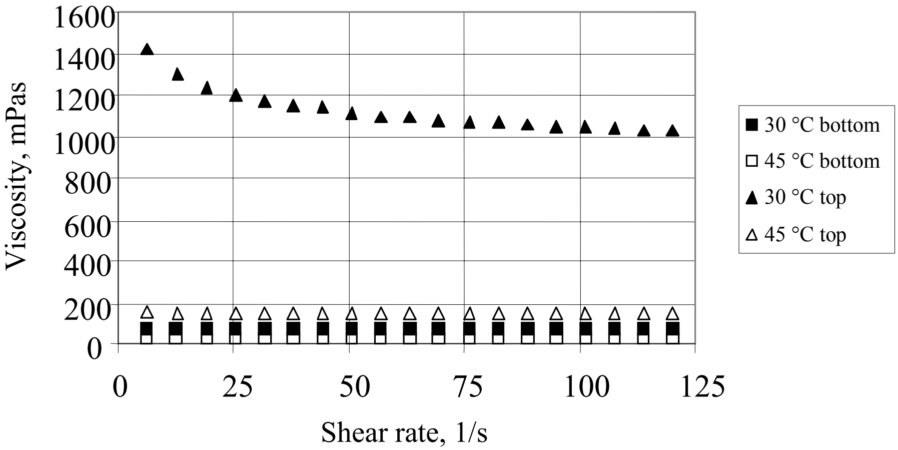


Figure 5. Dynamic viscosity (η) as a function of shear rate (τ) for the two phases (top and bottom) of forest residue liquid (water content: top 6.8 wt%, bottom 24.1 wt%).

The comparison of the two capillaries was carried out for one hardwood pyrolysis liquid. At 20°C, there was a small variation between viscosity results obtained either by Cannon-Fenske or Ubbelohde method. At 50–80°C, no significant difference was observed in the viscosity of pyrolysis liquid measured by these methods. The small difference in viscosities measured by the two capillary methods according to ASTM D 445 may be explained by difficulties in reading the volume in the Ubbelohde method (downward flow) [Oasmaa et al. 1997]. Another reason for this may be that a small error in temperature causes higher error at 20°C than at 40°C (Figure 6.)

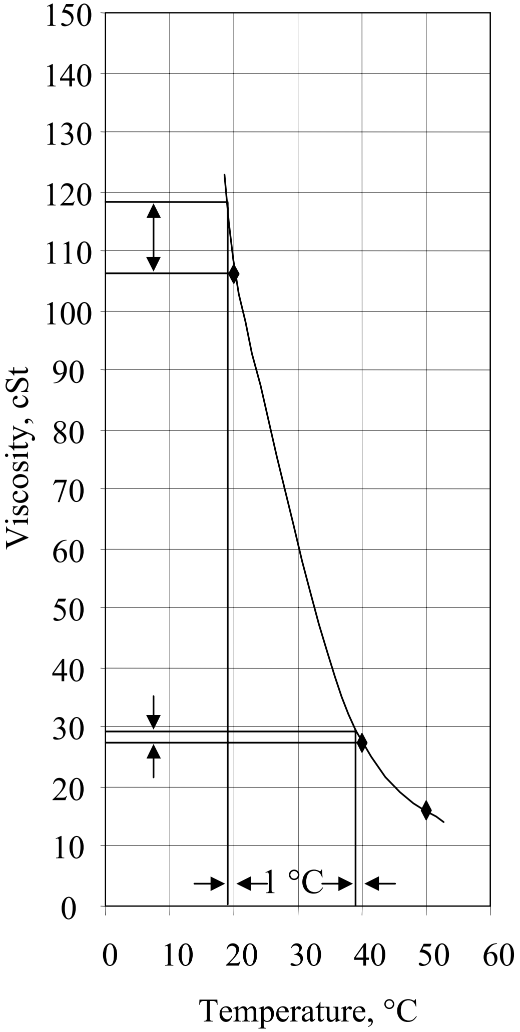


Figure 6. Viscosity curve of a softwood pyrolysis liquid.

The determination at near-ambient temperature may be disturbed by air bubbles, especially for forest residue liquids, and therefore vigorous shaking of the sample just before the analysis should be avoided. The sample can be instead rotated carefully. At elevated temperature the air bubbles can easily be removed during preheating of the liquid.

When comparing the kinematic viscosities with the dynamic viscosity obtained by a rotaviscotester (Haake VT 550 controlled rate rotaviscotester, 8 ml NV cup, 46 ml MV-DIN cup, Tmax 100°C) the precision was good below 50°C. At 80°C, the evaporation of volatiles was observable already during sample equilibration. The viscosity of the sample increased by almost 1% in a minute during measuring at 80°C. The stdevp at 80°C was also higher than by using the capillary system, where the evaporation of volatiles is not as significant due to the small open surface of the capillary. The equilibration times of 15 minutes for 20°C and 40°C, and 10 minutes for 80°C were used [Oasmaa et al. 1997].

Viscosities of pyrolysis liquids are a function of water content [Oasmaa et al. 1997]. Viscosities for various pine and forest residue liquids are shown in Figure 7.

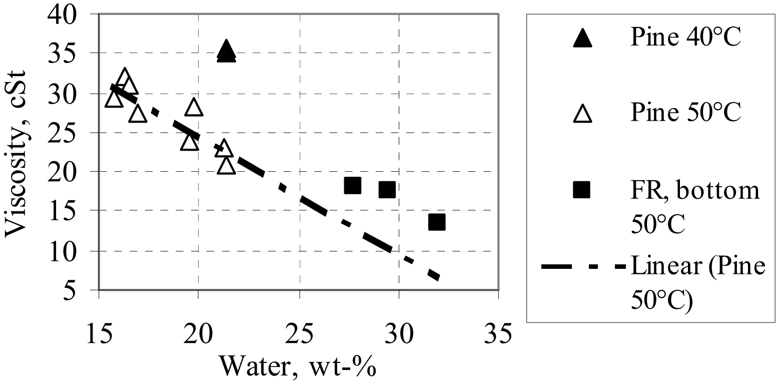


Figure 7. Viscosity of pyrolysis liquids from pine and forest residue (FR, bottom phase).

6.3 Pour point

The pour point of a fuel is an indication of the lowest temperature, at which the fuel can be pumped [Dyroff 1993]. The upper limit for pumpability is about 600cSt [Rick & Vix 1991]. The pour point was determined according to ASTM D 97. In the method, a preheated sample was cooled at a specific rate and examined at intervals of 3°C for flow characteristics. The lowest temperature, at which oil movement was observed, was recorded as the pour point. The setting point is the temperature, at which the oil cannot be pumped, and it is 2–4 K lower than the pour point.

Preheating of the sample was laborious for some pyrolysis liquids, as it may cause separation of water on the surface of the sample. The water froze before the actual pour point and hence disturbed the measurement. The pour point for wood (hardwood, softwood, forest residue) pyrolysis liquids ranged from –12°C to -33°C. For straw (wheat) liquids -36°C was measured for two different batches. For the pyrolysis liquids analysed the low viscosity was an indication of a low pour point.

6.4 Cloud point

Under low temperature conditions, paraffin constituents of a mineral fuel oil may precipitate as a wax, forming a cloud in the liquid. The wax settles out and blocks the fuel system lines and filters causing malfunctioning or stalling of the engine. The temperature, at which the precipitation occurs, depends on the origin, type, and boiling range of the fuel. The more paraffin in the fuel, the higher the precipitation temperature and the less suitable the fuel for low temperature operation [Dyroff 1993].

The cloud point is determined as the temperature, at which a cloud of wax crystals first appears in a liquid, when it is cooled under conditions described in the method ASTM D 2500. Despite low levels of paraffin compounds in pyrolysis liquids, the cloud point was measured for the pyrolysis liquid according to this method to check, if other components can cause a similar phenomenon. The sample was cooled at a constant rate down to -21°C, at which the sample was no more fluid. No "clouding" was observed, which may be due to the dark colour of pyrolysis liquid. It was concluded that this test is not suitable for dark pyrolysis liquids [Oasmaa et al. 1997].

6.5 Conradson carbon residue

The carbon residue is a measure of carbonaceous material left in a fuel after all the volatile components are vaporised in the absence of air. There is no real correlation between Conradson carbon results for diesel fuels and deposit formation on injector nozzles. Fuels with up to 12 wt% Conradson carbon residues (CCR) have been used successfully in slow speed engines [Dyroff 1993]. The significance of the Conradson carbon test results also depends on the type of the engine, in which the fuel is used. Pressure jet and steam atomising type burners are not very sensitive to the carbon residue of the fuel used.

The Conradson carbon residue was measured according to ASTM D 189. In the method, a weighed quantity of sample is placed in a crucible and subjected to destructive distillation. The residue undergoes thermal cracking and coking reactions during a fixed period of severe heating. At the end of the specified heating period, the crucible containing the carbonaceous residue is cooled in a desiccator and weighed. The residue is calculated as a percentage of the original sample, and reported as CCR.

Due to the high water content of pyrolysis liquids, causing foaming, the standard sample size was reduced from 3–5 g to 1 g. For heterogeneous liquids, a larger sample size (3–5 g) is needed, and the water should be evaporated carefully from the crucible on a heating plate to avoid spilling of the liquid sample.

The accuracy of the method according to the standard is ± 2 wt%, when CCR is above 20 wt%. The CCR has typically ranged 18–23wt% (22–23 wt% on dry pyrolysis liquid) for pyrolysis liquids from hardwood and softwood and 17–18 wt% (22–23 wt% on dry basis) for pyrolysis liquids from forest residue or wheat straw. Low CCR values (17–22 wt% on dry basis) have been determined for hot-vapour filtered pyrolysis liquids from hardwood (poplar), softwood (pine), and straw (wheat) [Oasmaa et al. 1997]. This may be an indication of change in the chemical composition of the liquid, e.g., sticking and possibly also thermal cracking of heavy compounds on the filter cake during hot vapour filtration, as the amount of solids alone does not explain it.

Normally Conradson Carbon is only specified for light diesel fuels. The pyrolysis liquids are of different chemical nature compared to mineral oil based heavy diesel fuels. There is not yet adequate information of diesel performance data for pyrolysis liquids, and therefore also this test was selected for evaluation [Oasmaa et al. 1997]. CCR can only be taken as a qualitative comparison between pyrolysis liquids.

6.6 Heating value

The heat of combustion of the fuel is the amount of heat produced, when the fuel is burned completely. It may be determined by bomb calorimetric techniques. There are two values for the heat of combustion, or calorific value, for every fuel. They are referred as the gross (or HHV, higher heating value) and net (or LHV, lower heating value) heats of combustion. The difference between the two calorific values is equal to the heat of vaporisation of water formed by combustion of the fuel.

The heating value is measured as HHV by DIN 51900. A Parr adiabatic bomb with a Parr Calorimeter Controller 1720 is employed. The heat of combustion is determined by measuring the temperature increase in the water jacket and then calculated from the energy balance for the system. The high water content of the pyrolysis liquids may lead to poor ignition, and therefore a fine cotton thread can be used as a wick. The heat content of the thread is subtracted from the result. The lower heating value (LHV) is calculated from HHV and the hydrogen content [ASTM 529192] by equation (5). No subtraction of free water has to be done [Rick & Vix 1991] because the water in the pyrolysis liquid cannot be removed by centrifugation as for heavy petroleum fuel oils.

$$\text{LHV [J/g]} = \text{HHV [J/g]} - 218.13 \times \text{H\% [wt\%]} \qquad (5)$$

The heating values correlate with the water content of pyrolysis liquids [Oasmaa et al. 1997]. The LHVs of pine and forest residue liquids are shown in Figure 8. The heating value of the bottom phase of the forest residue liquid correlates with the water similar to that of pine liquids. The maximum water content for forest residue liquids (bottom phase) is around 33 wt-% after which a phase separation happens. The heating value of the extractive-rich top phase is higher than that of the bottom phase. The difference is larger for lower water contents (higher extractive content in the top phase). The heating value of the pyrolysis liquid is roughly half (of dry matter) that of petroleum fuels (Table 1).

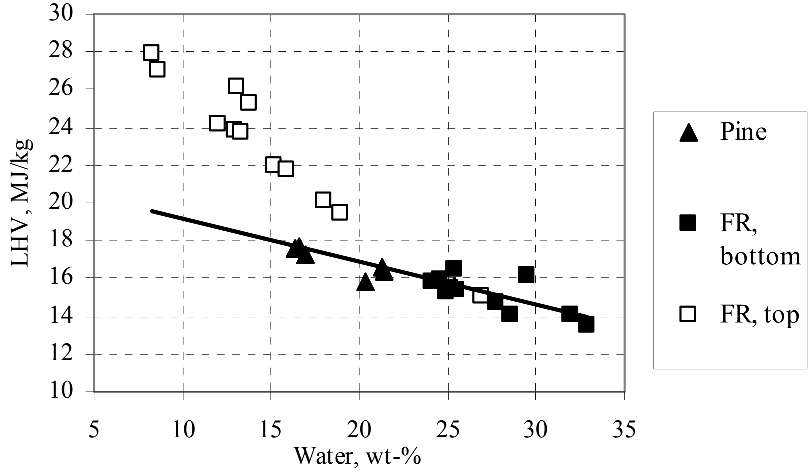


Figure 8. Heating value of pine and forest residue liquids (FR) as a function of water content.

