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Anja Oasmaa & Cordner Peacocke

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Key words pyrolysis liquid, biomass, fast pyrolysis, physical properties, fuel oil properties, test methods, characterisation, homogeneity, sampling, specifications

Abstract

This publication is an updated version of a study on testing and modifying standard fuel oil analyses (Oasmaa et al. 1997, Oasmaa & Peacocke 2001). Additional data have 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. In addition, information on specifications and registration is provided. Physical property data on a range of pyrolysis liquids from published sources have been added to provide a more comprehensive guide for users.

Preface

The Technical Research Centre of Finland has had a central role in analysing liquid and solid fuels for the Finnish industry for over three decades. In view of these experiences, the standard fuel oil analyses developed for petroleum-based fuels were applied to pyrolysis liquids. The first study was published as VTT Publication 306 in 1997 and an updated version, VTT Publication 450, in 2001. 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, transport and storage were also added to aid users and transporters of the liquids.

Conversion And Resource Evaluation Ltd. (CARE Ltd.) has been operating since 1996 in thermal conversion of biomass and wastes for energy, chemicals and speciality-derived products. CARE Ltd. has extensive experience of liquid production from a range of feedstocks on a bench scale and has worked on two pilot-scale (250 kg/h) fast pyrolysis projects in the UK and numerous research laboratory units.

The VTT project was funded by the National Technology Agency (Tekes). The analytical work at the VTT was carried out by Jaana Korhonen, Eeva Kuoppala, Sirpa Lehtinen and Elina Paasonen.

Douglas C. Elliott (PNNL, USA) is acknowledged for his valuable comments and review.

Espoo, October 2010

Authors

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Appendices

List of symbols

49 CFR	United States regulations relating to the standards for hazardous materials transportation – Hazardous Materials Safety Regulations and Interpretations
ADN	The European Provisions concerning the International Carriage of Dangerous Goods by Inland Waterways
ADR	EU Agreement on the Carriage of Dangerous Goods by Road
CAA	Civil Aviation Authority
CCNR	Central Commission for the Navigation of the Rhine
IATA	International Air Transport Association
IMO	International Maritime Organisation
IMDG	International Maritime Dangerous Goods

1. Introduction

Biomass fast pyrolysis liquids are completely different from petroleum fuels in their physical properties (Table 1) and chemical composition (Table 4). These liquids are typically high in water, can have substantial levels of suspended solids, have a density higher than conventional fossil fuels, are acidic, have a heating value of about half of that of mineral oils, and are chemically unstable when heated. Pyrolysis liquids are highly polar, containing about 35–40 wt% oxygen (dry basis), while mineral oils contain oxygen at ppm levels. Pyrolysis liquids are not miscible with mineral oils. The unusual properties of the liquids must therefore be taken into careful consideration in a range of applications.

Table 1. Physical properties of fast pyrolysis bio-oils and mineral oil U.S.#4 FO.

Analysis	Typical bio-oil	U.S.#4 FO
Water, wt%	20–30	0.5 (water and sediment)
Solids, wt%	Below 0.5	0.5 (water and sediment)
Ash, wt%	0.01–0.2[a]	0.1 max
Nitrogen, wt%	Below 0.4	–
Sulphur, wt%	Below 0.05	Varies
Stability	Unstable[b]	–
Viscosity (40°C), cSt	15–35[c]	5.5–24
Density (15°C), kg/dm^3	1.10–1.30[c]	–
Flash point, °C	40–110	55 min
Pour point, °C	$^{-}9$–$^{-}36$	$^{-}6$ min
LHV, MJ/kg	13–18[c]	–
pH	2–3	–
Distillability	Not distillable	–

[a] Note that metals form oxides during ashing and may yield ash values that are larger than the total solids in the liquid. [b] Unstable at high temperatures and for prolonged periods of time. [c] Depends on water content.

Due to these differences, standard fuel oil analyses developed for mineral oils are not always suitable as such for pyrolysis liquids. Research analysing physical properties of pyrolysis liquids has been carried out since the 1980s (Elliott 1983, Chum & McKinley 1988, Milne et al. 1990, Czernik et al. 1994, McKinley 1989, McKinley et al. 1994, Rick and Vix 1991, Fagernäs 1995, Diebold et al. 1997, Oasmaa et al. 1997, Meier et al. 1997, Bridgwater et al. 1999 and 2001, Oasmaa & Peacocke 2001, Oasmaa 2003).

Several round robins have been carried out in order to verify the relevant analytical procedures for pyrolysis liquid analyses (McKinley et al. 1994, Meier 1999, Oasmaa & Meier 2005). Based on these round robins, the following conclusions were drawn: liquid sample handling plays a very important role, the precision of carbon and hydrogen is good if properly calibrated, oxygen by difference is more accurate than by direct determination, and water by Karl Fischer titration and density are accurate. High variations were obtained for nitrogen, viscosity, pH, solids, water insolubles and stability.

This publication is an updated version of a study on testing and modifying standard fuel oil analyses (Oasmaa et al. 1997, Oasmaa & Peacocke 2001). Additional data have 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. Information on specifications, requirements and implications of REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) is provided. Data on properties of other bio-oils have also been included for comparison.

All comments concerning the significance of some specific methods or suggestions for further developments are greatly appreciated (Anja.Oasmaa@vtt.fi). Research on ignition properties of pyrolysis liquid is going on at VTT. Within IEA Pyrolysis project (lead by D. C. Elliott, PNNL, USA) toxicological data of pyrolysis liquids will be further processed. The aim is to write a more precise MSDS for pyrolysis liquid. Hence, this publication will be updated within a year and be available as an online version from VTT at http://www.vtt.fi/inf/pdf/publications/2010/P731.pdf.

2. Pyrolysis liquids production

An extensive review article is available for alternatives being developed for bio oil production (Bridgwater & Peacocke 2000), and this has been subsequently updated in varying degrees by others (Ringer et al., 2006, Venderbosch and Prins, 2010). A brief summary is given below.

Developments in fast pyrolysis may be traced back to a development programme by Occidental Petroleum, which was carried out in the US during the late 1960s and early 70s. The most important development work in this field, however, is indebted to the development at the University of Waterloo, Canada, by Professor Scott and his co-workers (Scott & Piskorz 1982). Another important development started at the University of Western Ontario and eventually led to the establishment of Ensyn Technologies (Freel & Graham 1991). Considerable early fundamental work was also carried out at NREL in the US (Diebold & Power 1988). In Europe, development work initiated at the University of Twente, the Netherlands, has led to process development at the BTG.

To date, commercial operation has only been achieved from a transport and circulating fluid-bed system, and only for food and flavouring products (Underwood & Graham 1989). A few companies are currently pushing for the commercialisation of bio-oil for energy applications: Ensyn Technologies, Dynamotive, Forschungszentrum Karlsruhe (KIT), BTG and Metso Power probably have the most advanced initiatives to pursue larger scale operations. Metso Power has built the world’s first integrated pyrolysis pilot plant in Finland in co-operation with the UPM, Fortum and the VTT (Lehto et al. 2009).

Pyrolysis liquids can be produced with a range of processes including fluid beds, ablative, entrained and circulating fluid beds, and screw reactors, each with its own specific features (Table 2) (Boukis 1997, as outlined by Bridgwater 2007).

Table 2. Fast pyrolysis reactor types and example organisations.

Reactor type	**Example Organisations (not all are currently active)**
Fluid bed	Aston University (UK), Biomass Engineering Ltd. (UK), Dynamotive (Canada), Hamburg University (Germany), INETI (Portugal), Leeds University (UK), Sassari University (Italy), ZSW-Stuttgart University (Germany), East China University of Science and Technology (China), FZK (Germany), vTI (Germany), Iowa State (USA), University of Maine (USA), University of Seoul (Korea), MARA Institute of Technology (Malaysia), Metso (Finland), Institute of Chemical Industry of Forest Products (China), University of Western Ontario (Canada), PNNL (USA), Virginia Tech (USA), VTT (Finland)
Cyclonic reactor	University of Nancy (France)
Ablative	PyTec (Germany), Aston University (UK), NREL (USA)
Circulating fluid bed	CRES (Greece), Ensyn (Canada and USA)
Screw reactor	FZK (Germany), Mississippi State University (USA), Renewable oil International (USA), ABRITech (Canada)
Rotating cone	Twente University (the Netherlands), BTG (the Netherlands), Genting (Malaysia)
Transported bed	Ensyn (Canada), Red Arrow (USA), VTT (Finland)
Vacuum moving bed	Laval University/Pyrovac (Canada)

The essential features of a fast pyrolysis reactor are very high heating rates at the reaction interface coupled with high heat transfer rates, moderate and carefully controlled vapour temperature, and rapid cooling or quenching of the pyrolysis vapours (Bridgwater 1995, Diebold & Bridgwater 1997).

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. Char contributes to secondary cracking by catalysing the cracking reactions 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.

Unless it is 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. This can be problematical, however, due to rapid filter blockage. Char may also be removed by centrifugation. Almost all of the biomass ash is retained in the char and, hence, successful char removal generally involves removal of almost all the ash, although some selective leaching of metals from the char into the liquids is possible (Elliott 1994, Agblevor et al. 1995, Garcìa-Pèrez et al, 2002). Solids removal may not be necessary in all applications, i.e., chemical and other non-fuel applications.

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, which is mostly in the form of aerosols rather than a true vapour. Quenching, i.e., contact with a cooled liquid, is effective, but careful design and temperature control are needed to avoid blockage from differential condensation and early deposition in cooler transfer pipework. High-volatility components are important in reducing liquid viscosity and therefore need to be recovered. Electrostatic precipitation has been shown to be extremely efficient in recovering aerosols. In fluid-bed systems, the organic vapour/aerosol concentration can be very low (< 5 vol%), further increasing the difficulty of product separation due to the low vapour pressure of gas phase species and broad condensation temperature range of the organics, significantly increasing the size of product recovery equipment. The pyrolysis processes in operation, commissioning or under design (2010) are listed with capacities and applications in Table 3. Note that this is an indicative list and not a complete list of all plants operating worldwide.