6.7 Flash point

The flash point of petroleum oil is measured to indicate the maximum temperature, at which it can be stored and handled without serious fire hazard. Too low a flash point causes the fuel to be subject to flashing, and possible continued ignition and explosion. In spite of its importance from a safety standpoint, the flash point of the fuel is of no significance to its performance in an engine. The autoignition temperature is not generally affected by variations in flash point, neither are other properties, such as fuel injection and combustion performance [Dyroff 1993].

The flash point can be determined according to ASTM D 93 using a Pensky-Martens closed-cup tester [ASTM D 93/IP 34]. The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature, at which the test flame ignites the vapour above the sample.

Flash points from 40°C up to above 100°C have been measured for pyrolysis liquids [Oasmaa et al. 1997]. The low flash point of pyrolysis liquids (40–50°C for forest residue liquids) is due to a high amount of low-boiling volatile compounds. A low flash point also indicates a high vapour pressure. For liquids low in volatile, the flash point is much higher (above 100°C). The flash point cannot be measured at 70–100°C, where the evaporation of water suppresses the ignition.

6.8 Ignition temperature

Unlike the petroleum-based fuels, the pyrolysis liquids do not spontaneously ignite in a typical compression ignition engine. The ignition temperature for aromatic-rich oils is much higher than for paraffin-based fuels [Rick & Vix 1991]. In addition, the high water and oxygen contents with a substantial amount of non-volatiles contribute to poor ignition.

The cetane number is used for light oils and diesel fuels and can be measured according to ASTM D 613. In the method, the tested fuel is ignited by compression, the ignition delay is measured and the results are then compared with those of known fuels. Autoignition of a pyrolysis liquid has been tested in a single cylinder diesel engine instrumented for cylinder pressure analysis [Solantausta et al. 1993]. The pyrolysis liquid ignited only after adding ignition-improver.

Properties of pyrolysis liquids vary significantly depending on feedstock, process, and product recovery. Hence, autoignition with a higher-quality pyrolysis liquid may succeed as stated by Shihadeh [Ph.D.Thesis]. Shihadeh's work was carried out with a combustion bomb to simulate the diesel engine environment, but not with a diesel engine.

The Ignition Quality Tester ($\mathrm{IQT}_{\mathrm{TM}}$) is a combustion-based analytical instrument, by which the ignition delay and cetane number (CN) of diesel and alternative fuels (including cetane improved diesel fuels) can be accurately determined. The American Society for Testing and Materials (ASTM) has approved the establishment of a study group to implement an ASTM standard test method for use of $\mathrm{IQT}_{\mathrm{TM}}$ to determine the cetane number of diesel fuels. CanMet and AET (Advanced Engine Technology Ltd.) in Canada have carried out IQT tests with pyrolysis liquid emulsions. Based on these results and by linear interpolation they ended up to a cetane number of 5.6 for the tested hardwood pyrolysis liquid [Ikura et al. JOR3-CT98-0253, Final report].

Instituti Motori (Italy) has studied the combustion characteristics of pyrolysis liquids by evaluating the ignition delay as the time lag between the start of the needle lift and the start of combustion. By means of a Reference Fuel Correlation, the Cetane Number of about -10 was evaluated from the Ignition Delay [Bertoli et al. JOR3-CT98-0253, Final report].

The method for determination the ignition temperature of pyrolysis liquids is under testing at VTT employing a thermobalance (TG).

The test developed to characterise gasoline properties (octane number) in spark ignition engines is not appropriate for pyrolysis liquids, as significant improvements on the pyrolysis liquid quality would be required. Antiknock rating or the octane number can be measured in a single-cylinder engine test according to ASTM D 2699 - 68 (IP 237/69). The fuel used should possess the following characteristics: high volatility, good stability in preheating (135 ± 8.5°C), good miscibility with hydrocarbons, stability with air, neutrality, stability during the test, a low amount of carbon deposit, and easy to clean. Pyrolysis liquid does not fulfill these requirements.

6.9 Thermal conductivity, specific heat capacity and electrical conductivity

Thermal conductivity and specific heat capacity are essential in the design and evaluation of transport units and sizing process equipment, i.e., heat exchangers, atomisers and combustors. There are two methods for measuring thermal conductivity [Jamieson 1975] – absolute or comparative. In the absolute method the heat conducted across a film of the test fluid located in the annular space between two vertical copper cylinders is measured. Thermal conductivity of pyrolysis liquids was determined using the more common comparative method where the heat conducted across a thin film of the test fluid in the space between a nickel coated sphere and a surrounding block using a relative method is measured [as described in Peacocke et al. 1994].

The chemical reactivity of pyrolysis liquids leads to erroneous results and values can vary even within batches of liquids, due to poor mixing and phase separation. Results from the work of Peacocke give an average thermal conductivity of

0.386 W/mK over the temperature range 44–63°C for mixed hardwood-derived fast pyrolysis liquids.

Measurements for specific heat capacity of pyrolysis liquids were carried out using a test-rig [Peacocke et al. 1994] where pyrolysis liquid was pumped around a closed loop at approximately 0.1 g/s. The liquid passed through the cell where it was heated and returned to the reservoir. Heat losses were minimised by sealing the cell body under high vacuum and covering it with aluminium. The pyrolysis liquid temperature change across the heater was measured. Power input was calculated by measuring the potential difference across the heater and a thermally stable resistor connected in series with the heater. The mass flow rate was measured at 2°C intervals by sampling the oil flow rate for two minutes. The system was calibrated using Shell Thermia B oil. Results of the work of Peacocke give an average value of 3.2 kJ/kgK [±300 J/kgK] over the temperature range of 26–61°C.

Electrical conductivity is a property that is of no direct use for fuel applications, but is required by some instruments for level measurement and control. There are no published data for values. However, Wellman Process Engineering Ltd. has provided some data as indicated in Table 5.

Table 5. Electrical conductivity of pyrolysis liquids.

Sample code	Water content wt%	Char content wt%	Conductivity µS/cm
DYN1002	28.54	1.49	50
BTG2G	22.97	0.77	60
BK40/90W7	21.33	--	200

Data supplied by Wellman Process Engineering Ltd. [measured using a standard electrical conductivity meter] Water and char content data supplied by Aston University.

6.10 Lubricity

Viscosity does not describe the lubricating properties of the oils. Lubrication properties are crucial, for example, for selection of supply pumps [Rick & Vix 1991]. Two methods measuring lubricating properties of diesel fuels have been tested for pyrolysis liquids [Oasmaa et al. 1997]: Cameron Plint TE77 High Frequency Friction equipment, and a fourball wear test according to IP 239/69T [ASTM D 278388] were used. The former method is not suitable, because it is a totally open system and the evaporation of pyrolysis liquid disturbs significantly the measurement. The latter method may be used. Considering the preliminary tests, it seems that the pyrolysis liquids possess some lubricating properties. It should be borne in mind that the viscosity of the sample affects the results and no exact conclusions can be drawn due to the great difference in viscosity between pyrolysis liquids and diesel fuels [Oasmaa et al. 1997].

7. Unique properties of pyrolysis liquids

7.1 Acidity and material corrosion

The pH of pyrolysis liquids is low (2–3) due to high amounts (8–10 wt%) of volatile acids, mainly acetic and formic acid [Sipilä et al. 1998, Fagernäs 1995]. These acids with water are the main reasons for the corrosiveness of pyrolysis liquids especially at elevated temperatures [Aubin & Roy 1980].

When producing pyrolysis liquids an even black coating can be formed on the steel surface of the process equipment. This “coating”, analysed by ESCA (Electron Spectroscopy for Chemical Analysis), contained metals from pyrolysis liquid, mainly silica, potassium, and calcium. No corrosion was observed.

The corrosion test specified for fuel oils is empirically based (colour changes for copper strips) and bears little significance to the corrosion potential of a pyrolysis liquid. The colour changes observed, resulting from copper reacting with different chemicals (primarily sulphur-containing compounds) found within the petroleum. The calibration of this type of test or the development of an entirely new test is required, before the corrosion potential of pyrolysis liquids can be set down in a specification [Diebold et al. 1997].

In the standard corrosion test at 60°C (ASTM D 665 A), no rust was formed, but a clear weight loss in carbon steel (AISI 01) was observed. Aubin and Roy [1980] reported no corrosion for carbon steel at ambient temperature in low acid (3.6%) and water (4.4%) concentrations, but they observed clear corrosion at elevated temperature (45°C) in high acid (17.5%) and high water (55.7%) contents.

The acid-resistant steel AISI 316 (17% Cr, 11% Ni, 2.2% Mo, 0.05% C) can be used. AISI 316 may be a little better than AISI 304 because of the small amount of Mo that serves to make the steel more resistant to general corrosion in non-oxidising acids, to stress corrosion and especially to localised corrosion (pitting and crevice corrosion) caused by aggressive components like halogens [Oasmaa et al. 1997]. It is difficult to find suggestions for corrosion allowances for pyrolysis liquids in the literature. Rates have been suggested for "pyroligneous acid – wood distillation products": < 0.0001 cm/y for 304 and 316 SS [Polar 1961].

Extensive testing of various metals (brass, mild steel, aluminium and stainless steel) has been carried out by Orenda [Fuleki 1999]. Brass and stainless steel were relatively unaffected, but aluminium and mild steel suffered severe weight loss at higher temperatures and prolonged exposure (17.8 and 15.8 wt% loss respectively during 360 hours, 70°C). If the surface deposits on the mild steel were removed, then even higher corrosion rates were reported (19.6 wt% loss during 360 hours, 70°C). It was noted that brass might not be suitable in fuel combustion systems, due to the potential erosion by particulate matter in the liquids. Soltes and Lin [1984] also reported that the pyrolysis liquids are corrosive to mild steel and aluminium.

Jay et al. [1995] carried out material testing related to Wärtsilä's diesel engine tests. The nozzle would be a critical component with respect to abrasive wear due to high particle content and corrosion. The tests in a 400 bar injection test rig showed M390 to be suitable material for the nozzle. M390 is Martensitic Sintered Stainless steel with a composition of 1.90% C : 20% Cr : 1% Mo : 4% V : 0.6% W, which can be through hardened to achieve a 62 HRc and can withstand soak temperatures of up to 500°C. X90CrMoV18 (AISI 440B) stoff 1.4112 Martensitic Stainless steel, 57 HRc hardness is suitable for engine pushrods and injection needles [Jay et al. 1995].

Nickel and nickel-based materials are not resistant to pyrolysis liquids even at room temperature. On the other hand, cobalt-based HAYNES 188 (39.4% Co, 22% Cr, 22.9% Ni, 14.5% W, 1.2% Fe) was resistant in the corrosion tests at < 80°C [Oasmaa et al. 1997].

In the copper corrosion test (ASTM D 130) no corrosion or weight loss on copper stem (99.9% electrolytic copper) was observed for different pyrolysis liquids (hardwood, softwood, straw) at 40°C. Copper is a noble metal and hence has generally a good corrosion resistance to non-oxidising acids. Copper is suitable for washers [Jay et al. 1995]. However, if connected with other metals, there is a possibility of electrochemical corrosion. Copper and its alloys (brass, bronze, cupronickel) are widely used in piping applications (tubes, valves, etc.) mostly because of the excellent availability of different components. However, it should be borne in mind that copper and brasses are subject to erosion and corrosion, when high fluid velocities are used or abrasive particles are present especially at higher temperatures. It should also be pointed out that brass with 15% Zn or more could not be used with pyrolysis liquids due to dezincification.

Many plastics like PTFE (polytetrafluoroethylene), PP (polypropylene), PE (polyethylene), HDPE (high density polyethylene), and polyester resins are very resistant to pyrolysis liquids [Oasmaa et al. 1997, Czernik 1994]. They are excellent materials for containers in storing, transportation and sampling of pyrolysis liquids. EPDM (Ethylene Propylene Diene Monomer rubber) and Teflon O rings can be used in sealing [Jay et al. 1995]. Viton O rings react with pyrolysis liquid causing material expansion [Jay et al. 1995]. The use of plastics could possibly be extended to replacing copper or, in special cases, also AISI 316.

7.2 Solubility

7.2.1 Water solubility

Water is chemically dissolved in pyrolysis liquids [Oasmaa et al. 1997]. Pyrolysis liquids can be considered as mixtures of water and water-soluble organic compounds with water-insoluble, mostly oligomeric material (Table 6). The ratio of these fractions depends on the feedstock, on the process and storage conditions. The lignin-derived oligomers usually account for 30–40 wt% of the liquid, while water concentration ranges from 20 to 30 wt%. In such cases, pyrolysis liquids are typically in single phase because of the presence of polar carboxyl and hydroxyl compounds. However, phase separation can take place in higher water and/or lignin-derived material concentrations [Oasmaa & Czernik 1999]. In phase separation, the heavy mainly lignin-derived fraction separates out from the aqueous fraction. This type of phase separation occurs for example in fresh liquid, when the moisture content of the feedstock has been too high (>15 wt%).

Table 6. Compound classes in pyrolysis liquids (D. Radlein in Bridgwater et al. 1999).

Compound class	Composition range (wt% of organic fraction of pyrolysis liquid	Hydrophilicity (arbitary scale 4 is highest)
C_1 compound (formic acid, methanol and formaldehyde, CO_2)	5–10	4
C_2–C_4 linear hydroxyl and oxo substituted aldehydes and ketones	15–35	4
Hydroxyl, hydroxymethyl and/or oxo substituted furans, furanones and pyranones (C_5–C_6)	10–20	3
Anhydrosugars, incl. anhydro-oligosaccharides (C_6)	6–10	4
Water-soluble carbohydrate derived oligomeric and polymeric material	5–10	4
Monomeric methoxyl substituted phenols	6–15	2
Pyrolytic lignin	15–30	1

Pyrolysis liquids differ to some extent in their ability to dissolve water [Oasmaa et al. 1997]. A typical phase diagram for a pyrolysis liquid – water system is shown in Figure 9. The weight percent of organics (or water) in each phase is presented as a function of the global organic material concentration in the liquid. The segment of the diagonal in the upper right corner corresponds to a single-phase liquid. With the addition of water to this particular pyrolysis liquid, the phase separation occurs at 25 wt% of water (75 wt% of organics) in the liquid. The bottom layer, which is represented by the upper branch in the diagram, contains more organic, mostly lignin-derived compounds, while the upper layer (lower branch) is the aqueous fraction, with mostly carbohydrate-derived components. For example, in the overall water content of 50% the aqueous fraction would contain 27% of organics and 73% of water, while the organic phase would contain 72% of organics and 28% of water [Oasmaa & Czernik 1999].

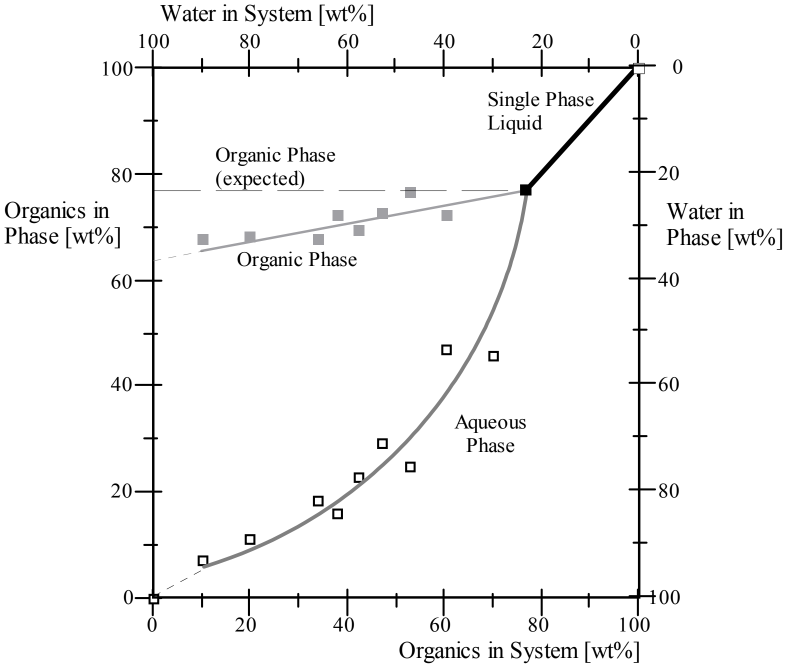


Figure 9. Pyrolysis liquid - water phase diagram [Peacocke et al. 1994].

By adding increasing amounts of water to pyrolysis liquids, a phase separation can be forced to occur (Appendix C/1). When adding excess water, the water-insoluble lignin-derived fraction separates out of the aqueous phase (Appendix G). The amount of water insolubles varies for different pyrolysis liquids: 34–35 wt% (dry basis) for hardwood, 32–35 wt% (dry basis) for softwood (pine) and forest residue (pine/spruce), and 17–28.5 wt% (dry basis) for straw liquids. Extractives are included to water insolubles [Oasmaa & Kuoppala 2002b].

7.2.2 Solubility in other solvents

The solubility of pyrolysis liquids in solvents other than water is significantly affected by the degree of polarity. Good solvents for highly polar white wood and straw pyrolysis liquids are alcohols, like ethanol and methanol. These solvents dissolve practically the whole pyrolysis liquid excluding solids (char). Acetone is also a good solvent for white wood liquids, but causes a precipitation/reaction in straw liquid (see Chapter 5.2).

White wood pyrolysis liquids do not dissolve in hydrocarbons like hexane, diesel fuels and polyolefins. However, forest residue and bark liquids contain extractives which are soluble in n-hexane. For dissolving forest residue liquids a mixture of a polar (alcohol) and a neutral (dichloromethane, dioxane, hexane) solvent is needed (see 5.2 and Appendix D).

For cleaning-up and washings basic solvents, like NaOH (Sodium Hydroxide) and machine wash agents, are efficient in laboratory.

7.3 Stability

Pyrolysis liquids are not stable like conventional petroleum fuels due to their high amount of reactive oxygen containing compounds and low-boiling volatiles. A comprehensive overview on stability of pyrolysis liquids is given by Diebold in Bridgwater et al. 2001. The instability of pyrolysis liquids can be seen as:

- Evaporation of volatile components under air. Possible reactions with air.
- Slow increase in viscosity and phase-separation ("aging").
- Fast increase in viscosity/polymerisation and phase-separation by heating.

Exposure to air must be prevented for several reasons, e.g., loss of light compounds causing strong odours in the environment and oxygen causes polymerisation reactions with consequent sedimentation of heavy compounds. Hence, storage, handling and transport must be performed in air-tight, non-ventilated containers and transfer from the storage tank to a transport vehicle and reverse must be carried out with a simultaneous exchange of gas to prevent air inlet and exhaust to ambient air [Oasmaa et al. 1997, Hägerstedt & Jakobsson 1999].

Pyrolysis liquids contain compounds that, during storage or handling at ambient temperatures, can react with themselves to form larger molecules. The main chemical reactions observed are polymerisation of double-bonded compounds [Polk & Phingbodhippakkiya 1981], as well as etherification and esterification occurring between hydroxyl, carbonyl, and carboxyl group components [Czernik et al. 1994], in which water is formed as a byproduct. These reactions result in undesirable changes in physical properties, such as increase of viscosity, molecular weight and water content with a corresponding decrease of volatility [Oasmaa & Czernik 1999]. Aging reactions are fastest in a fresh pyrolysis liquid (Figure 10) and retard in time (Figure 10). Due to the instability of the pyrolysis liquids, special care has to be taken in handling, transporting, storing, and using the liquids.

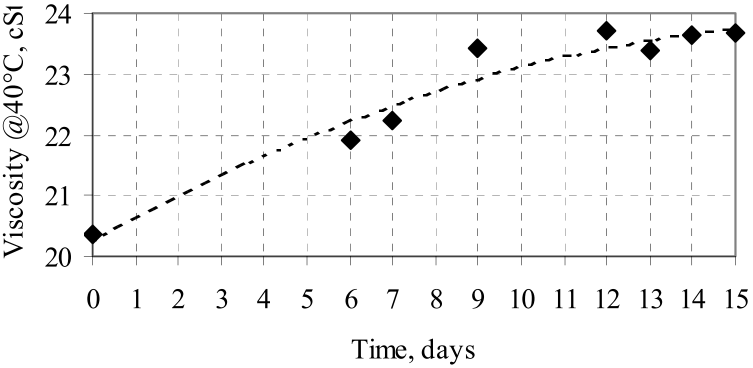


Figure 10. Viscosity increase of a forest residue liquid (bottom phase) during the first two weeks after production.

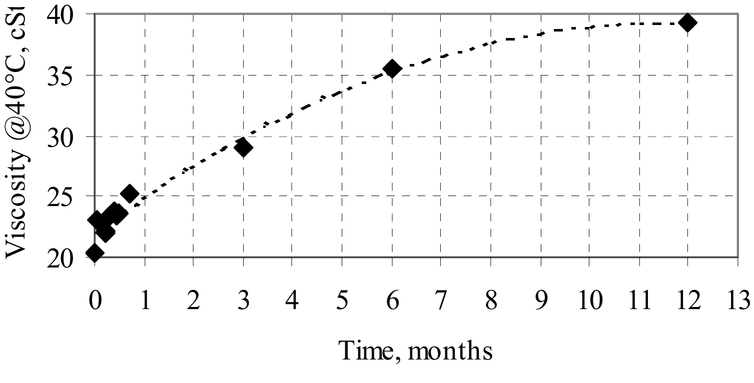


Figure 11. Viscosity increase of a forest residue liquid (bottom phase) during one year after production.

When heating pyrolysis liquid four stages are observed:

1. Thickening. The viscosity of the liquid increases because of mainly polymerisation reactions. At ambient temperatures the viscosity of a typical pyrolysis liquid roughly doubles in a year. The increase in viscosity is faster at elevated temperatures (Figure 12). The viscosity change is different for various pyrolysis liquids.
2. Phase separation. Water is formed as by-product in aging reactions (etherification, esterification, condensation reactions). An aqueous phase separates out of the heavy lignin-rich phase, when the total water content of the liquid exceeds about 30 wt% (see Chapter 7.2).
3. Gummy formation from the heavy lignin-rich-phase, if the temperature is raised (abt. 140°C).
4. Char/coke formation from the gummy phase at higher temperatures.

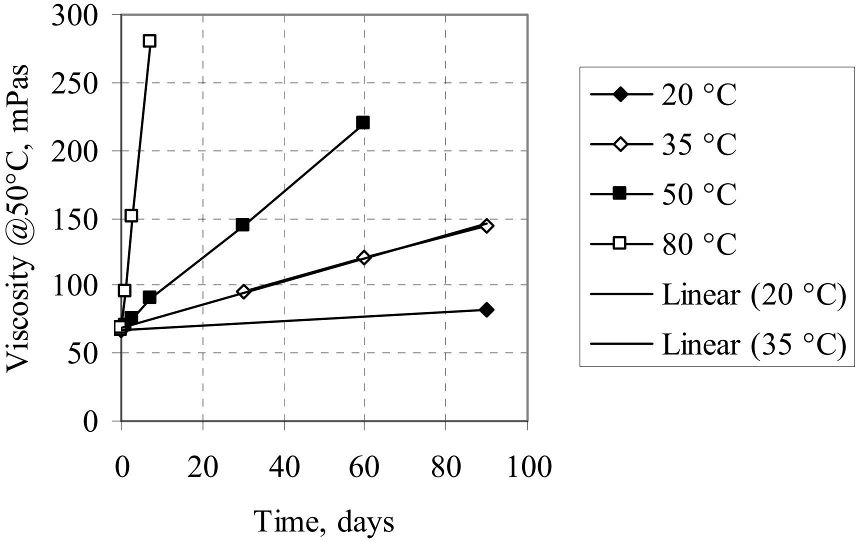


Figure 12. Viscosity change of a hardwood pyrolysis liquid at 20–80°C [Oasmaa et al. 1997].

Because of this thermal instability, heating should be done indirectly with a low-temperature surface, e.g., warm water heat exchanger, jacketed tanks. Temperatures below 50°C are recommended for storage and pumping.

A simple test (Appendix H/1) was developed for a quick comparison of the stability of different pyrolysis liquids [Oasmaa et al. 1997]. In the test, the pyrolysis liquid is kept at fixed temperature for a certain time, and the increase in viscosity is measured. The presence of air (10 vol%) increases only slightly the viscosity (Appendix H/2), and hence, for practical reasons, it is recommended to perform the test without any nitrogen-purge with a fixed (10 vol%) free-space volume. This test has been included to the round robin 2000 [Bridgwater et al. 2001] and the results showed that more precise instructions and more testing for stability test are needed. Other test conditions used were 6 hours at 80°C and 1 week at 40°C. The stability test is recommended to be used for internal comparison of pyrolysis liquids owing similar initial viscosities.