Table 3. Pyrolysis liquids production processes, 2010 (> 10 kg/h).

Host organisation	**Country**	**Technology**	**kg/h**	**Applications**	**Status**
ABRITech/ Advanced Biorefinery Inc., Forespect	Canada	Auger	70–700 2 000	Fuel	Operational Commissioning
Agri-Therm/ University of Western Ontario	Canada	Fluid bed	420	Fuel	Upgrade
Biomass Engineering Ltd.	UK	Fluid bed	250	Fuel and products	Construction
BTG	Netherlands	Rotating cone	200 5 000	Fuel and chemicals	Operational 5 t/h in design phase
BTG/Genting	Malaysia	Rotating cone	2 000	Fuel	Dormant
Dynamotive	Canada	Fluid bed	80 625	Fuel	Disassembled
Dynamotive	Canada	Fluid bed	4 200	Fuel	Operational
Dynamotive	Canada	Fluid bed	8 400	Fuel	Standby
KIT	Germany	Auger	1 000	Fuel	Operational
Metso	Finland	Fluid bed	300	Fuel	Operational
Pytec	Germany	Ablative	250	Fuel	Operational
Red Arrow/Ensyn several	USA	Circulating transported bed	125– 1 250	Fuel and chemical	Operational
University of Hamburg	Germany	Circulating transported bed	50	Waste disposal Fuel and chemicals	Operational
University of Science and Technology of China, Hefei	China	Fluid bed	120	Fuel	Operational
Virginia Tech	USA	Fluid bed	250	Fuel	Operational
VTT	Finland	Circulating transported bed	20	Fuel	Operational

Typical product yields from clean, white wood (wood without bark) under fast pyrolysis conditions are approximately 64 wt% organic liquids, 12 wt% product water (chemically dissolved in organic liquids), 12 wt% char and 12 wt% non-condensable gases (CO_2, CO, H_2, CH_4, trace C_3+'s). Variations in organic liquid yields are mainly due to differences in the physical and chemical composition of feedstock when operated within a normal fast pyrolysis regime (fast heat-up of feed, short residence time of solids, rapid cooling of product vapours, amount of inorganics and their composition). Reactor configuration plays a minor role in product liquid quality and composition, if all other process parameters remain constant. The liquid yields from pyrolysis of biomass are shown in Figure 1. The properties of various fast pyrolysis liquids are shown in Appendix G.

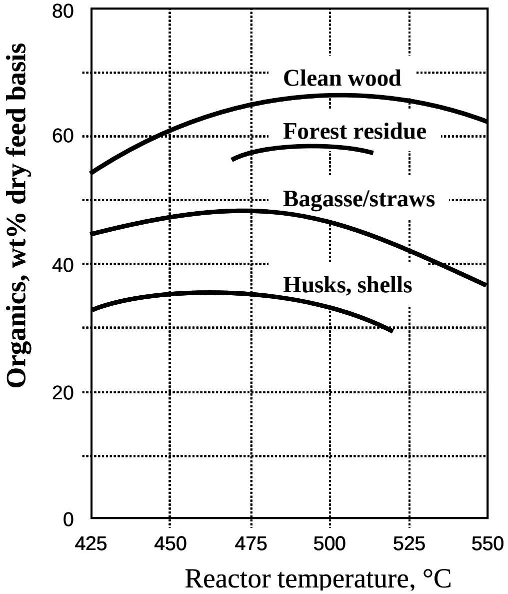

Figure 1. Approximative organic liquid yields from pyrolysis of wood and agro-biomasses.

3. Chemical composition of fast pyrolysis liquids

The chemical composition of fast pyrolysis liquids is difficult to analyse with conventional methods like GC/MSD due to low volatily resulting from the polarity and high molecular mass of the compounds in the liquid. A solvent fractionation scheme based on water-extraction (Piskorz et al. 1988) was developed (Oasmaa et al. 2003) for chemical characterisation of whole pyrolysis liquids (Appendix E).

In the method, pyrolysis liquid is divided into water-soluble (WS) and water-insoluble (WIS) fractions. The WIS fraction can be separated further by dichloromethane (DCM) extraction into two fractions with different molecular size distributions. The water-insoluble material consists mainly of lignin material, extractives (neutral substances) and solids. In aged liquids, this fraction also includes high-molecular-mass reaction products mainly derived from the pyrolytic lignin.

The water-soluble (WS) fraction consists mainly of water, “sugars” (sugar-type compounds, ether-insolubles), acids, aldehydes, ketones, pyrans and furans. The acids can be analysed by Capillary Electrophoresis (CE) directly from the WS fraction (Chapter 8). Acidity of pyrolysis liquids can also be measured by TAN (Total Acid Number) (Oasmaa et al. 2010, Agblevor 2010). The “sugars” are obtained with extraction of diethyl ether as an ether-insoluble (EIS) fraction. These “sugars” can also be measured roughly with the Brix method using a density meter (Oasmaa & Kuoppala 2008). The methods can be used to monitor the main differences in composition of various biomass-based pyrolysis liquids and to follow changes occurring in the liquids during storage (Figure 2).

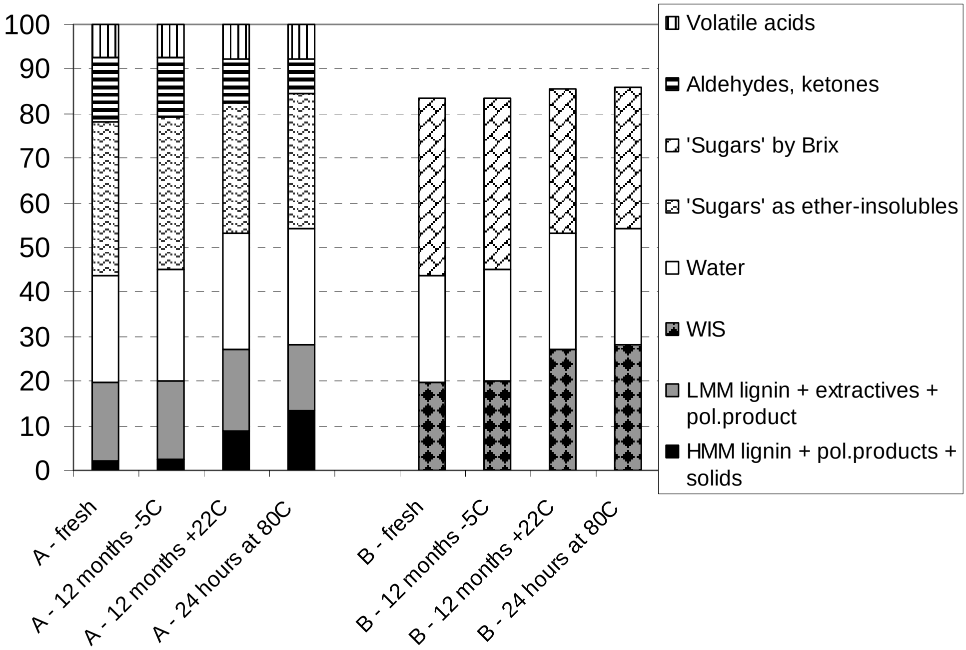

Figure 2. Follow-up of the main changes in the chemical composition of a pine pyrolysis liquid during one year of storage at various temperatures. A is the long (Oasmaa et al. 2003) and B the short (Oasmaa & Kuoppala 2008) solvent fractionation method.

The results of solvent fractionation and GC/MSD complete each other as shown in Table 4.

Table 4. Composition of a pine pyrolysis liquid (CHNO of dry matter) when combining solvent fractionation and GC-MSD*.

Fast Pyrolysis Bio-Oil (Pine)		**wet**	**dry**	**C**	**H**	**N**	**O**	**pKa**
Whole oil		**23,9**	**0**	**53,3**	**6,5**	**0,08**	**40**	
Water	wt-%	23,9	0					**15,7**
Acids	**wt-%**	**4,3**	**5,6**	40,0	6,7	0	53,3	**3 - 5**
Formic acid	wt-%		1,5					3,8
Acetic acid	wt-%		3,4					4,7
Propionic acid	wt-%		0,2					
Glycolic acid	wt-%		0,6					3,8
Alcohols	wt-%	**2,2**	**2,9**	37,5	12,5	0	50,0	**15 - 16**
Ethylene glycol	wt-%		0,3					15
Methanol	wt-%		2,6					16
Aldehydes, ketones, furans, pyrans	wt-%	**15,4**	**20,3**					**16 - 36**
Nonaromatic Aldehydes	wt-%		9,72	40,0	6,7	0,0	53,3	17
Aromatic Aldehydes	wt-%		0,009					17
Nonaromatic Ketones	wt-%		5,36	48,6	8,11	0,0	43,2	20
Furans	wt-%		3,37					32 - 36
Pyrans	wt-%		1,10					32 - 34
Sugars	wt-%	**34,4**	**45,3**	44,1	6,6	0,1	49,2	**3 - 16**
Anhydro-ß-D-arabino-furanose, 1,5-	wt-%		0,27					
Anhydro-ß-D-glucopyranose(Levoglucosan)	wt-%		4,01					
Dianhydro-α-D-glucopyranose, 1,4:3,6-	wt-%		0,17					
Hydroxy, sugar acids	wt-%							3 - 5
LMM lignin	wt-%	**13,4**	**17,7**	68	6,7	0,1	25,2	**9 - 10**
Catechols	wt-%		0,06					
Lignin derived Phenols	wt-%		0,09					10
Guaiacols (Methoxy phenols)	wt-%		3,82					10
HMM lignin	wt-%	**1,95**	**2,6**	63,5	5,9	0,3	30,3	
Extractives	wt-%	**4,35**	**5,7**	75,4	9,0	0,2	15,4	**7 - 16**
Fatty acids	wt-%							9-10
Triglyserides	wt-%							
Resin acids	wt-%							7

* Analysed at the vTI (Germany). LMM = Dichloromethane soluble lower-molecular mass fraction of water-insolubles (WIS). HMM = Dichloromethane insoluble higher molecular mass fraction of water-insolubles (WIS).