For a pine liquid (water content 21 wt%, viscosity @40°C 35 mPas) the viscosity increase (95%) in the test conditions 24 hours at 80°C correlated to the viscosity increase in one year storage at room temperature. Addition of an organic solvent, e.g. methanol, ethanol, or isopropanol, improves the stability of the pyrolysis liquid (Diebold & Czernik 1997, Oasmaa et al. 1997). For example, addition of 2, 5, and 10 wt% ethanol to the pine pyrolysis liquid mentioned above the viscosity increase decreased to 56, 48, and 15%, respectively. At higher temperatures, the ethanol addition had also a favourable effect on viscosity (Oasmaa et al. 1997).

For forest residue liquid (bottom phase) the correlation (stability test compared to room temperature storage) has been similar. Because of higher water content of forest residue liquid test conditions 24 hours at 80°C has often yielded to phase-separation and the viscosity of the liquid could not be determined for aged sample. Hence, test conditions 1 week at 40°C has been used for forest residue liquid. At these conditions the viscosity increase correlates to three months storage at room temperature.

8. Fuel oil specifications

At present, there are no national or internationally recognised standard of fuel specifications for biomass-derived fast pyrolysis liquids. Progress is being made in this area, but due to the lack of a wide availability of consistent pyrolysis liquids, coupled with ongoing developments in the methods for fast pyrolysis liquids, standards are not expected for another 1–3 years. Commercial application of biomass pyrolysis liquids requires an adequate description of their relevant properties. The specifications for standard fuel oils have been established by ASTM and similar organizations in respective countries. They define property ranges for different classes of fuels marketed for different specialized applications [Oasmaa & Czernik 1999].

The significance of the specification standards relate to their development for petroleum-derived fuel applications. When considering the applications of these standards to a non-petroleum-derived fuel, one must understand the basis for the standard and justify the appropriateness of its application [Elliott 1983]. Elliott assessed the specification standards for various pyrolysis liquids in IEA BLTF (International Energy Agency Biomass Liquefaction Test Facility) project. The classification was based on ASTM standards D-396 for fuel oils, D-975 for diesel fuels, and D-2880 for gas turbine fuels. The IEA PYRA group suggested [Diebold et al. 1997] specifications shown in Table 7. Feedback from pyrolysis liquid end-users was requested.

Based on the diesel engine and boiler tests performed, an engine manufacturer, Wärtsilä NSD Oy, and a potential bio-oil user, Birka Energi (former Stockholm Energi AB), set the requirements for heating values and water, solids, and ash content that are presented in Table 8 [Oasmaa & Czernik 1999]. For combustion, tighter specifications, less property variation, has recently been acknowledged [Oasmaa & Kytö 2000, Oasmaa & Meier in Bridgwater 2001].

It is necessary to conduct large-scale and long-duration tests on boilers, engines and turbines before accepting pyrolysis liquids as commercial fuels. These tests will require a substantial supply of liquids with specified properties established by the producers and users.

Table 7. Proposed specifications for biomass pyrolysis liquids [Diebold et al. 1997].

	Light bio-oil (~ASTM #2)	Light-Medium bio-oil (~ASTM #4)	Medium bio-oil (~PORL100)	Heavy bio-oil (~Can. #6)
Viscosity, cSt	1.9-3.4 FO 1.9-4.1 D 1.9-4.1 GT @ 40 °C	5.5-24 @ 40 °C	17-100 @ 50 °C	100-638 @ 50 °C
Ash, wt%	0.05 FO 0.01 D 0.01 GT	0.05 FO 0.10 D	0.10 FO	0.10 FO
Pour point, °C min	report	report	report	report
CCR, wt%	report	report	report	report
Max. 0.1 μm filtered ethanol insolubles	0.01 FO	0.05	0.10	0.25
Accelerated aging rate @ 90 °C cSt/h	report	report	report	report
Water, wt% of wet oil, max.	32	32	32	32
LHV, MJ/L min., wet oil	18	18	18	report
C, wt% dry	report	report	report	report
H, wt% dry	"	"	"	"
O, wt% dry	"	"	"	"
S, wt% dry	0.1 max.	0.1 max.	0.2 max.	0.4 max.
N, wt% dry	0.2 max.	0.2 max.	0.3 max.	0.4 max.
K + Na, ppm	report 0.5 GT	report	report	report
Phase Stability @ 20 °C 8 h @ 90 °C	single phase	single phase	single phase	single phase
Flash point, °C min.	52	55	60	60
Density, kg/m3	report	report	report	report

Table 8. Specifications for biomass pyrolysis oil for diesel engines and boilers.

	Diesel engine tests by Wärtsilä		Tests at Birka Combustion
	Specifications	Allowable variation (10%) for a container (surface/bottom)	Specifications
Homogeneity	7-day storage	no phase-separation	-
Water, wt%	max 26	max 10% difference, max 26	max 25
HHV, MJ/kg LHV, MJ/kg	min 18 min 16	max 10% difference, min 18 and 16	min 19 min 17
Ash, wt%	max 0.1	0–0.1	max 0.1
Solids, wt%	max 1	0–1	max 1
<50 µm	100	-	-
<25 µm	min 90	-	-

9. Recommendations

Pyrolysis liquids exhibit unusual properties, which are not apparent in conventional hydrocarbon liquids. The aim of this guide is to highlight the difficulties with the standard methods for property determination and to elucidate and propose modified standard and new test methods as appropriate, based on the current state of knowledge. Further developments in the test methods will continue, however, this guide provides basic data for the producer, tester and end-user of the liquids.

Based on the wide range of properties assessed and evaluated in this guide, the following modifications to the standard methods are recommended:

Table 9. Analytical methods for wood-based pyrolysis liquids.

Analysis	Method	Comment	Sample size
Water, wt%	ASTM E 203	1	1 g
Solids, wt%	Ethanol insolubles	2	30 g
	Methanol-Dichloromethane insolubles	2	30 g
Particle size distribution	Microscopy+Particle Counter	3	1 g
Conradson carbon, wt%	ASTM D 189	4	2–4 g
Ash, wt%	EN 7	5	40 ml
CHN, wt%	ASTM D 5291	6	1 ml
Sulphur and chlorine, wt%	Capillary electrophoresis	7	2–10 ml
Alkali metals, wt%	AAS	8	50 ml
Metals, wt%	ICP, AAS	9	50 ml
Density (15°C), kg/dm^3	ASTM D 4052	10	4 ml
Viscosity (20, 40°C), cSt	ASTM D 445	11	80 ml
Viscosity, mPas	Rotational viscometry	12	40 ml
Pour point, °C	ASTM D 97	13	80 ml
Heating value, MJ/kg calorimetric (HHV) effective (LHV)	DIN 51900	14	1 ml
Flash point, °C	ASTM D 93	15	150 ml
pH	pH meter	16	50 ml
Water insolubles, wt%	Water addition	17	5 ml
Stability	80°C 24 hours	18	200 ml
	40°C 1 week	18	200 ml

Sample size = Minimum amount of pyrolysis liquid needed for carrying out the analysis including duplicates.

Comments to Table 9.

Note 1: When handling reagents in the procedures described in the following appendices, please observe all relevant health and safety procedures (Appendix A) applicable.

Note 2: Extractive-rich samples, like forest residue liquids, foam easily. A gentle mixing, like rolling the sample bottle carefully, is recommended. See Appendix B.

1. *Karl-Fischer titration. Methanol-Chloroform (3:1) as a solvent. Water addition method for calibration. HYDRANAL K reagents (Composite 5K and Working Medium K) in case of a fading titration end-point. 50 ml solvent for two determinations. Sample size about 0.25 g (water content >20 wt%). Stabilisation time 30 s. See appendix C.*
2. *Millipore or multi-place filtration system, 1 µm filter, sample size 1–15 g in order to obtain 10-20 mg residue, sample:solvent = 1:100, solvent: ethanol for white wood liquids, methanol-dichloromethane for forest residue liquids (Appendix D).*
3. *Microscopy with photo analysis programme (Appendix E).*
4. *Controlled evaporation of water to avoid foaming. The implication of carbon residue is unclear.*
5. *Controlled evaporation of water to avoid foaming.*
6. *Proper homogenisation. For forest residue liquids careful rolling of the sample bottle. Large sample size as possible. Triplicates.*
7. *Sample pretreatment by combustion according to ASTM D 4208*
8. *Wet combustion as a pretreatment method. See appendix F.*
9. *Wet combustion (Appendix F) as a pretreatment method. In samples with a high amount of silicates, silicon can precipitate as SiO_2 during the sample pretreatment. This may yield an error in silicon. For accurate determination of Si the sample should be ashed by dry combustion and a fusion cake prepared from the ash.*
10. *Careful mixing of foam-prone forest residue liquids in order to avoid air bubbles.*
11. *Cannon-Fenske viscometer tubes at room temperature and for non-transparent liquids, Ubbelohde tubes may be used for transparent liquids.*

No prefiltration of the sample if visually homogenous. Elimination of air bubbles before sampling. Equilibration time 15 minutes.

12 *Precise temperature measurement. Cover to the sample holder above 40°C.*

13 *No preheating of the sample.*

14 *Use of a fine cotton thread for ignition. Lower heating value (LHV) obtained from calorimetric heating value and hydrogen analysis.*

15 *Elimination of air bubbles before sampling.*

16 *Frequent calibration of the pH meter.*

17 *Addition of 5 g pyrolysis liquid into water, see Appendix G*

18 *90 ml (45 ml) pyrolysis liquid in 100 ml (50 ml) tight glass bottles, heating in a heating oven (Appendix H). Measuring of increase in viscosity and water. Viscosity determination at 40°C according to ASTM D 445.*

Other analyses from literature, which were not tested within this study, are presented in Table 10. Properties of pyrolysis liquids are summarised in Table 11.

Table 10. Analytical methods for wood-based pyrolysis liquids. Literature data [Bridgwater et al. 1999].

Property	Standard method	Suitability of the method
Density	ASTM D941	Can be used
	ASTM D1298-85	Can be used
Thermal conductivity	No standard	Rough estimate
Specific heat capacity	No standard	Rough estimate
Setting point	DIN51583	Can be used
Boiling curve	ASTM D86-82	Cannot be used
Coke residue	ASTM D524-88	Can be used
Ignition limit	DIN51603	Limited testing
Vapour pressure	IP69/89	Can be used
Surface tension	ASTM D 971-50	Limited testing
Sulphur	ASTM D4208	Can be used

Table 11. Properties of pyrolysis liquids.

Property	Range (wet basis)
Density (15°C), kg/dm^3	1.11–1.30
Lower heating value, MJ/kg	13–18
Viscosity-kinematic, cSt	10–80 @50°C
Thermal conductivity, W/mK	0.35–0.43
Specific heat capacity, J/gK	2.6–3.8 @ 25–60°C
Pour point	$^{-}9$–$^{-}36$
Coke residue, wt%	14–23
Flash point, °C	40–110
Ignition limit, °C	110–120
Ignition temperature, °C	600–700
Water, wt%	20–35
Char, wt%	0.01–1
Vapour pressure, kPa	5.2 @33.5°C
Surface tension, mN/m	29.2
Carbon, wt% (dry)	32–49 (48–60)
Hydrogen	6.9–8.6 (5.9–7.2)
Nitrogen	0–0.4
Oxygen	44–60 (34–45)
S, ppm	60–500
Cl, ppm	3–75
Ash, wt%	0.01–0.20
pH	2.0–3.7
K+Na, ppm	5–500

The use of biomass-derived pyrolysis liquids in heating and electricity generation applications is increasing significantly. For the producer, a ready reference for the determination of properties and how to handle the liquids is essential. It is hoped that this guide will allow those active in research, development and commercial applications to better understand how to evaluate the properties of the liquids, relevant to the application and allow the liquids to be used in a safe and environmentally compliant way.

The use of the modified methods [derived from conventional fuel oil methods] proposed in this guide is aimed to avoid some of the more common problems associated with the liquids and improve their usability in a range of applications.

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LIST OF APPENDICES

Where appropriate for methodologies, looked at: Oasmaa, A. Leppämäki, E., Koponen, P., Levander, J. & Tapola, E. Physical characterisation of biomass-based pyrolysis liquids. Application of standard fuel oil analyses. Espoo: VTT Energy, 1997. 46 p. + app. 30 p. (VTT Publications 306.) http://www.inf.vtt.fi/pdf/publications/1997/P306.pdf

Note: When handling reagents in the procedures described in the following appendices, please observe all relevant health and safety procedures applicable.

Appendix A:

MSDS – Material health and safety data sheet for pyrolysis liquids

Prepared by Dr.C.Peacocke and Dr.A.V.Bridgwater, Aston University, UK. Modifications to Chapters 2.0 and 10.0 based on IEA PyNe MSDS [Bridgwater et al. 1999].

NOTE:

There is at present no official recognition of the information contained within this document. The Health and Safety Executive do not have an official designation for pyrolysis liquids.