4. Homogeneity and sampling

4.1 Pyrolysis liquid phases

Pyrolysis liquids are typically considered to be in single phase. There are a number of reasons why two or more phases can be formed during product recovery, handling or storage, and may cause serious problems in combustion. Multi-phase liquids can be due to the chemical composition of the original biomass feedstock, e.g., a high content of extractives, i.e., neutral substances originating mainly from bark and needles, or higher than normal lignin content, or a high water yield causing phase separation. Although this type of phase-separation cannot usually be prevented, its consequences can be minimised.

The amount and type of extractives (lipids, resin acids, etc.) in the wood feedstocks cause the formation of a distinct top layer (Oasmaa et al. 2003a, b, Oasmaa et al. 2004, Garcia-Pérez et al. 2006). Forest residues, in particular, yield a pyrolysis liquid with a 5–20 wt% top phase that is low in polarity. The amount of top phase depends on the feedstock composition, process and product collection conditions. Compared with the bottom phase, the top phase is low in water and density and high in heating value and solids content. Some extractives (e.g., C_{18}–C_{26} fatty acids) can appear as crystals in the liquid (Oasmaa et al. 2003b).

Phase separation can also take place during long storage or severe heating (see Chapter 9) or upon the addition of water to the liquids.

4.2 Homogenisation and sampling

In the case of fresh, single-phase, low-to-medium viscous pyrolysis liquid, the liquid remains fairly homogenous under the proposed storage conditions for 6 to 12 months without any mixing. The solids in the liquid settle to the bottom or rise to the top depending on the density difference (see Section 6.2).

Mixing and sampling methods depend on the type and size of the pyrolysis liquid container (Appendix A). Small samples can be homogenised in routinely used laboratory mixers. Pyrolysis liquid in barrels or in large totes can be homogenised by propeller mixers. Recirculating is not that efficient and care must be taken that the whole liquid is in movement (Oasmaa et al. 1997).

The homogeneity of the liquid after mixing can be verified by microscopic determination and/or by sampling from different depths and analysing the moisture and solids contents. The sampling device should be wide-mouthed to obtain a homogenous sample.

5. Solubility

5.1 Water solubility

Pyrolysis liquids can be considered as mixtures/solutions of water and water-soluble organic compounds with water-insoluble, mostly oligomeric, material (Table 4). The ratio of these fractions depends on the feedstock, the pyrolysis process, production and storage conditions. The water-insoluble fraction, mainly lignin-derived oligomers, usually accounts for about 20–25 wt% of the liquid (wet basis), while the water concentration typically ranges from 20 to 30 wt%.

Pyrolysis liquids differ, to some extent, in their ability to dissolve water. A typical phase diagram for a pyrolysis liquid water system is shown in Figure 3. (Peacocke et al. 1994). The weight percent of organics (or water), at 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, 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% organics and 73% water, while the organic phase would contain 72% organics and 28% water.

By adding increasing amounts of water to pyrolysis liquids, a phase separation can be forced to occur (Appendix B/1). When adding excess water, the water-insoluble lignin-derived fraction separates out of the aqueous phase, retaining some of the water as shown above.

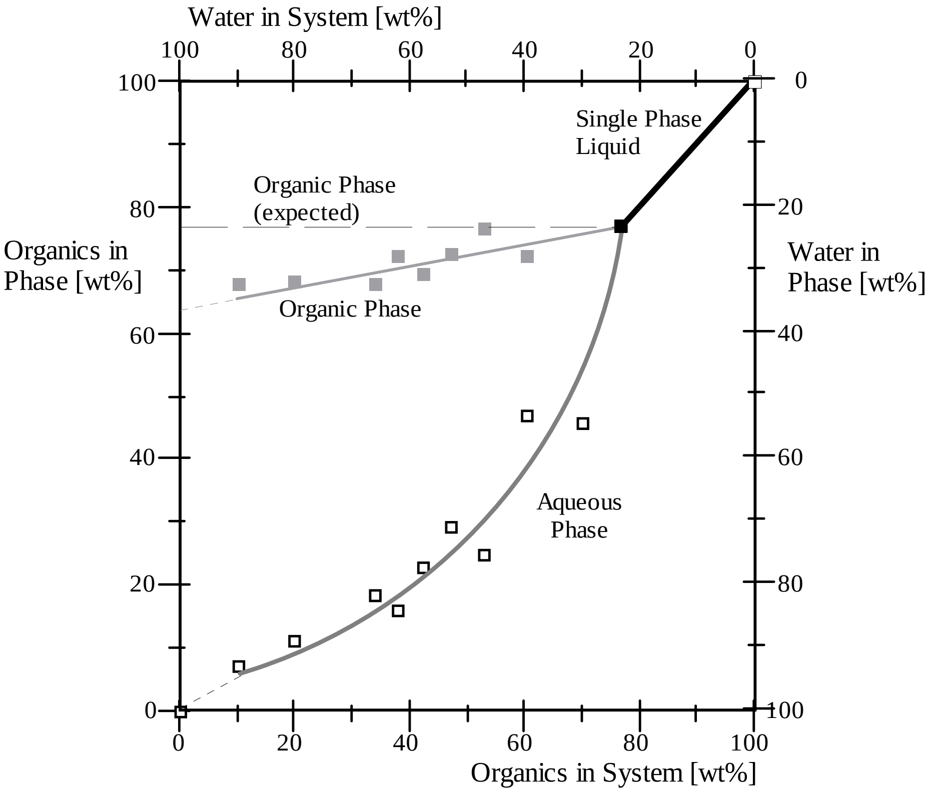

Figure 3. Pyrolysis liquid – water phase diagram (Peacocke et al. 1994).

5.2 Solubility in organic and inorganic solvents

The solubility of pyrolysis liquids in organic solvents is affected by the degree of polarity. Good solvents for highly polar biomass pyrolysis liquids are low molecular weight alcohols, such as methanol, ethanol and iso-propanol. These solvents dissolve practically the whole pyrolysis liquid excluding solids (char) and some extractives.

Polar biomass pyrolysis liquids do not dissolve in hydrocarbons such as hexane, diesel fuels or polyolefins. Neutral, mainly aliphatic, substances in forest residue and bark liquids (< 10 wt%) are soluble in n-hexane however. To dissolve forest residue liquids, a mixture of a polar (e.g., alcohol) and a neutral (e.g., dichloromethane) solvent is needed (Appendix C).

An increase in the pH of the liquids can, in principle, be carried out by adding basic organic solvents like amines or alkali hydroxides. The introduction of nitrogen or alkali metals is not recommended, however, if the final application of pyrolysis liquid is fuel. Use of strong inorganic bases may lead to rapid reaction and high instability in the liquids, leading to a dramatic increase in viscosity and temperature of the liquid. Addition of organic amines may not lead to phase-separation, but additional nitrogen is not desirable in combustion.

For cleaning up of equipment and washings, solvents such as methanol, ethanol, acetone and mixtures thereof are effective on fresh liquids, though materials compatibility must also be taken into account so as not to damage seals in pumps and gaskets in flanges. Lignin based deposits and heavy liquids can be solubilised with 5–10 wt% NaOH (Sodium Hydroxide) or machine washing agents. For large-scale cleaning of equipment, a dilute, i.e., 3–5 wt%, NaOH or KOH solution is recommended, subject to material compatibility and the use of other cleaning agents, reagents or other liquid media (i.e., incompatibilities with recirculation liquids in quench systems needs to be evaluated).

6. Fuel oil analyses for pyrolysis liquids

6.1 Water content

Water is regulated in petroleum fuels because it forms a separate phase that can cause corrosion, problems in burners or emulsion formation. With pyrolysis liquid, the water content is high (> 20 wt%) and needs to be regulated because of its influence on other properties and phase stability.

In pyrolysis liquids, water is dissolved or exists as an emulsion. It cannot be removed by physical methods such as centrifugation (Oasmaa et al. 1997). Pyrolysis liquids contain low-boiling (below 100°C) and water-soluble compounds, and hence conventional drying methods or xylene distillation (ASTM D 95) cannot be used (Oasmaa & Peacocke 2001, Qiang et al. 2008) without a significant loss of low molecular weight chemicals and secondary reaction within the liquids.

The water content of pyrolysis liquids can be analysed by Karl Fischer (KF) titration according to ASTM E 203-96: Standard Test Method to Water Using Volumetric KF Titration. With a proper choice of sample size, KF reagent concentration and apparatus, volumetric titration is suitable for the measurement of water over a wide concentration range, that is, parts per million to 100% water. In some cases for increased accuracy, use of a coulometric KF titrator can be used for low concentrations (< 1 wt% 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:

$$\text{Titre t } = \frac{\text{mg of water}}{\text{mg of KF solution}} \tag{1}$$

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

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

The anion of the alkyl sulphurous acid oxidises into alkyl sulphate by iodine (3). This reaction consumes water. To ensure the reaction occurs in the optimum pH range (5–7), imadazol is used.

$$H_2O + I_2 + (RNH)SO_3CH_3 + 2\ RN \text{ -> } (RNH)SO_4CH_3 + 2(RNH)I \qquad (3)$$

ROH	an alcohol, e.g., methanol, ethanol, ethylene-glycol-mono-ethyl-ether
RN	a caustic solution, e.g., 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 have been tested for forest residue liquid (Oasmaa & Peacocke 2001). There was no significant difference in the measured water contents. The titration end point was easier to detect when chloroform was present however. The recommended sample solvent for KF titration (ASTM E203) is therefore a mixture (3:1) of methanol and chloroform. It must be noted that new KF reagents, including those containing no pyridine, are also available. In order to verify the use of another sample solvent or reagent, the use of the water addition method (Appendix B/1) for calibration is recommended.

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

The accuracy of titration for good quality white wood liquids can be ±0.1 wt% (Oasmaa et al. 1997). For extractive-rich forest residue liquids, errors of ±0.5 wt% deviation for 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 approximately 20 wt% water for use in a volumetric titrator. 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, i.e., no globules, single phase with very low particulates (< 0.1 wt%), the 0.01 mg/ml deviation in the 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).