This MSDS has no legal validity and represents a consensus view of those active in biomass fast pyrolysis, that using publicly available information represents the best effort that can be made at this time.

1.0 Chemical Identification

Pyrolysis liquid (also known as pyrolysis oil, bio-crude-oil, bio-oil bio-fuel-oil, pyroligneous tar, pyroligneous acid, wood liquids, wood oil, liquid smoke, wood distillates)

2.0 Composition/Information on Ingredients

Complex mixture of highly oxygenated hydrocarbons. A mixture of three to four hundred chemicals derived by the thermal decomposition of biomass. A typical pyrolysis oil may be composed as follows:

Composition	wt%
organic acids	5–10
aldehydes and hydroxyaldehydes	5–20

ketones and hydroxyketones	0–10
anhydrosugars	5–30
degraded lignin, phenolics	20–30
hydrocarbons	0–5
water	15–35

A list of components which may be found in pyrolysis oils is appended (Appendix 1).

3.0 Synonyms

Bio-oil, pyrolysis liquid, pyroligneous oil, bio crude oil, pyroligneous liquid, liquid wood, bio-fuel oil, wood tar, wood oil.

4.0 Hazards Identification

Label Precautionary Statements

- Harmful by inhalation, in contact with skin and if swallowed.
- Irritating to eyes, respiratory system and skin.
- Corrosive (pH 1.5–3).
- Only flammable with additional fuel source at 5wt% concentration such as methanol, ethanol, acetone, or diesel and upon heating with suitable ignition source.
- Possible mutagen, contains potentially carcinogenic compounds.
- Keep container tightly closed in a cool well ventilated place.
- Do not empty into drains.
- Wear suitable gloves and eye/face protection when handling.
- Avoid continuous exposure.

5.0 First Aid Measures

- In case of contact with eyes flush with copious amounts of water for 15 minutes. Remove contaminated clothing.
- In case of contact with skin flush with copious amounts of water. Remove contaminated clothing.
- If inhaled remove to fresh air. If breathing is difficult give oxygen. If not breathing give artificial respiration.

- If swallowed, wash out mouth with water. Consume water to dilute. Call doctor immediately.

6.0 Fire Fighting Measures

Extinguishing Media
Water, Carbon Dioxide, Foam, Powder

Special Fire Fighting Precautions

- Wear self contained breathing apparatus and protective clothing to prevent contact with eyes and skin. Do not inhale smoke from fire.
- Use water spray to cool fire exposed containers.

7.0 Accidental Release Measures

7.1 Small Quantities (<100ml)

- Wear rubber gloves and suitable eye and face protection.
- Cover contaminated area with sawdust.
- Take up sawdust and place in closed container.
- Transport to approved landfill or incinerator.

7.2 Large Quantities (>100ml)

- Evacuate area.
- Wear rubber boots, rubber gloves, suitable eye/face protection and NIOSH/MSHA approved respirator.
- Cover contaminated area with sawdust. Take up sawdust and place in closed container. Transport to approved landfill or incinerator.

8.0 Handling and Storage

- Store in sealed container in darkness at room temperature.
- Immiscible with water above 50% weight concentration. Soluble only in solvents such as acetone or ethanol. Immiscible in hydrocarbon solvents.
- Reacts with mild steel and impure copper due to high acidity. Attacks buna rubber and in some cases causes rubber seals to swell.

9.0 Exposure Controls/Personal Protection

- Wear appropriate NIOSH/MSHA approved respirator, rubber gloves, rubber apron, and suitable eye/face protection.
- Use in a well ventilated area or fume cupboard.
- Safety shower and eye bath.
- Do not breath vapour.
- Wash thoroughly after handling.

10.0 Physical and Chemical Properties

Dark brown, viscous liquid with a smoky odour.

(All values are typical, not definitive, values)

pH	2.5–3.5
Density (kg/dm3)	1.2 @ 15°C
Viscosity (cSt)	20–100 @ 40°C
Pour point (°C)	¯20
Flash point (°C)	50–70
Boiling Curve	Starts boiling below 100°C. Forms 20–50% of solid residue.
Autoignition Temperature	High. Approximately above 500°C.
Upper Explosion Level:	Unknown
Lower Explosion Level:	Unknown
Vapour Pressure:	Similar to water
Vapour density:	Unknown

11.0 Stability and Reactivity

Incompatibilities

Heat - 50% char formed upon continuous heating above 100°C

Hazardous Combustion or Decomposition Products.

Fumes of:

Carbon dioxide

Carbon monoxide

Light organics-2-propenal, acetic acid, formaldehyde, methanol, acetaldehyde

12.0 Toxicological Information

- Liquids produced at reactor temperatures greater than 600°C contain condensed polyaromatic ring compounds which have mutagenic effects.
- Harmful if swallowed, inhaled, or absorbed through the skin.
- Vapour is irritating to the eyes, mucous membranes and upper respiratory tract.
- Can sensitise skin.
- Laboratory test have shown mutagenic properties.

13.0 Ecological Information

Very high BOD - no exact value yet

14.0 Disposal Considerations

Burn in a chemical incinerator observing all environmental regulations.

15.0 Transport Information.

Transport in sealed translucent container in cool conditions. Avoid prolonged exposure to strong sunlight and heat.

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Appendix 1

Some Chemicals Identified in Pyrolysis Liquid.

Acids

oxopentanoic acid
acetic acid
benzoic acid
butyric acid
formic acid (methanoic acid)
glycolic acid
hexadecanoic acid
hexanoic acid
propanoic (propionic) acid
valeric acid (pentanoic acid)

Sugars

1,6-anhydroglucofuranose
cellobiosan
D-arabinose
D-glucose
D-xylose
fructose
oligosacharides
levoglucosan

Ketones

1-hydroxy 2-propanone
2,5-hexanedione
2-butanone
2-ethylcyclopentanone
2-methyl-2-cyclopenten-1-one
2-methylcyclohexanone
2-methylcyclopentanone
3-ethylcyclopentanone
3-methyl-2-cyclopenten-1-one

3-methylcyclohexanone
3-methylcyclopentanone
3-methylindan-1-one
C8 (=) cyclic ketones
C8 cyclic ketones
C9 (=) cyclic ketones
C9 cyclic ketones
cyclohexanone
cyclopentanone
dimethylcyclopentanone
hydroxyacetone
methylcyclopentene-ol-one
trimethylcyclopentanone

Phenolics

(4-hydroxyphenyl)-1-ethanone
2,3,5-trimethylphenol
2,3,6-trimethylphenol
2,3-dimethyl phenol
2,4,6-trimethylphenol
2,4-xylenol
2,5,8-trimethyl-1-naphthol
2,5-dimethyl phenol
2,6-dimethoxy phenol
2-methoxy-4(1-propenyl)phenol
2-methoxy-4-n-propylphenol
3-methyl-1-naphthol
4-ethyl-1,3-benzenediol
4-ethyl-2-methoxyphenol
4-ethylguaiacol
4-hydroxy-3,5-dimethoxyphenylethanon
4-hydroxy-3-methoxybenzaldehyde (Vanillin)
4-methyl-2-methoxyphenol
4-propylguaiacol
6,7-dimethylnaphthol
C2 dihydroxybenzene

C3 dihydroxybenzene
C3 phenols
C4 dihydroxybenzene
C4 phenol
C4 phenols
C5 (=) phenols
C5 dihydroxybenzene
C5 phenols
C6 (=) phenols
C6 dihydroxybenzene
C6 phenols
catechol
dimethyldihydroxybenzene
dimethylnaphthol
ethylmethylphenol
eugenol
guaiacol
hydroquinone
isoeugenol
m-cresol
methylbenzenediol
o-cresol
p-cresol
p-ethylphenol
phenol
resorcinol
syringaldehyde
trimethyldihydroxybenzene
trimethylnaphthol

Other Oxygenates

1-acetyloxy-2-propanone
2,3-dihydro-1,4-benzodioxin
2-butoxyethanol
2-furaldehyde
2-furanone

2,5-dimethylfuran
2-methyl-2-butenal
2-methylcyclopentanol
2-methylfuran
3-hydroxy-2-methyl-4-pyrene
4-butyrolactone
5-hydroxymethyl-2-furanone
5-methyl furfural
5-methyl-2(3H)furanone
acetal
acetaldehyde
angelicalactone
acetol
dibenzofuran
ethylene glycol (ethan-1,2-diol)
formaldehyde
furfuryl alcohol
glyoxal (ethan-1,2-dial)
hydroxyacetaldehyde
methanol
methyl glyoxal
methyl formate

Hydrocarbons

1-eicosene
1-heneicosene
1-heptadecene
1-hexacosene
1-nonadecene
1-octadecene
1-pentacosene
1-tetracosene
1-tricosene
1-tridecene
2,6,10,14-tetramethylpentadecane
4-methylanisole

benzene
dimethylcylopentene
eicosene
heneicosene
heptadecene
hexadecene
methylindane
nonadecene
octadecene
pentacosene
pentadecene
styrene
tetracosene
tetradecene
tetrahydrocyclopropyl(a)indene
toluene
tricosene

Appendix B: Homogenisation and sampling

B.1 Homogenisation

A small (containers <10 l) sample vessel is homogenised in a laboratory mixer (about one hour at room temperature). Exractive-rich samples, like forest residue liquids, foam easily. Hence a gentle mixing, like rolling the sample bottle carefully, is recommended.

Larger (10-100 l) containers can be turned upside down overnight, if the liquid is old (> 6 months) and a sticky solids layer has settled at the bottom. The pyrolysis liquid is mixed by a propeller mixer with top-mounted slow revolving propeller stirrer. The pyrolysis liquid is mixed (abt. one hour at room temperature) or using nitrogen purge (stainless steel pipe which has a closed end and has been bent roundthrough 180° and perforated) for a shorter (15 minutes) time. Care is taken to mix also the very bottom layer of the barrel.

Large (> 1 m^3) containers can be homogenised with a top-mounted slow revolving propeller stirrer. If circulation is used, the pump (vane pump, eccentric pumps e.g. ‘mono’-pumps, low speed centrifugal pumps) is connected by hoses to the bottom and upper opening of the container. One sample valve is connected to the bottom opening. The liquid sample should be at room temperature. If the viscosity of the liquid is still too high for pumping, a warm water (30–40°C) circulation on the container discharge may be used. The pyrolysis liquid is pumped from the bottom of the container and circulated for about one hour. The homogeneity of the liquid is ensured by analysing the water and solids content from upper and lower part of the liquid. If the difference in water and solids between the upper and lower parts of the liquid is more than 5%, homogenisation of the sample is continued. For very viscous liquids, a propeller mixer is recommended.

B.2 Sampling and homogeneity verification

Material suitable for sample bottles/containers:

PP (polypropylene), HDPE (high-density polyethylene), PTFE (polytetrafluoroethylene) or other resistant polymeric materials, stainless steel AISI316SS, glass (if trace levels of alkalis are not to be analysed).

Sampling

See B.1 Homogenisation. Samples are suggested to be taken at following depths: 5 vol% from surface, middle, 5 vol% above the bottom. Several sampling devices can be used, like piston pump or large syringe. An easy and exact method for sampling is to adjust thin glass pipes to different depths in the sample and suck the sample slowly to a sample bottle using a slow-speed suction pump after the sample bottle.

Microscopic determination

Samples from various layers (surface, 5 vol% from surface, middle, 5 vol% above the bottom, bottom) of pyrolysis liquid are taken and the homogeneity is checked by microscopy (see B.3–B.4). The very surface and bottom may be little different from the rest of the liquid, which is accepted.

7-day standing test

The homogenised liquid sample is placed in a 100 ml measuring bottle, sealed, and left to stand at room temperature for seven days.

The water content is analysed by Karl-Fischer titration (see Appendix C) from top, middle, and bottom layers.

If the difference in water from top and bottom is less than 5% the sample is accepted. See B.3.

If the difference in water from top and bottom is more than 5% the sample is abandoned. See B.4.