6.2 Solids and ash

6.2.1 Occurrence of solids and ash in pyrolysis liquid

There are varying amounts of solids in pyrolysis liquids. This may affect erosion in pumps and injection nozzles, blockages and high particulate emissions (Hallgren 1996, Suppes et al. 1996, Gust 1997, Oasmaa & Kytö 2000, Oasmaa et al. 2005).

Pyrolysis liquids typically contain less than 0.5 wt% solids having an average particle size of approximately 5 µm when cyclone(s) are used to remove the char from the hot products during pyrolysis. In fast pyrolysis, about 12 wt% char is typically produced as a by-product from clean, bark-free wood. Some char comes directly from the solid biomass and there is also evidence that secondary cracking gives coke or soot, which may be associated with the primary char. There are a range of cyclone designs and preference should be made to high efficiency cyclones designed for high temperature use to remove low density solids (char/ash particles) at low solids concentrations in the gas phase. In entrained bed processes, and some fluid bed processes, some attrited sand may also end up in the product liquid. The amount of solids (residual char and sand) in the product liquid is due to the feedstock (type and particle size distribution), process type (fluidised bed, entrained bed, etc.), and effect of cyclones or other type of char removal techniques. Depending on the densities and storage time, solids can be found on the surface or at the bottom of the liquid (see Figure 4).

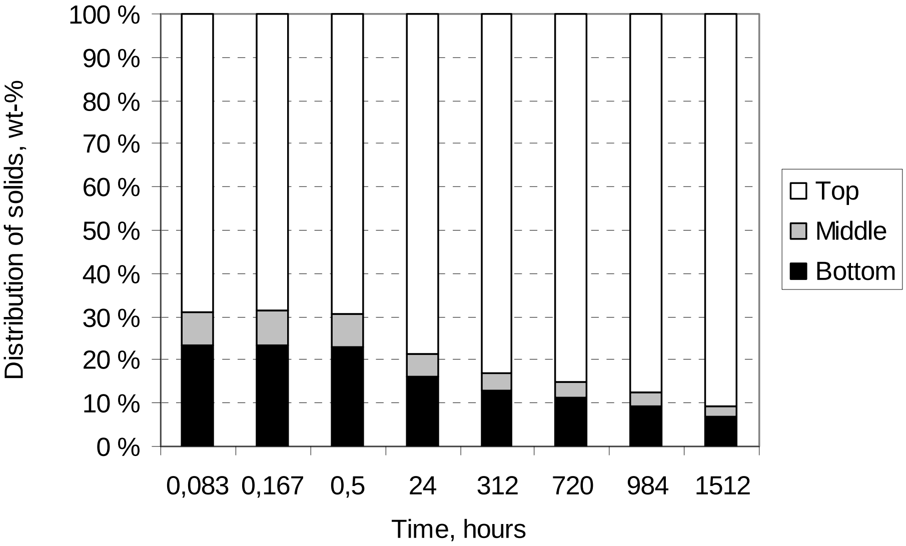

Figure 4. Distribution of solids as wt% of total solids (0.32 wt% measured as insoluble in methanol-dichloromethane) by storage time in a pine pyrolysis liquid at room temperature. Amount of samples: 5 wt% top, 90 wt% middle, 5 wt% bottom.

The solids present in the liquids may contain condensed carbon residual material, elutriated sand and metals. Depending on the use of the fuel, ash and/or char, the content and composition have a considerable bearing on whether there will be any detrimental effects.

6.2.2 Determination of solids and ash

Various solvents and their combinations for solids determination have been tested earlier (Oasmaa & Peacocke 2001). A mixture of methanol and dichloromethane has been chosen as the most effective solvent for various biomass-derived pyrolysis liquids. A 1 µm filter is used because of the residual fine particles in the liquid. A sample size yielding 10–20 mg residue and a sample to solvent ratio of 1:10 with several washings are recommended (Appendix C). A maximum difference of 10 wt% between duplicates can be accepted. This method is a base for the ASTM D7579 standard for solids content.

The ash content of the liquids 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 significant amount of water in pyrolysis liquids can cause foaming or splashing during the heating of the sample, leading to erroneous results. Controlled evaporation of the water is therefore needed. A sample of 20 ml pyrolysis liquid may initially be heated in a porcelain crucible on a heating plate or in a temperature-controlled small sand bath for evaporation of the water and other volatile components. The addition of isopropanol or ash-free filter paper for absorbing the water can also prevent splashing.

Ash is always made up of the oxides of the elements; in reality it is always results in over-reporting the elements. Ash contents have typically been low (< 0.2 wt%) for white wood pyrolysis liquids and higher (< 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 the very high removal efficiency of hot vapour filtration of char fines with alkali (Na, K, Ca, Mg) metals (below 10 ppm).

For alkali metal analyses, different sample pretreatment methods for ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) and Atomic Absorption Spectrometer (AAS or AA) have been tested previously (Oasmaa et al. 1997). It was found that the standard approach with dissolution in isopropanol (IPA) was inaccurate due to incomplete dissolution of the sample. Dry combustion was shown to be good but time-consuming, as the water has to be evaporated carefully before ashing or the liquid would foam out of 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 may be partially ejected or completely lost. Wet oxidation was the easiest and fastest method tested. Large samples are difficult to handle with acids, however, and a sample size of 3–5g is suggested as adequate. The same acid or acid mixture and concentrations should be used in both the sample and standard solutions.

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

Metals may be analysed by ICP-AES, ICP-OES (Optical Emission Spectroscopy) or AAS. Wet oxidation (Oasmaa & Peacocke 2001) is suggested as a fast and easy pretreatment method, especially for analysing alkali metals and easily volatilised toxic metals such as Cr, As, Pb, Hg and Cd. For a semi-quantitative analysis, XRF (X-ray fluoresence) can be used.

It should be pointed out that for an accurate analysis of trace alkali metals, the whole procedure from recovery of the pyrolysis liquid to sample pretreatment should be re-checked in detail. Contamination from glass containers and dust in the air may influence the results (as observed by 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, such as neutron activation (NA) analysis, may be advantageous.

6.3 Carbon residue

The carbon residue is a measure of the carbonaceous material left in a fuel after all the volatile components have been vaporised in the absence of air. It may be expressed as Conradson Carbon Residue (CCR) or Micro Carbon Residue (MCR). Numerically, the CCR value is the same as that of MCR.

No real correlation between the Conradson carbon results for pyrolysis liquids and the deposit formation on injector nozzles has been reported. Fuels with up to 12 wt% 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 engine in which the fuel is to be used. Pressure jet and steam-atomising-type burners are not very sensitive to the value of the carbon residue of the fuel to be used.

Conradson carbon is normally only specified for light diesel fuels. The pyrolysis liquids are of a different chemical nature than mineral-oil-based heavy diesel fuels. There is not yet adequate information on diesel engine performance data for pyrolysis liquids, and this test was therefore also selected for evaluation (Oasmaa et al. 1997). MCR has been successfully used in hydrotreatment studies (Mercader at al. 2010), however, in which it is an important property when aiming to process a feed for FCC in an oil refinery.

The CCR of pyrolysis liquids was measured according to ASTM D 189 and MCR according to ASTM D 4530. The methods are similar. 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 or MCR. The sample size for MCR is 0.15 ± 0.05 g if the residue is > 5%. The optimum amount of residue for MCR in about 25 mg. For a pine pyrolysis liquid MCR of 20.8 wt% with stdev of 0.27 (six duplicates) was obtained.

The accuracy of the method according to the standard is ±2 wt% when the CCR is above 20 wt%. The CCR typically has a range of 18–23 wt% for pyrolysis liquids from hardwood and softwood, and 17–18 wt% for pyrolysis liquids from forest residue or wheat straw. Low CCR values 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 a 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. It has been observed that the molecular weight average for hot-vapour-filtered pyrolysis liquids is lower than liquids recovered using a standard quench arrangement.

6.4 Particle size distribution

Optical methods have been tested for determining particle size distribution for pyrolysis liquids (Oasmaa et al. 1997, Oasmaa & Peacocke 2001). Optical microscopy or particle size laser analysis may be useful tools for qualitative off-line assessment and on-line follow-up (Chapter 10) of solids during pyrolysis, but they cannot be used for exact quantitative determination of solids.

6.5 Elemental composition

An elemental analysis of carbon, hydrogen and nitrogen is carried out at the VTT with Elementar VARIOMAX 785-500 according to ASTM D 5291. With the method, carbon, hydrogen and nitrogen are determined simultaneously as gaseous products (carbon dioxide, water vapour and nitrogen). Oxygen (dry basis) is calculated by difference.

The accuracy of carbon and hydrogen is good. The accuracy of nitrogen depends on its content. Liquids from wood biomass typically contain low concentrations of nitrogen (≤ 0.1 wt%) that are practically the same as the nitrogen detection limit (0.1 wt%) of the method. Pyrolysis liquids from straw and some forest residues contain higher (0.2–0.4 wt%) concentrations of nitrogen and hence the δ_{dev}% is lower. Due to the small sample size used in the analysis method, the reproducibility of the elemental analysis is dependent on the homogeneity of pyrolysis liquids. At least triplicates and representative standards are recommended (Oasmaa et al. 1997).

X-Ray Fluoresence (XRF) is a semi-quantitative and fast method for screening elements. The error varies between 10 and 30% and the detection limit is 100 ppm. The analysis is conducted straight from the sample (5 ml). For sulphur, the LECO SC 432 analytical instrument according to ASTM D 4239 can be used as a fast method. The oil sample is analysed without any pretreatment. The detection limit is 100 ppm.