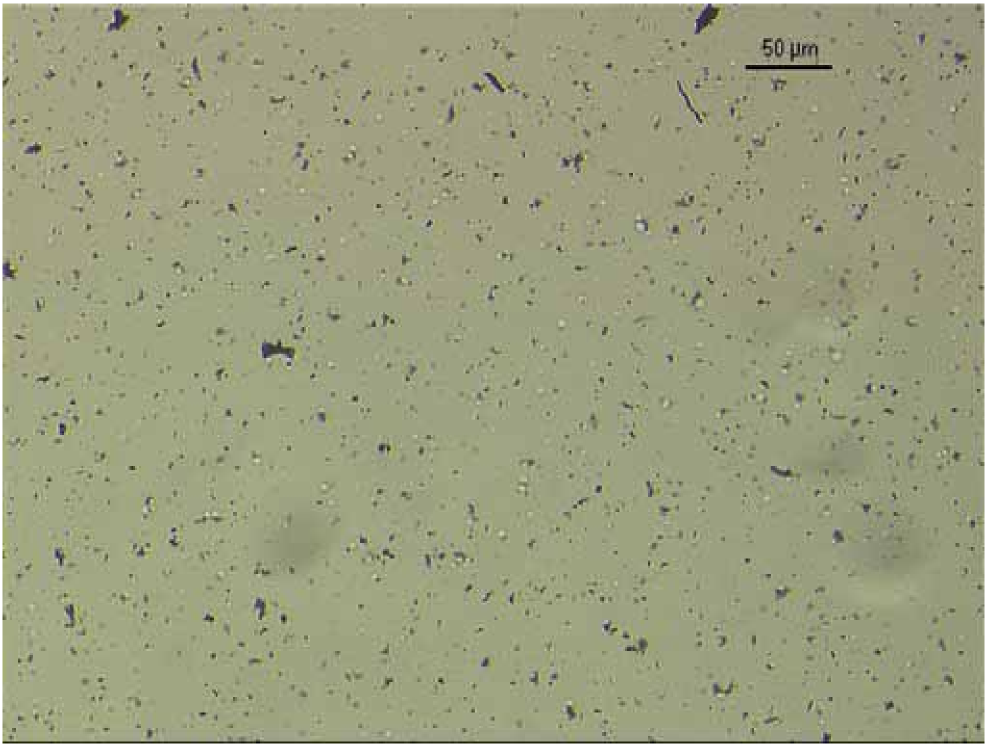
B.3 Homogeneity determination

Good-quality liquid

The liquid is single-phase liquid determined by microscopy from various layers (top-middle-bottom). The difference in water content by 7-day standing test is below 5 wt% (as a% of the absolute values).

The 7-day standing test is continued. Before using the liquid batch the homogeneity of the test sample is verified.

A homogenous pyrolysis liquid by Leica DM LS microscopy.



Water, wt%

	Before mixing	After mixing containers
Top	20.9	21.1
Middle	21.1	
Bottom	20.7	

B.4 Homogeneity determination

Inhomogenous liquid

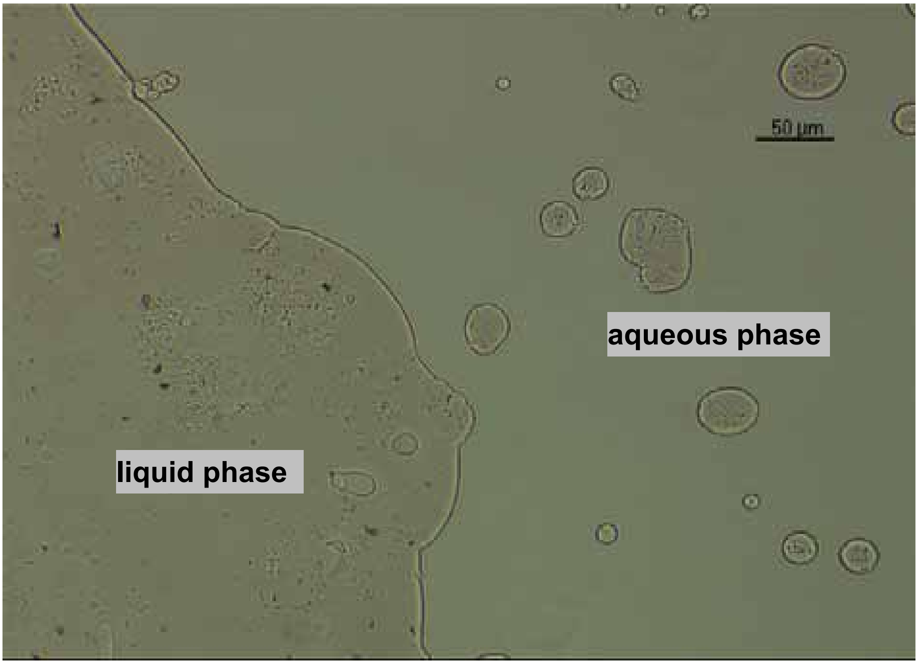
The difference in water contents in the 7-day standing test is more than 5% and phase-separation is observed by microscopy. The liquid cannot be stored.

Poor-quality liquid

A clear phase-separation can be observed visually and liquid is abandoned.

A phase-separation can be observed by microscopy. Samples from top, middle, and bottom layers of the unhomogenised pyrolysis liquid are taken. Water content by Karl-Fischer titration is determined from the samples and microscopic observation is carried out. If the difference in water is more than 5% and phase-separation is observed by microscopy the liquid is abandoned.

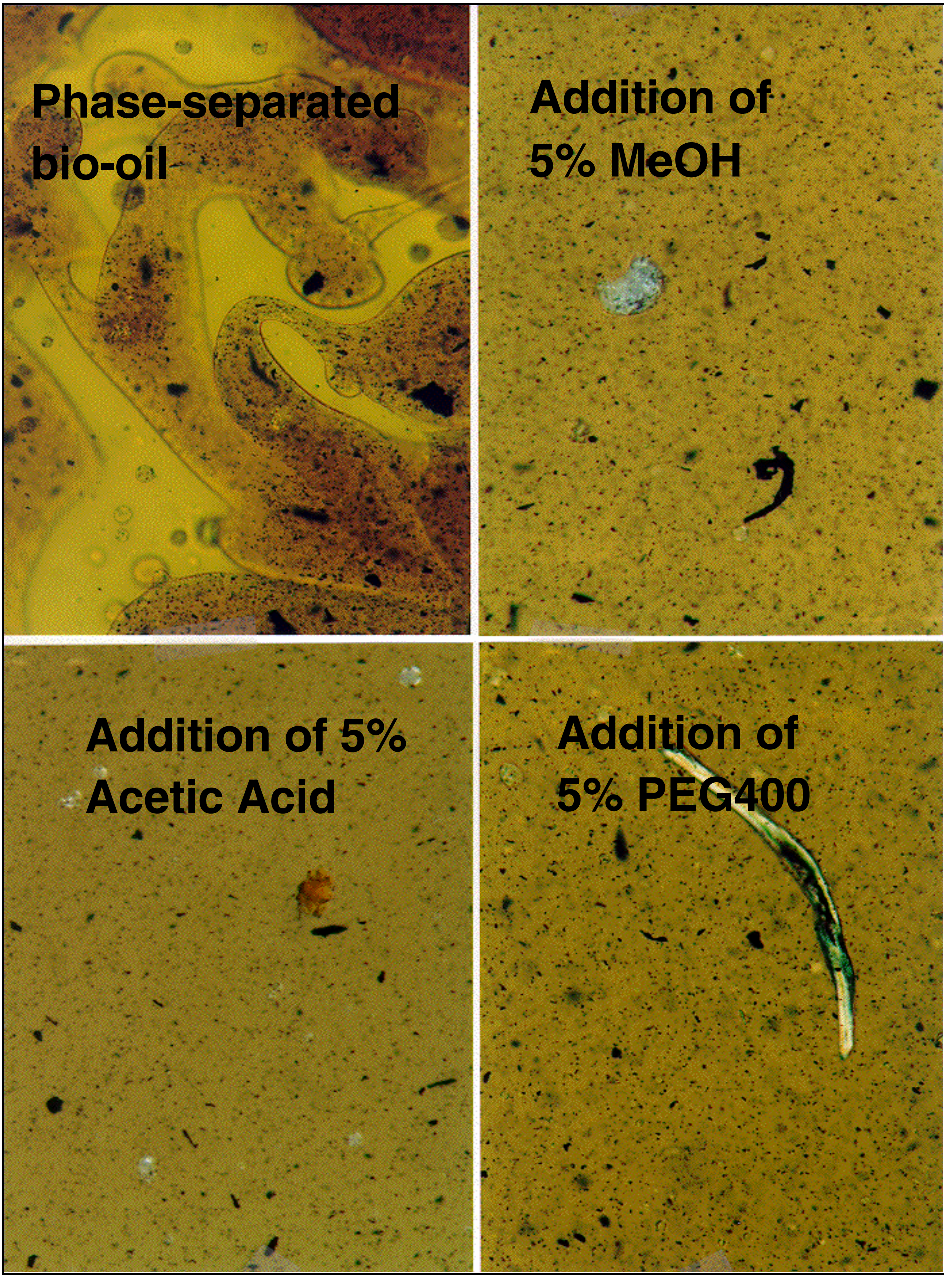
A phase-separated pyrolysis liquid by Leica DM LS microscopy.



Water, wt%

	Before mixing	After mixing containers
Top	31.1	28.3
Middle	32.4	
Bottom	20.3	

B.5 Homogenisation of phase-separated pyrolysis liquid by solvent addition (wt%). MeOH = Methanol. PEG400 = Polyethylene-glycol 400



Appendix C:

Determination of water content

C.1 Method

Karl-Fischer titration ASTM E 203

Water addition test

Water is added to pyrolysis liquid. Samples are shaken in a mixer for about 30 minutes and left to stand overnight in air-tight bottles at room temperature. Before water determination the samples are mixed again by hand. The water content obtained mathematically or analytically should be the same for single-phase liquids.

Water addition test results.

No.	Forest residue	Water		Water		Difference
	g	g		wt%		wt%
		Added	Total	Calculated	Analysed	
0		0			24.3	
1	10.294	0.317	2.816	26.5	26.4	-0.14
2	10.645	0.588	3.173	28.2	28.2	-0.07
3	10.866	0.869	3.507	29.9	29.6	-0.30
4	11.194	1.183	3.901	31.5	31.3	-0.19
5	11.545	1.547	4.350	33.2	34.0	0.77
6	11.865	1.873	4.753	34.6	37.0	2.35
7	12.275	2.272	5.252	36.1	two phases	

Forest residue = VTT PDU 10/01, bottom (90 wt% of total liquid)

Problem solving in Karl-Fischer titration

Observation	Possible reason	Action
Fading titration end-point/ End-point not clear	Wet drying agent Air leakage Unhomogenous sample Reactions of aldehydes/ketones with the KF reagent Moisture on the walls or on the cover	Change/dry the material Check gaskets, septum Repeat homogenisation Use proper reagent e.g. Hydranal solvents Wash the vessel and titrate the water
Long titration time	Too large sample size/too much water Sample dissolves slowly in KF working medium	Take smaller sample Add dissolving solvent or extract the moisture from the sample with suitable solvent beforehand
Unclear titration end-point	Dirty electrode Unhomogenous sample Dirty solvent	Clean the electrode Repeat homogenisation Change the solvent, 2 - 4 determinations/solvent
Too high/low water content	Unadequate sample homogenisation/sampling Burette reading error Dirty electrode Variation in water equivalent Wrong titration end-point	Repeat homogenisation/sampling Calibrate burette Clean the electrode Check water equivalent Calibration/water addition test
Difference in duplicates	Water in titration solvent or in sample vessel/cover Non-homogenous sample Dirty solvent Splashing of sample to the walls of the titration vessel	Titrate the solvent Use as large sample size as possible Change the solvent, 2–4 determinations/solvent Carefull sample injection

Testing of sample solvent for KF water determination of forest residue liquids

Bottom phase

Chloroform:Methanol	3:1	1:1	1:3	0:1
	28.97	28.39	28.86	29.03
	29.03	28.67	28.90	28.96
	28.98	28.64	29.21	28.76
	28.91	28.57	28.77	28.98
	29.01	28.6	28.82	28.79
	28.96	28.58	28.86	28.98
	28.97	28.75	28.92	28.86
	29.07	28.74	28.67	28.90
			28.86	
Average, wt%	29.0	28.6	28.9	28.9
Stdev	0.05	0.11	0.15	0.10

Top phase

Chloroform:Methanol	1:3	0:1
	7.80	7.81
	7.73	7.82
	7.75	7.86
	7.76	7.73
	7.80	7.88
	7.75	7.79
	7.71	7.82
	7.70	7.73
Average, wt%	7.8	7.8
Stdev	0.04	0.05

Appendix D:

Determination of solids content

Solvent choice

- Ethanol - white wood liquids from softwood or hardwood, straw pyrolysis liquids
- Methanol (CH_3OH) - Dichloromethane (CH_2Cl_2) - extractive-rich liquids like forest residue and bark.

Method

1. The sample size (1, 5, 10 g) is determined in order to obtain 10–20 mg dry solid residue.

2. A representative sample of pyrolysis liquid is dissolved in about 100 ml of solvent.

3. The solution is filtrated through a 1 µm pore size filter (Scleicher & Schöll, GF50, ф 47 mm, Glass Fibre papers, Ref.No. 10428026, Lot: CF0401-1). The rough side of the filter paper is faced upwards. The filter paper is soaked on to the filter by the solvent used. If the filtration time is very long, due to high solids content, a larger pre-filter (3 µm) may be used. The filtrate is then filtered through a 1 µm filter. The two solids contents are combined.