Sulphur and chlorine can both be analysed accurately either by ion chromatography (IC) or by Capillary Electrophoresis (CE) based on standard CEN/TS 15289 and on modified CEN/TS 15408. The sample solutions for both methods are prepared by combustion of the sample in an oxygen bomb according to ASTM D 4208. The detection limits for both of the elements are 30 ppm if the contamination in the oxygen bomb is eliminated, that is, the bomb is used only for these analyses. Table 5 presents the comparative results for S and Cl by various methods. It can be seen that the two Leco methods gave different results even though the detection limit is same. IC was chosen for further analyses because of its low detection limit and that both S and Cl can be determined by the same analysis.

Lower amounts (detection limit 5 ppm) of chlorine can be analysed by ion neutron activation analysis (INAA). Sulphur cannot be analysed by INAA. Lower concentrations of sulphur can be analysed by Inductively Coupled Plasma (ICP) for which the detection limit is 20 ppm with a sample dissolution in HNO_3 and H_2SO_4 using a microwave oven. Metal analyses are discussed in Section 6.2.2.

The sulphur content of pyrolysis liquids from wood and agro-biomass is typically low (60–500 ppm). The chlorine content of pyrolysis liquids from different feedstocks has been determined to be below 10 ppm for hardwood (oak maple) liquid: below 100 ppm for softwood (pine) liquid, and 100–400 ppm for forest residue (high content of green material) and for straw (wheat) liquid.

Table 5. Analysing sulphur and chlorine of two fast pyrolysis liquids (Oasmaa et al. 2011).

	Forest residue liquids						
Sulphur	PR09-12-1					Average	δ_{dev}
Leco SC-432/VTT	0.0179	0.0172	0.0221	0.0219	0.0202	0.0199	0.002
Leco/Ramboll	0.026	0.025	0.026	0.023	0.024	0.0248	0.0012
Halogen combustion+IC	0.012	< 0.01	< 0.01	< 0.01	0.01	0.01	
Chlorine							
Halogen combustion+IC	0.0063	0.0057	0.0064	0.012	0.0089	0.0079	0.0026
	Pine Liquid						
Sulphur	PR09-51-2					Average	δ_{dev}
Leco SC-432/VTT	0.03	0.0267	0.0266	0.0292	0.0304	0.0286	0.002
Leco/Ramboll	0.063	0.071	0.051	0.044	0.045	0.0548	0.0118
Halogen combustion+IC	0.024	0.022	0.025	0.026	0.026	0.0246	0.0017
Chlorine							
Halogen combustion+IC	0.0077	0.0084	0.008	0.0071	0.0072	0.0077	0.0005

6.6 Density

The specific gravity is of little significance as an indication of burning characteristics, but it 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 in tests. A viscous pyrolysis liquid with large particles may disturb the measurement and cause erroneous results. Air bubbles may also disturb the determination near ambient temperatures. Vigorous shaking of the sample just before the analysis should therefore be avoided. Instead, the sample can be rotated carefully. At an 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 about 1.2 kg/dm^3 for water contents of ~25 wt%. The precision of density measurements is good (variation below ±0.1%). Densities of biomass pyrolysis liquids are a function of water content (Oasmaa et al. 1997). Figure 5 shows the densities of various pine and forest residue liquids (top:bottom = 1–2:8–9) as a function of original water content. It shows that the bottom phase of forest residue liquid has a similar density-water correlation to 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 (e.g., the oleinic acid, present in the extractive layer is 0.89 kg/dm^3) in the top phase while water with water-soluble compounds moves to the more polar bottom phase.

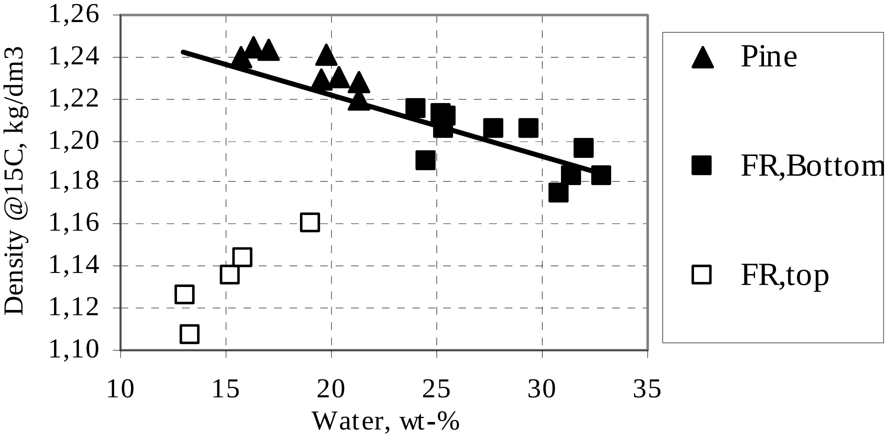

Figure 5. Density of pine and forest residue (FR, top:bottom = 1-2:8-9) pyrolysis liquids as a function of water content.

6.7 Viscosity and pour point

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 fuel (Dyroff 1993).

The viscosity of standard fuels 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.

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:

$$\nu = \frac{\eta}{\rho} \tag{4}$$

where

ν kinematic viscosity (cSt) at temperature T
η dynamic viscosity (mPa s) at temperature T
ρ density (kg/l) of the liquid at temperature T.

Due to the high extractive content of forest residue liquids, the Newtonian behaviour of the liquid was tested (Oasmaa and Peacocke, 2001). The bottom phase is chemically similar to the white wood pine liquid and its Newtonian behaviour was not unusual. The top phase containing most of the extractives showed a slight non-Newtonian behaviour at 30°C. At 45°C however, the non-Newtonian behaviour was undetectable.

Cannon-Fenske or Ubbelohde capillaries can be used. The basic difference between these methods is the flow direction of the sample. For non-transparent liquids, Cannon-Fenske is easier to use at room temperature because of the 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.

The viscosity determination at near-ambient temperature may be disturbed by gas bubbles, especially for forest residue liquids, and vigorous shaking of the sample just before the analysis should therefore be avoided. The sample can instead be rotated carefully. The air bubbles are let to be removed before sampling. At an elevated temperature, the gas bubbles can easily be removed during the preheating of the liquid. The tempering time in the heating bath is 15 minutes. The maximum allowed difference of duplicates is 5%.

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, T_{max} 100°C), the precision was good below 50°C. At 80°C however, the evaporation of volatiles was observable during sample equilibration. The viscosity of the sample increased by almost 1% in a minute during measuring at 80°C. The δ_{dev} at 80°C was also higher than when using the capillary system, for which the evaporation of volatiles is not as significant due to the small exposed surface of the capillary (Oasmaa et al. 1997).

Viscosities of pyrolysis liquids are a function of water content (Oasmaa et al. 1997). The viscosities for various pine and forest residue liquids are shown in Figure 6.

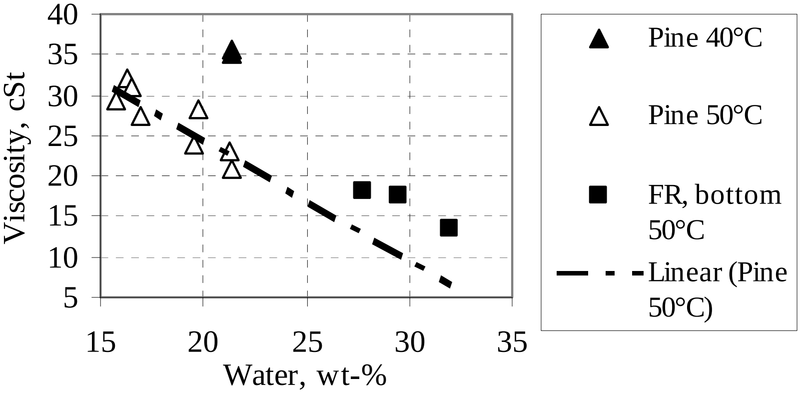

Figure 6. Viscosity of pyrolysis liquids from pine and forest residue (FR, bottom phase).

The pour point of a fuel is an indication of the lowest temperature at which the fuel can be pumped (Dyroff 1993). The recommended upper limit for pumpability is about 600cSt (Rick & Vix 1991). The pour point was determined at the VTT 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 typically 2–4 K lower than the pour point.

Preheating of the sample is laborious for some pyrolysis liquids, as it may cause separation of water on the surface of the sample. The water on the surface can then freeze before the actual pour point and hence disturb the measurement. The pour point of wood and straw pyrolysis liquids is typically below –30°C. For the analysed pyrolysis liquids, the low viscosity was an indication of a low pour point.

6.8 Lubricity and surface tension

Viscosity does not describe the lubricating properties of the oils. Lubrication properties are crucial for, for example, the 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 four-ball wear test according to IP 239/69T (ASTM D 278388). The former method is not suitable because it is a totally open system and the evaporation of pyrolysis liquid significantly disturbs the measurement. The latter method may be used. Considering the preliminary tests, it seems that the pyrolysis liquids possess some lubricating properties. Work on lubricity testing of liquids derived from rice husk with the four-ball method was recently reported (Lu et al. 2008). The EP (extreme-pressure), AW (antiwear performance) and friction-reducing properties of the liquid fuels were evaluated by the Pb (maximum non-seizure loads). A WSD (wear scar diameter) and friction coefficient with results of 470N, a WSD of 0.57 mm and a friction coefficient of 0.082 were measured. A surface tension value of 35.3 mN/m at 30°C for liquids derived from rice husk was also reported (Lu et al. 2008).

6.9 Heating value

The combustion heat of the fuel is the amount of heat produced when the fuel is burned completely. It is typically determined by bomb calorimetric techniques. There are two values for combustion heat, or calorific value, for every fuel. They are referred to 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 the water formed by the combustion of the fuel.

The heating value of pyrolysis liquid can be measured as HHV by DIN 51900. 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 pyrolysis liquids may lead to poor ignition, and a fine cotton thread can therefore advantageously be used as a wick. The heat content of the thread is subtracted from the result. The lower heating value (LHV) is calculated from the HHV and the hydrogen content (ASTM 529192) by equation (5). No subtraction of free water has to be made (Rick & Vix 1991) because the water in the pyrolysis liquid cannot be removed by physical methods, as is the case 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 (Figure 7). 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 a dry organics basis) that of petroleum fuels.