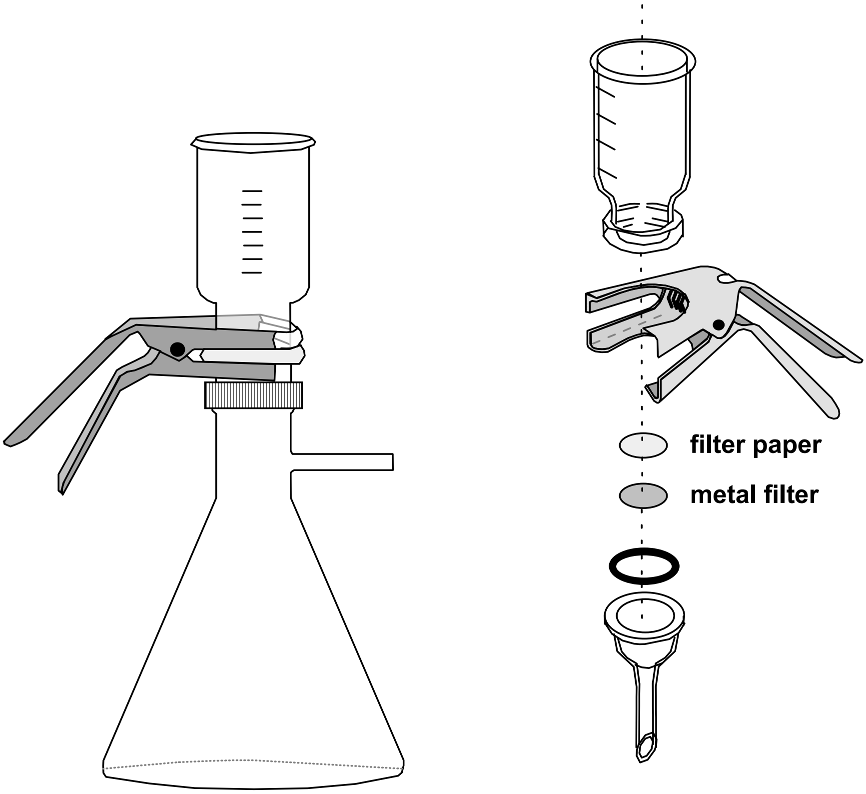
4. The sample bottle, filter and residue are washed with solvent until the filtrate is clear.

5. The filter paper with the residue is air-dried for 15 min and in an oven at 105°C for 30 minutes, cooled in a desiccator and weighed.

6. The solids content is calculated based on the original pyrolysis liquid sample.

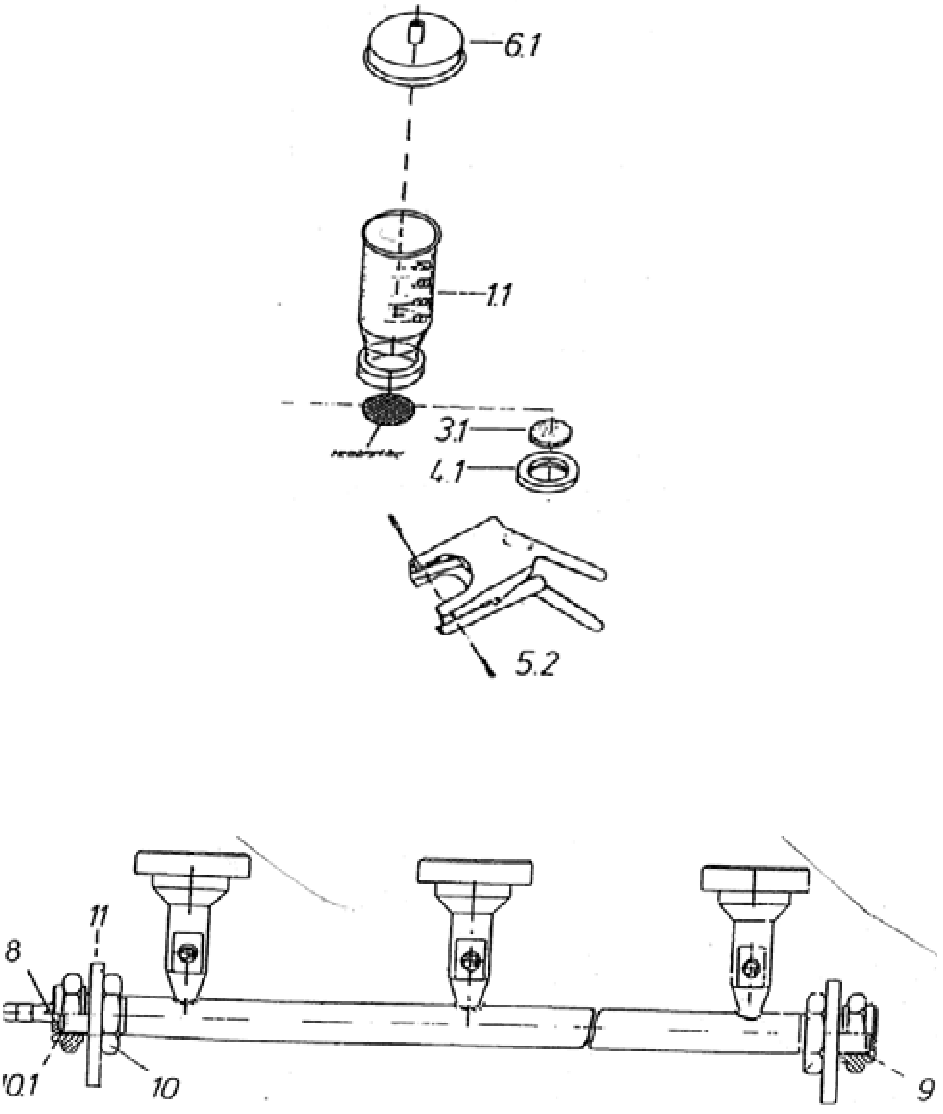
Filtration apparatus at VTT

Millipore filtration system. The original Millipore filter was too slow and was replaced by a larger porosity metal sinter.



Millipore filtration system.

6-place filtration system. Scleicher & Schuell, AS 600/2. Filtration system complete with six 250 ml glass funnels with rubber lid, for 47 and 50 mm filters, Teflon-coated support screen. A vacuum pump is used instead of water suction.



Six-place filtration system.

Testing of solids content of forest residue liquids

Bottom phase

Sample	Solvent	Sample size g	Residue mg	Solids wt-%	Average wt-%
bottom phase	Methanol (MeOH)	15.3405	17.70	0.12	0.12
"	Ethanol (EtOH)	14.8577	30.20	0.20	0.20
"	MeOH-Dichloromethane (MeCl2);(1:1)	16.1387	16.30	0.10	0.09
		10.9274	9.30	0.09	
		10.6254	9.40	0.09	
		11.5852	9.30	0.08	
"	**MeOH-20 vol-% MeCl2**	15.9757	6.20	0.04	**0.04**
		29.5361	10.30	0.03	
		30.1381	11.20	0.04	
		30.5504	10.90	0.04	
		30.0461	11.20	0.04	
"	EtOH-20 vol-% MeCl2	9.7542	18.10	0.19	0.16
		9.7786	15.30	0.16	
		13.0855	18.70	0.14	
"	EtOH-MeCl2 (1:1)	11.1632	15.70	0.14	0.15
		11.9167	18.80	0.16	
		10.7893	16.50	0.15	
"	Isopropylalcohol (IPA) -Industol* (1:1)	15.1620	70.70	0.47	0.47
"	IPA-20 vol-% MeCl2	15.5704	59.10	0.38	0.38
"	IPA-hexane (1:1)			Not soluble	
"	Methanol-20 vol-% hexane	14.9014	16.50	0.11	0.11
"	Methanol-hexane (2:1)	16.5295	15.50	0.09	0.09
"	Acetone	15.2881	144.20	0.94	0.94
"	Dioxane (1,4-)-Acetone (1:1)	15.0626	63.30	0.42	0.42
"	Dioxane-20 vol-% IPA	15.1776	62.00	0.41	0.41
"	Industol*	15.9160	30.00	0.19	0.19
"	Industol-20 vol-% Dioxane	15.7802	25.50	0.16	0.16
"	Methoxy propanol	15.9512	40.60	0.25	0.25
"	Methoxy propanol-20 vol-% Dioxane	15.8626	36.50	0.23	0.23

* Industol = Industol PE2, a trade name, 88.3% ethanol, 2.7% methyl-isobutylketone, 1.8% acetone

Testing of solids content of forest residue liquids

Whole Liquid *

*Samples from the process before phase-separation, efficient mixing before fast sampling

Sample	Solvent	Sample size g	Residue Mg	Solids wt-%	Average wt-%
whole liquid 1	Methanol	10.6482	39.5	0.37	0.37
"	**MeOH-MeCl2 (1:1)**	11.0005	23.0	0.21	**0.21**
"	**MeOH-20 vol-% MeCl2**	10.9994	23.4	0.21	**0.21**
"	MeOH-hexane (2:1)	11.3703	45.4	0.40	0.40
"	Industol- 20 vol-% Dioxane	10.3156	40.0	0.39	0.39
"	IPA-MeCl2 (1:1)	9.4711	43.2	0.46	0.46
"	Methoxy propanol-Dioxane (1:1)	9.8952	36.7	0.37	0.37
"	Industol-Dioxane (1:1)	9.4445	29.2	0.31	0.31
whole liquid 2	EtOH-20 vol-% MeCl2	4.6223	30.2	0.65	0.63
"		6.1577	37.6	0.61	
"	**MeOH-MeCl2 (1:1)**	7.2408	21.5	0.30	**0.25**
"		4.9475	10.9	0.22	
"		4.6785	11.4	0.24	
"	MeOH-20 vol-% MeCl2	7.0694	30.1	0.43	0.37
"		5.6691	20.6	0.36	
"		6.1134	23.4	0.38	
"		2.9725	10.2	0.34	
"		3.1904	10.9	0.34	
"		3.7888	13.5	0.36	
"	MeOH-10 vol-% MeCl2	5.5636	25.3	0.45	0.45
"		5.3646	23.6	0.44	
"	EtOH	5.0351	36.0	0.71	0.70
"		5.6706	39.1	0.69	
"	EtOH-MeCl2 (1:1)	5.4433	21.5	0.39	0.42
"		6.0428	23.5	0.39	
"		3.1736	14.8	0.47	
whole liquid 3	EtOH-MeCl2 (1:1)	3.1772	13.6	0.43	0.43
"		3.5979	15.5	0.43	

Testing of solids content of forest residue liquids

Top/extractive-rich phase

	Solvent	Sample size	Residue	Solids	Average
		g	Mg	wt-%	wt-%
Top phase	Methanol (MeOH)	2.922	77.8	2.66	2.68
"		2.827	73.8	2.61	
"		1.951	53.3	2.73	
"		2.1171	57.3	2.71	
"		3.095	83.5	2.70	
"	**MeOH-Dichloromethane (MeCl2) (1:1)**	0.95	10.6	1.12	**1.22**
"		1.0222	12.6	1.23	
"		1.3045	16.6	1.27	
"		1.0924	13.9	1.27	
"	MeOH-MeCl2 (20vol % MeCl2)	1.677	34.3	2.05	2.03
"		1.7868	36.8	2.06	
"		1.5454	30.7	1.99	
"	Isopropanol alcohol (IPA)	2.255	107.0	4.75	4.54
"		2.57	121.8	4.74	
"		2.041	84.2	4.13	
"	**IPA-MeCl2 (1:1)**	2.306	20.8	0.90	**1.01**
"		2.945	28.7	0.97	
"		3.183	31.2	0.98	
"		2.12	19.0	0.90	
"		2.47	22.7	0.92	
"		1.912	18.4	0.96	
"		1.1592	13.4	1.16	
"		0.8016	9.0	1.12	
"		1.586	18.6	1.17	
"	**IPA-Dioxane (1:1)**	1.348	10.4	0.77	**0.76**
"		1.223	9.2	0.75	
"		1.274	9.6	0.75	
"	IPA- Hexane (2:1)	1.325	112.2	8.47	8.65
"		1.1943	106.0	8.88	
"		1.6666	143.3	8.60	
"	**Industol*-Dioxane (1:1)**	1.66	12.6	0.76	**0.75**
"		1.489	11.3	0.76	
"		1.601	11.7	0.73	
"	MeCl2-Dioxane (1:1)	1.419	69.2	4.88	5.19
"		1.801	100.5	5.58	
"		1.302	66.6	5.12	
"	**Methoxy propanol-Dioxane (1:1)**	1.868	12.5	0.67	**0.73**
"		1.563	12.1	0.77	
"		1.254	9.3	0.74	

* Industol is a Trade name for ethanol containing a small amount of acetone.

Appendix E:

Particle size distribution for pyrolysis liquid

Equipment

Leica DM LS microscopy with the Leica Qwin Lite Standard photo analysis programme.