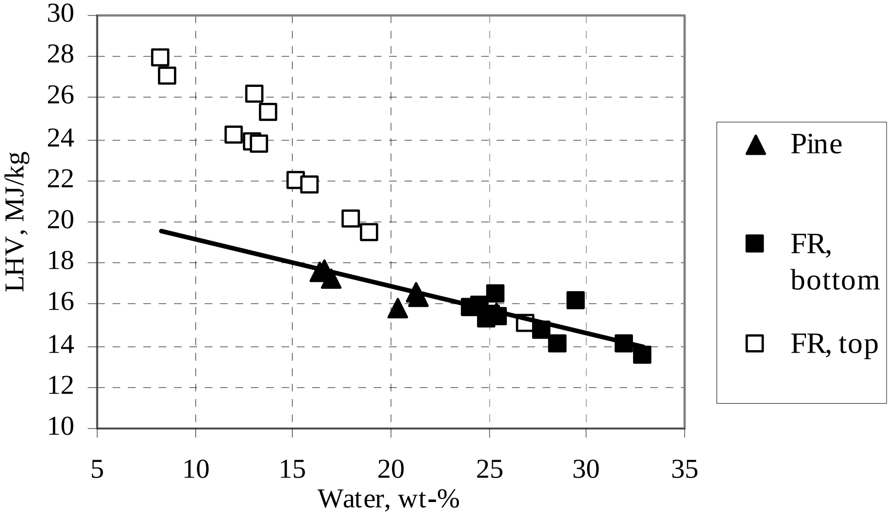

Figure 7. Heating value of pine and forest residue liquids (FR) as a function of water content.

7. Ignition properties of pyrolysis liquids

7.1 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. If the flash point is too low it 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 the flash point, nor are other properties such as fuel injection and combustion performance (Dyroff 1993).

The flash point of pyrolysis liquids has been 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 the stirring. The flash point is the lowest temperature at which the test flame ignites the vapour above the sample.

Flash points from 40°C to above 100°C have been measured for pyrolysis liquids (Oasmaa et al. 1997). Even for one pyrolysis liquid the flash point may range from 40 to 110°C depending on the laboratory. With pyrolysis liquids the low-boiling volatile compounds flash slightly before the evaporated water suppresses ignition. The flash may be too difficult to distinguish. Research work at VTT is going on for studying the flash point detection and ignition qualities of pyrolysis liquids.

7.2 Ignition temperature

Unlike the petroleum-based fuels, 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. The 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 is only ignited after adding an ignition-improver.

The properties of pyrolysis liquids vary significantly depending on the feedstock, the pyrolysis process (and the reaction parameters) and the product recovery system. Autoignition with a higher quality pyrolysis liquid may therefore succeed as stated by Shihadeh (1998). Shihadeh’s work was carried out with a combustion bomb to simulate the diesel engine environment.

The Ignition Quality Tester (IQT) is a combustion-based analytical instrument by which the ignition delay and cetane number 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 using the $\mathrm{IQT}_{\mathrm{TM}}$ to determine the cetane number of diesel fuels. CanMet and Advanced Engine Technology Ltd. in Canada have carried out IQT tests with pyrolysis liquid emulsions. Based on these results and linear interpolation, they ended up with a cetane number of 5.6 for the tested hardwood pyrolysis liquid (Ikura et al. 1998).

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. The Cetane Number of ~10 was evaluated from the Ignition Delay by means of a Reference Fuel Correlation (Bertoli et al. 2001).

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. The antiknock rating or 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 being easy to clean. Raw pyrolysis liquid does not fulfil these requirements due to its inherent chemical instability, lack of miscibility, low pH, water and O_2 adsorption.

7.3 Conductivity and specific heat capacity

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 and 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. The thermal conductivity of pyrolysis liquids was determined using the more common comparative method in which 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. An average thermal conductivity of 0.386 W/mK over the temperature range 44–63°C for mixed hardwood-derived fast pyrolysis liquids was determined (Peacocke 1994). Recent work by Qiang et al. (2008) on rice husk derived liquids gave a similar value: 0.389 W/mK. The chemical reactivity of pyrolysis liquids leads to erroneous results when heat flow occurs across the sample (Peacocke et al. 1994).

Electrical conductivity is a property that is of no direct use to fuel applications but is required by some instruments for level measurement and control. There are no published data for values. Wellman Process Engineering Ltd. has provided some data, however, as indicated in Table 6.

Table 6. 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). The water and char content data were supplied by Aston University.

Measurements for the specific heat capacity of pyrolysis liquids were carried out using a test rig (Peacocke et al. 1994) in which 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. The 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 intervals of 2°C by sampling the oil flow rate for two minutes. The system was calibrated using Shell Thermia B oil. The results of the work by Peacocke give an average value of 3.2 kJ/kgK (±300 J/kgK) over the temperature range of 26–61°C. Recent work by Qiang et al. (2008) reports a similar value, 2.8 kJ/kgK, for liquids derived from rice husk.

8. Acidity

8.1 Measurement

The acidity of fast pyrolysis liquids is typically determined as pH. The pH is a representation of how corrosive the oil may be, but it does not indicate the concentration of acidic constituents. The pH test method is useful in applications in which corrosive oil could cause considerable damage. The pH of fast pyrolysis liquids from untreated biomass is low (2–3).

The total acid number (TAN) can also be used for measuring the acidity of fast pyrolysis liquids. The TAN is the amount of potassium hydroxide (KOH) in milligrams that is needed to neutralize the acids in one gram of liquid.

ASTM D664 measures acidic constituents using a potentiometer to determine the end point. To prepare the sample (an appropriate sample size is presented in Table 7), a mixture (= TAN solvent) of toluene (50%), isopropyl alcohol (49.5%) and water (0.5%) is dissolved into a sample. This solvent mixture is the one developed for petroleum and is used here for consistency to allow comparison of methods and results. Potassium hydroxide (0.1-N potassium hydroxide in isopropanol, Mercantile product Merck 1.05544.1000) is then titrated into the solution using a burette with constant rate. The potentiometer output is monitored while the KOH is titrated into the solution.

Fast pyrolysis liquid was dissolved in 90 ml of TAN solvent. The amount of solvent is not important because KOH is only consumed when neutralizing the sample and the TAN will be calculated based on the amount of sample used. The TAN for water, methanol and hexane was 0.

Table 7. Sample size for TAN analysis.

Expected acid number, mg KOH/g sample	Sample weight, g	Weighing accuracy, g
0.05–0.9	10 ± 2	0.100
1–4.9	5 ± 0.5	0.020
5–19	1 ± 0.1	0.005
20–99	0.25 ± 0.02	0.001
100–250	0.1 ± 0.01	0.0005

The TAN is determined for the TAN solvent (Figure 8a). The result (< 0.1 mg KOH/g) is subtracted from the TAN of the sample. The determination of the TAN of fast pyrolysis liquids differs from that of mineral oils. There are no inorganic acids in biomass fast pyrolysis liquids. First, a pre-curve without the window set-up is drawn (Figure 8a). This is important for an unknown sample in order to identify the window area where the strongest derivative peak locates. The reduction in the U value at about 0.1 ml is due to the solvent which can be noticed from the blank test. The inflexion around 3 ml in Figure 8a is due to weak acids. A tangent is drawn to the steepest point on the curve and, based on that, the window (Figure 8b) for the titration end point (EP) is chosen. The window should be as tight as possible and the higher point on the curve is particularly important. A derivative curve from Figure 8b provides a clear end point. Table 8 shows the TAN results of a pine and a forest residue liquid.

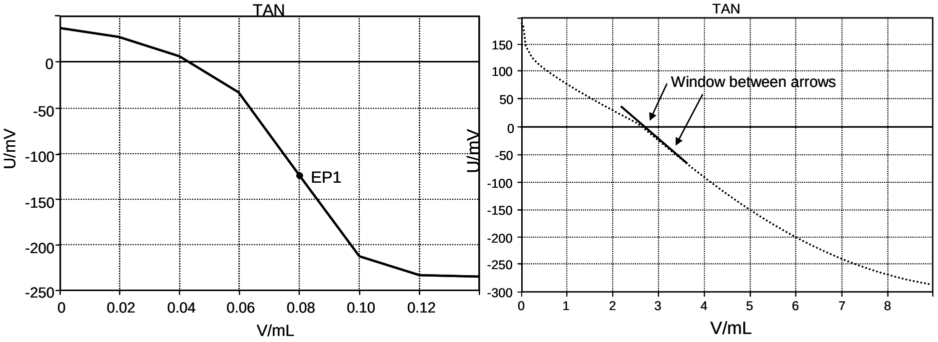

Figure 8a. Window "off". Blank test for solvent (left). TAN curve of pine fast pyrolysis liquid (right). The window is chosen from the steepest point on the curve. The window should be as tight as possible. (Oasmaa et al. 2010.)

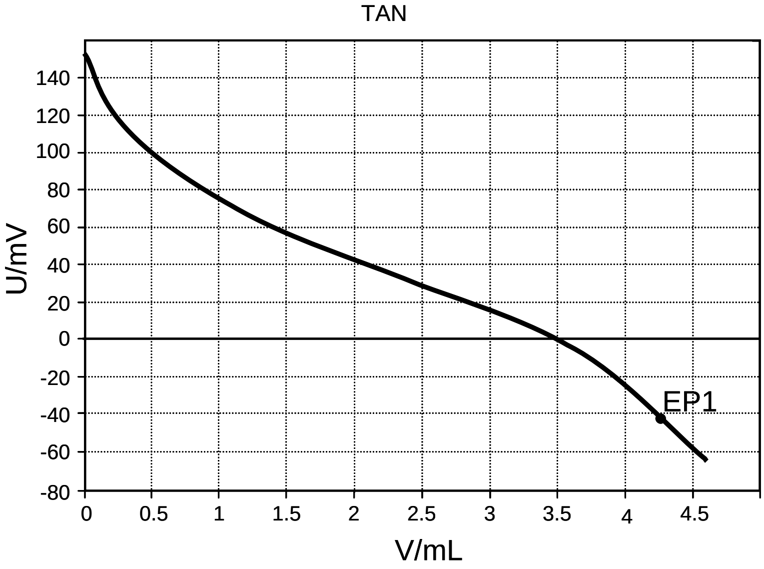

Figure 8b. Window “on” and set-up between 0 and –100. The titration end point (EP1) will be detected automatically.

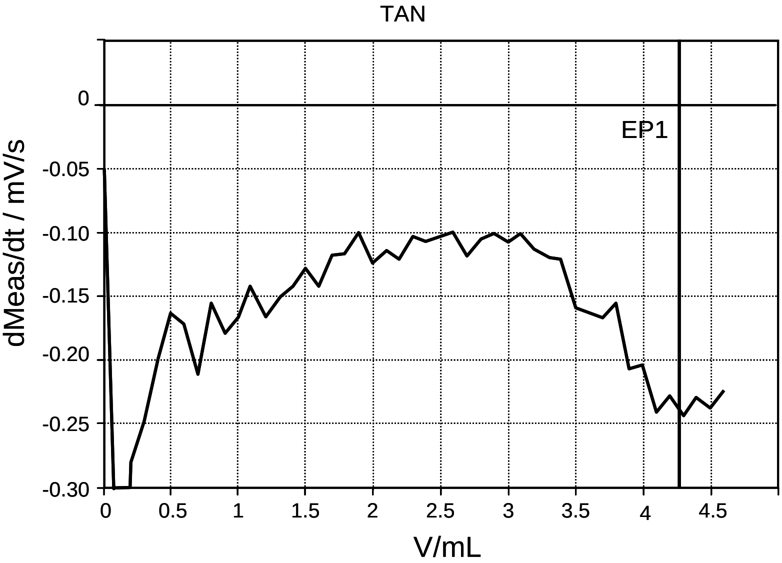

Figure 8c. Derivative curve of Figure 8b (Oasmaa et al. 2010).

TAN, mg KOH/g = (EPn-C31) x C01xC03/C00, where:

EPn = consumption of KOH at final equivalent point, ml
C00 = weight of the sample, g
C01 = 0.1 (concentration of the titrant, mol/l)
C03 = 56.106 [M(KOH) in g/mol]
C31 = consumption in zero titration, ml.

Table 8. TAN of pine and forest residue fast pyrolysis liquids by the ASTM D664 (Oasmaa et al. 2010).

	Ref.Pine PR06-27-10	**Forest residue** PR07-4-3
Acetic acid, wt-%	2,6	5,62
Formic acid, wt-%	1,50	0,92
Glycolic acid, wt-%	0,51	0,21
Total, wt-%	**4,6**	**6,8**
TAN, mg KOH/g	**71**	**97**
No of duplicates	11	20
Stdev	1	2

The solvents suggested by Agblevor (2010) were also tested for comparison with the ASTM D664 standard method. Aqueous potassium hydroxide (0.1 M KOH) was used as standard titrant instead of 0.1M KOH in alcoholic solution, and acetone was used as titration solvent instead of mixtures of toluene and 2-propanol. The same results (pine pyrolysis liquid TAN 70 ± 2) were obtained as when using the standard methods. Both of the methods were simple and fast ones.

The ASTM D 3339 – 07 test method covers the determination of acidic constituents in new or used petroleum products and lubricants soluble or nearly soluble in mixtures of toluene (50%), and isopropyl alcohol (49.5%), and water (0.5%). The test method is especially intended for cases in which the amount of sample available to be analyzed is too small to allow accurate analysis by Test Methods D 974 or D 664. It is applicable for the determination of acids having dissociation constants in water larger than 10^{-9}. Extremely weak acids having dissociation constants smaller than 10^{-9} do not interfere. Salts titrate if their hydrolysis constants are larger than 10^{-9}. To determine the acid number a sample (0.1 to 5 g weighed to 0.1 mg) of well mixed liquid is dissolved in 40 mL of the toluene, isopropyl alcohol, and water solvent. The resulting single-phase solution is titrated at room temperature under a nitrogen atmosphere with standardized 0.01 *M* potassium hydroxide (KOH) in isopropyl alcohol to the stable green color of the added *p*-naphtholbenzein indicator.

The acidity of fast pyrolysis liquids is derived mainly (60–70%) from the volatile acids, whose pKa values are the lowest of all the compounds in the liquid. This is the reason for the good correlation between the TAN and the amount of acids (Figure 9). There are also other groups of compounds in fast pyrolysis liquids that influence acidity, like phenolics (5–10%) and fatty and resin acids (< 5%). The acidity of the "sugar" fraction, mainly due to hydroxy acids, covers about 20% of the total acidity. (Oasmaa et al. 2010.)

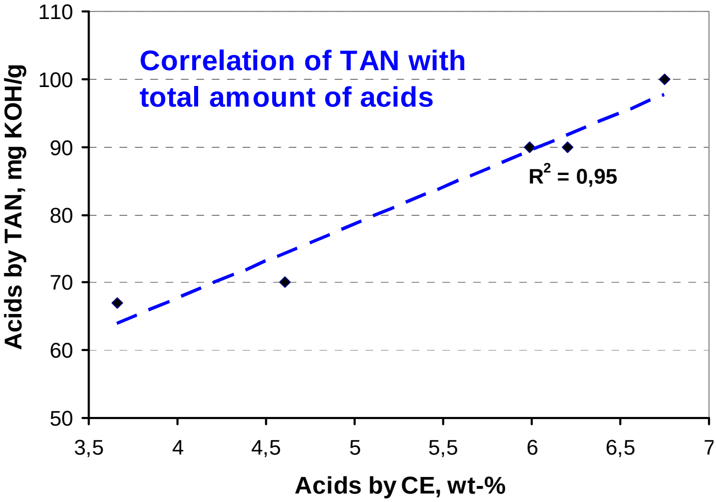

Figure 9. Correlation of TAN with volatile acids in pyrolysis liquid (Oasmaa et al. 2010).

8.2 Material resistance

Acids with water are the main reason for the corrosiveness of pyrolysis liquids, especially at elevated temperatures (Aubin & Roy 1980). The standard corrosion tests specified for fuel oil are empirically based – colour changes on copper strips or visible rust/oxidation on carbon steel rod AISI01 – and bear little significance to the corrosion potential of a liquid. In the standard corrosion test (ASTM D 665 A) at 60°C with pyrolysis liquid, a clear weight loss in carbon steel (AISI 01) takes place. There is a need for a corrosion test that is specific to pyrolysis liquids before the corrosion risk of pyrolysis liquids can be set down in a specification (Diebold et al. 1997).

The acid-resistant steel AISI 316 can be used in most applications. AISI 316 may be a little better than AISI 304 because of the small amount of Mo, which 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).

Extensive testing of various metals (brass, mild steel, aluminium and stainless steel) has been carried out by Orenda Aerospace Corporation (Fuleki 1999). Brass and stainless steel were relatively unaffected, but aluminium and mild steel suffered severe weight loss at higher temperatures and prolonged exposure (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) reported that pyrolysis liquids are corrosive to mild steel and aluminium. Work by Das et al. (2004) on a liquid fraction produced from the pyrolysis of cashew nut shells gave a liquid that exhibited corrosion rates of 0.232 mm/y for copper and 0.021 mm/y for stainless steel at 50°C. Kirk et al. (2001) immersed various materials at 80°C for 15 days in pyrolysis liquids. Their conclusions were that 304L stainless steel, 316L stainless steel, 430 stainless steel and 20M04 stainless steel have corrosion rates of less than 0.007 mm/y and are suitable for use with pyrolysis liquids. Low chromium alloy steel (C 0.16%, Cr 12%, Mn 0.53%, Mo 0.52%, Ni 1.8%, Si 0.8%, V 0.3%, bal Fe) corroded at rates up to 3.7 mm/y. At room temperature, the alloy showed good resistance with a corrosion rate of less than 0.009 mm/y.

Nickel is not resistant to pyrolysis liquids even at room temperature. Some nickel based alloys, like Hastelloy C 276 (57% Ni, 16% Cr, 16% Mo, 4% W, 5% Fe, max 2.5% Co, max 1% Mn, 0.08% Si, 0.01% C) are resistant to acid (Elliott 2010). 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 for a week (Oasmaa et al. 1997).

In the copper corrosion test (ASTM D 130), no corrosion or weight loss was observed on the copper stem (99.9% electrolytic copper) for different pyrolysis liquids (hardwood, softwood, straw) at 40°C. Copper is a noble metal and hence generally has good corrosion resistance to non-oxidising acids. Copper is suitable for washers (Jay et al. 1995). If it is connected to other metals, however, 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 the different components. It should be borne in mind, however, 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.

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 the high particle content and corrosion. The tests in a 400-bar injection test rig showed M390 to be a 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.

Many plastics like PTFE (polytetrafluoroethylene), PP (polypropylene), PE (polyethylene), HDPE (high-density polyethylene) and polyester resins are very resistant to pyrolysis liquids (Kirk et al. 2001, Oasmaa et al. 1997, Czernik 1994). They are excellent materials for containers for storing, transportation and sampling of pyrolysis liquids. Kirk et al. (2001) concluded that PTFE was the most resistant of the polymers tested (PTFE, HDPE, PP) and PP the least resistant.

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). Kirk et al. (2001) concluded that Viton, Buna-N and EPDM had volume changes of up to 100% during a 10-day test. Viton and EPDM, however, have been used very successfully at VTT as sealing material in pyrolysis units. Once inserted, it seems to have good sealing properties. It may become fragile, however, and has to be changed when opening the connection. The use of plastics could possibly be extended to replace copper and, in special cases, also AISI 316.

9. Stability of pyrolysis liquids

9.1 Phenomena

Pyrolysis liquids are not as chemically or thermally stable as conventional petroleum fuels due to the high content of reactive oxygen containing compounds and low-boiling volatiles. The instability of pyrolysis liquids can be observed as evaporation of volatile components under air, possible reactions with air due to O_2 adsorption, increase in viscosity and possible phase-separation ("aging") by time, or a rapid increase in viscosity/polymerisation and phase-separation when heated.