Method description

Particles are marked, and the computer programme measures (based on length), calculates and classifies them. If the solids content is high, overlapping of particles may cause error to the results.

Sample

Forest residue liquid, PDU19/01 8.5.01 11:30 P1, solids content (insolubles in methanol-dichloromethane, 1:1) 0.47 wt%

Measurement 1

Bin	Length (µm)		Count (%)	Count
1	1.00	1.58	613	31.75
2	1.58	2.51	299	15.48
3	2.51	3.98	472	24.44
4	3.98	6.31	305	15.79
5	6.31	10.0	131	6.78
6	10.0	15.8	77	3.99
7	15.8	25.1	23	1.19
8	25.1	39.8	8	0.41
9	39.8	63.1	2	0.10
10	63.1	100	1	0.05

Undersize Count: 713.00 Total Count: 1 931.00
Oversize Count: 0.00

Total 7 288.19
Mean 3.77

Std Dev	4.17
Std Error	0.10
Max	72.92
Min	1.39
2-s Range	16.70
Median	3.16
Mode	1.26
Skewness	5.59
Kurtosis	56.79
Features	1 931.00
Spec. Area	173 018.89
Norm. Count	11 160.63

Measurement 2

Bin	Length (µm)		Count (%)	Count
1	1.00	1.58	421	31.54
2	1.58	2.51	237	17.75
3	2.51	3.98	269	20.15
4	3.98	6.31	238	17.83
5	6.31	10.0	92	6.89
6	10.0	15.8	47	3.52
7	15.8	25.1	28	2.10
8	25.1	39.8	1	0.07
9	39.8	63.1	1	0.07
10	63.1	100	1	0.07

Undersize Count: 458.00 Total Count: 1 335.00
Oversize Count: 0.00

Total	5 108.33
Mean	3.83
Std Dev	4.10
Std Error	0.11
Max	65.28
Min	1.39
2-s Range	16.40
Median	3.16
Mode	1.26
Skewness	4.95
Kurtosis	47.21
Features	1 335.00
Spec. Area	173 018.89
Norm. Count	7 715.92

Measurement 3

Bin	Length (µm)		Count	Count (%)
1	1.00	1.58	490	31.15
2	1.58	2.51	247	15.70
3	2.51	3.98	370	23.52
4	3.98	6.31	283	17.99
5	6.31	10.0	108	6.87
6	10.0	15.8	51	3.24
7	15.8	25.1	19	1.21
8	25.1	39.8	3	0.19
9	39.8	63.1	2	0.13
10	63.1	100	0	0.00

Undersize Count:	510.00	Total Count:	1 573.00
Oversize Count:	0.00		

Total	5 829.86
Mean	3.71
Std Dev	3.84
Std Error	0.10
Max	60.42
Min	1.39
2-s Range	15.35
Median	3.16
Mode	1.26
Skewness	5.32
Kurtosis	51.15
Features	1 573.00
Spec. Area	173 018.89
Norm. Count	9 091.49

Appendix F:

Alkali metals and metals

Sample pretreatment:

Wet oxidation [Oasmaa et al. 1997]

The procedure must be carried out in a suitable fume cupboard. 20 ml of concentrated (65%, pro analysis-grade) nitric acid is added to a homogenised sample of pyrolysis liquid (3–5 g) in a conical flask. After the formation of vapours (nitric oxides) has ceased (about 30 minutes) 10 ml of concentrated (70%, pro analysis grade) perchloric acid is slowly added. The mixture is boiled evenly for 1–1.5 hours until the volume of the mixture is below 5 ml and the residue is clear and colourless. The solution is diluted with distilled water to total volume of 50 ml. The solution is transferred to a plastic bottle and 5 ml of hydrogen fluoride is added. The solution is let to stand overnight and analysed by AAS or ICP. The minimum sample size needed is 10 g.

In samples with a high amount of silicates, silicon can precipitate as SiO_2 during the sample pretreatment. This may yield error in silicon. For accurate determination of Si the sample should be ashed by dry combustion and a fusion cake prepared from the ash for further analysis.

Standard solutions should contain the same acids in the same proportions as when dissolving the pyrolysis liquid sample.

Detection limits for the metals (wet oxidation and ICP-analysis):

Metal	Detection limit mg/kg	Metal	Detection limit mg/kg
Na	5–10	Pb	5–10
K	5–10	Cd	1–3
Ca	0.2–0.5	As	5–10
Mg	0.2–0.5	Co	0.5–1
Fe	0.5–1	Cu	0.5–1
Si	5–10	Ni	0.5–1
Zn	0.5–1	V	0.5–1
Al	3–5	Cr	0.5–1
P	5–10	Hg	0.5–1

Appendix G:

Water extraction method for pyrolysis liquids

1. 400 g water is poured in a 500 ml Erlenmeyer or 500 ml Schott flask.
2. 5 g of pyrolysis liquid (A, water content a wt%) is added to the water stirring continuously by a propeller stirrer.
3. The bottle is closed and placed to a mixer at least for two hours. The solution may stand overnight.
4. The solution is filtered through a Büchner funnel (blue ribbon filter paper, filter pore size about 2 μm) into a suction flask. An intermediate flask, e.g., Wulff flask, is used for water suction. Should the filtrate not be clear it is filtered again through a 0.1 μm filter to remove tiny particles disturbing the water analysis. If a weighable amount of precipitate remains on the filter paper, it is dried and added (D) to the total amount of solids.
5. The precipitate in the Erlenmayer/Schott flask and in the Büchner funnel are rinsed with water.
6. The wet precipitate is dried in a heating oven ≤ 40°C until no further weight loss (about 3 hours).
8. The precipitate is cooled in the desiccator and weighed immediately after cooling (B).
9. If a weighable amount of precipitate remains on the walls of the sample flask, the flask is dried in the vacuum oven ≤ 40°C for three hours, cooled in an desiccator and weighed. The weight of this precipitate (C) is added to the amount of the major part of the precipitate (B).

Analyses:

- pyrolysis liquid - water

Substance insoluble in water (dry basis), wt% = $(B+C+D)\bullet 100/[((100-a)\bullet A)/100]$

Appendix H:

Stability test method

The pyrolysis liquid sample is mixed properly(see B.1) and let to stand, until the air bubbles are removed. 90 ml of the sample is poured in 100 ml tight glass bottles (or 45 ml in 50 ml bottles). The bottles are firmly closed and pre-weighed before placing in a heating oven for a certain time. The bottles are re-tightened a few times during the heating-up period. After a certain time the closed sample bottles are cooled under tempered water, weighed, and analyses are performed. The samples are mixed and measured for viscosity and water. The viscosity of the liquid at 40°C is measured as kinematic viscosity by a standard method (ASTM D 445). The water content is analysed by Karl Fischer titration according to ASTM D 1744.

$$\Delta \text{ Viscosity (40°C) [\%]} = \frac{(\nu_2 - \nu_1)}{\nu_1} \bullet 100$$

$$\Delta \text{ Water [\%]} = \frac{(\omega_2 - \omega_1)}{\omega_1} \bullet 100$$

ν_1 = viscosity of the original sample, measured at 40°C, cSt
ν_2 = viscosity of the aged sample, measured at 40°C, cSt
ω_1 = water content of the original sample, wt%
ω_2 = water content of the aged sample, wt%

Note 1: The test is recommended to be used for internal comparison of liquid stability for pyrolysis liquids from one process. The test is more reliable if the initial viscosities of the samples tested are similar.

Note 2: The possible difference in the weights before and after the test is an indication of leakage and the test should be repeated if the net weight loss is above 0.1 wt% of original weight.

Test conditions: 24 hours at 80°C (white wood liquids) or 1 week at 40°C (forest residue liquids), optional conditions based on EU-IEA Round Robin 2001 [Bridgwater et al. 2001]: 6 or 24 hours at 80 °C, 1 week at 40°C.

Effect of gas athmosphere, pressure, and mixing on the viscosity of pyrolysis liquid in a stability test of 24 hours at 80°C

Test results using a 1 litre AE autoclave. 900 ml pine pyrolysis liquid.

Expt.	Gas	Pi	Mixing	T	Time	Viscosity @40°C mPas				Water wt%		
		bar	rpm	°C	h	Initial	Final	Change %	Aver. %	Initial	Final	Change %
1.1	Air	no	0	80	24	48	81	69	69	20.9	22.3	6
1.1.3	Air	no	0	80	24	48	81	69		20.9	22.4	7
1.2	Air	no	1.000	80	24	48	78	63	65	20.9	22.4	7
1.2.2	Air	no	1.000	80	24	48	80	67		20.9	22.0	5
1.3	N2	no	0	80	24	48	78	63	63	20.9	22.5	8
1.4	N2	no	1.000	80	24	48	79	65	63	20.9	22.2	6
1.4.2	N2	no	1.000	80	24	48	77	60		20.9	22.1	6
1.5	N2	100	1.000	80	24	48	76	58	59	20.9	22.3	7
1.5.2	N2	100	1.000	80	24	48	77	60		20.9	22.4	7
1.6	N2	100	0	80	24	48	74	54	60	20.9	22.8	9
1.6.2	N2	100	0	80	24	48	80	67		20.9	22.8	9
1.7	N2	150	1.000	80	24	48	77	60	64	20.9	22.3	7
1.7.2	N2	150	1.000	80	24	48	80	67		20.9	22.3	7

Published by

Vuorimiehentie 5, P.O.Box 2000, FIN-02044 VTT, Finland
Phone internat. +358 9 4561
Fax +358 9 456 4374

Series title, number and report code of publication

VTT Publications 450
VTT–PUBS–450

Author(s)
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Title

A guide to physical property characterisation of biomass-derived fast pyrolysis liquids

Abstract

This publication is a revised and updated version of VTT Publication 306: Physical characterisation of biomass-based pyrolysis liquids, issued in 1997. The main purpose of the on-going study is to test the applicability of standard fuel oil methods developed for petroleum-based fuels to pyrolysis liquids. New methods have also been tested and further developed. The methods were tested for pyrolysis liquids derived from hardwood, softwood, forest residue, and straw. Recommendations on liquid handling and analyses are presented. In general, most of the standard methods can be used as such, but the accuracy of the analyses can be improved by minor modifications. Homogeneity of the liquids is the most critical factor in the accurate analyses, and hence procedures for its verification are presented.

Keywords
pyrolysis liquid, biomass, fast pyrolysis, physical properties, fuel oil properties, test methods, characterization, homogeneity, sampling, specifications

Activity unit
VTT Energy, New Energy Technologies, Biologinkuja 3–5, P.O.Box 1601, FIN–02044 VTT, Finland

ISBN
951–38–5878–2 (soft back ed.)
951–38–6365–4 (URL:http://www.vtt.fi/inf/pdf)

Project number

Date	Language	Pages	Price
December 2001	English	65 p. + app. 34	B

Name of project

Commissioned by
Tekes

Series title and ISSN
VTT Publications
1235–0621 (soft back ed.)
1455-0849 (URL:http://www.vtt.fi/inf/pdf)

Sold by
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VTT PUBLICATIONS 450   A guide to physical property characterisation of biomass-derived fast pyrolysis liquids

A guide to physical property characterisation of biomass-derived fast pyrolysis liquids is a revised and updated version of VTT Publication 306: *Physical characterisation of biomass-based pyrolysis liquids. Application of standard fuel oil analyses* by Oasmaa et al. published in 1997. The objective of this work was to test the standard methods developed for characterization of petroleum fuels on biomass pyrolysis liquids and modify them if necessary to accommodate the significant differences in properties between these two groups of fuels. Compared to the previous publication, this work extends the method validation tests on more biomass-derived liquids and more physical properties. It includes the recommendations on testing procedures for two-phase liquids obtained from pyrolysis of forest residues, the most likely feedstock for producing pyrolysis liquids. A chapter on transporting and handling pyrolysis liquids that considers the health and safety aspects of the operations is included. The publication is mostly focused on practical issues related to pyrolysis liquid characterization such as sampling techniques and recipes for the tests. Summarizing, *A guide to physical property characterisation of biomass-derived fast pyrolysis liquids* will serve as a guide and a reference for the researchers and technicians working with biomass pyrolysis liquids.

Tätä julkaisua myy	Denna publikation säljs av	This publication is available from
VTT TIETOPALVELU	VTT INFORMATIONSTJÄNST	VTT INFORMATION SERVICE
PL 2000	PB 2000	P.O.Box 2000
02044 VTT	02044 VTT	FIN–02044 VTT, Finland
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ISBN 951–38–5878–2 (soft back ed.)
ISSN 1235–0621 (soft back ed.)

ISBN 951–38–6365–4 (URL: http://www.inf.vtt.fi/pdf/)
ISSN 1455–0849 (URL: http://www.inf.vtt.fi/pdf/)