Exposure to air must be prevented for several reasons, e.g., loss of light compounds causing strong odours in the environment, and oxygen causing polymerisation reactions with consequent sedimentation of heavy compounds.

Pyrolysis liquids contain compounds that can react to form larger molecules or cause cross-linking of lignin fragments into more polymeric material. The main chemical reactions observed are polymerisation of double-bonded compounds, condensation reactions, and etherification and esterification occurring between hydroxyl, carbonyl and carboxyl group components (Czernik et al. 1994) in which water is formed as a by-product. These reactions cause a decrease in carbonyl compounds and an increase in the water-insoluble fraction (Figure 10). These reactions result in undesirable changes to the physical properties, such as an increase in viscosity, molecular weight and water content with a corresponding decrease in volatility (Oasmaa & Czernik 1999, Oasmaa et al. 2003). Aging reactions are fastest within the first weeks after liquid production and slow with time (Figure 11.). The reactions enhance above and diminish below room temperature (Figure 2). At VTT pyrolysis liquids are stored between –5 and –10°C. No significant changes in liquid composition or properties have been observed. Due to the instability of the pyrolysis liquids, special care has to be taken in handling, transporting, storing and using the liquids. A comprehensive overview of the stability of pyrolysis liquids is given by Diebold (2001).

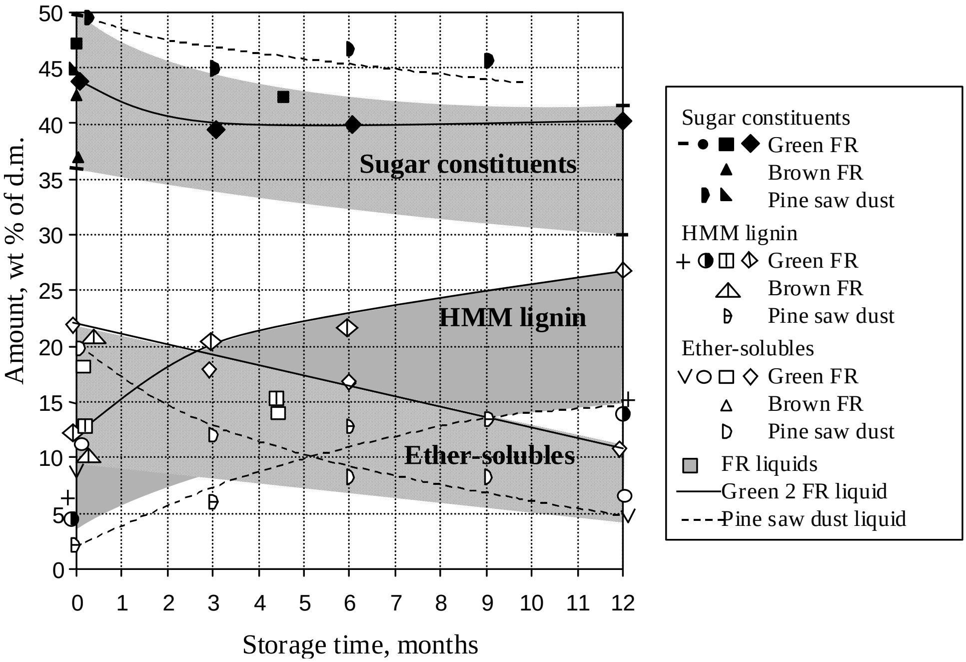

Figure 10. Main changes in softwood (forestry residue FR and pine sawdust) pyrolysis liquids during storage. The ranges are based on observing the changes in four FR liquids and two pine sawdust liquids. The continuous lines have been drawn for the same green FR liquid, and the dotted lines for pine sawdust liquid. (Oasmaa 2003.)

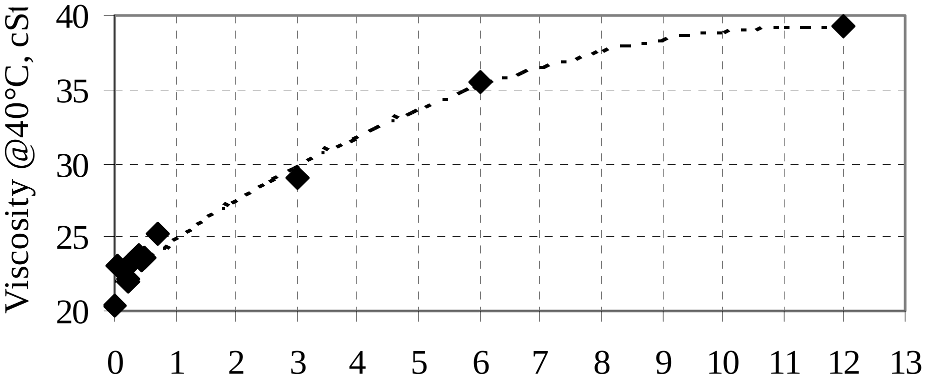

Figure 11. Increase in viscosity in a forest residue liquid (bottom phase) for one year after production.

When heating pyrolysis liquid, four stages are observed:

1. Thickening. The viscosity of the liquid increases mainly because of 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. The viscosity change and rate of change vary for different pyrolysis liquids.
2. Phase separation. Water is formed as a by-product in aging reactions. An aqueous phase separates out the heavy lignin-rich phase.
3. Viscous gummy-like "tar" formation from the heavy lignin-rich-phase if the temperature is raised above 100°C for a long time.
4. Char/coke formation from the "tar" phase at higher temperatures, i.e., over 100°C for a long time.

Due to the thermal instability, heating should be carried out indirectly with a low-temperature surface, e.g., warm water heat exchanger, jacketed tanks. Temperatures below 50°C are recommended for pumping to keep the viscosity low and reduce the rate of decomposition. Prolonged recycling of liquids with thermal cycling leads to a significant deterioration in quality and increases in viscosity.

The addition of polar solvents such as alcohols (Diebold & Czernik 1997, Oasmaa et al. 1997) stabilises pyrolysis liquids to some extent. The addition of water has a similar effect. Water cannot be added above ~30 wt% (depending on the liquids), however, without causing phase separation, i.e. the pyrolytic lignin crashes out of solution. This effect can only be offset if there is also a high concentration of a co-solvent such as an alcohol.

9.2 Test methods for stability

There is no standard method for measuring the stability of pyrolysis liquids. A simple test (Appendix D) has been developed for a quick comparison of the stability of different pyrolysis liquids (Diebold and Czernik 1997, Oasmaa et al. 1997). In the test, the pyrolysis liquid (45 ml in a 50 ml bottle) is kept at a fixed temperature for a set time (at the VTT 80°C for 24 hours) and the increase in viscosity (measured at 40°C) is measured. With pyrolysis liquids having a water content of about 25 wt%, the increase in viscosity under test conditions for 24 hours at 80°C correlates to the increase in one year stored at room temperature. Figure 12 represents the stability of various VTT PDU (20 kg/h) pyrolysis liquids produced from different softwoods (pine sawdust, forest residues). It can clearly be seen that the water content of the pyrolysis liquid has a big influence on the stability.

The results of a round robin test campaign in 2005 (Oasmaa & Meier 2005) showed a variation in the results. Since that the test method was specified in more detailed (Appendix D). If the same procedure is carried out every time in exactly the same way, fairly reproducible results (Table 9) are obtained. More testing and further development and consensus are needed among the producers and end-users of pyrolysis liquids however.

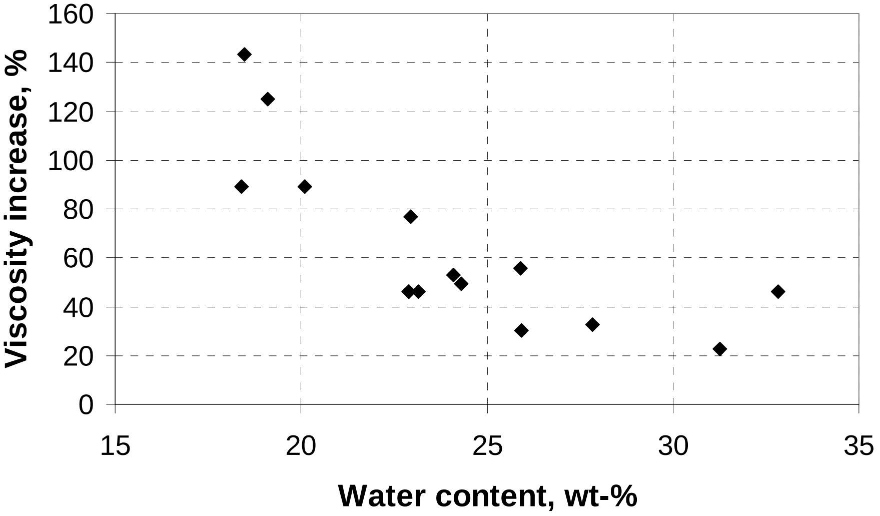

Figure 12. Stability of the VTT PDU (20 kg/h) pyrolysis liquids from various softwoods.

Table 9. Stability of a fast pyrolysis liquids.

Viscosity 40C, cSt		**Viscosity increase**
before	**after 24h 80C**	**%**
16,6	23,3	40
16,6	23,5	41
16,6	22,8	37
16,6	23,0	38
		39

10. Quality control

Quality follow-up during fast pyrolysis liquid production ensures the production of pyrolysis liquids of a constant quality and helps to avoid possible problems during production (Lehto et al. 2009).

Feedstock moisture is the main parameter to be followed. Feedstock that is too moist (> 15 wt%) may cause the formation of a multi-phase liquid product. VTT has good experience of the fast Sartorius MA 45 Moisture Analysis device, but there are other suitable analysers for moisture determination in the biomass. A rough indication of expected organic liquid yields (Lehto et al. 2009) can be obtained by analysing the volatiles/fixed carbon (Figure 13) of the feedstock to be pyrolysed. Standardisation of biomass analyses (Alakangas et al. 2007) is under development in CEN/TC 335.

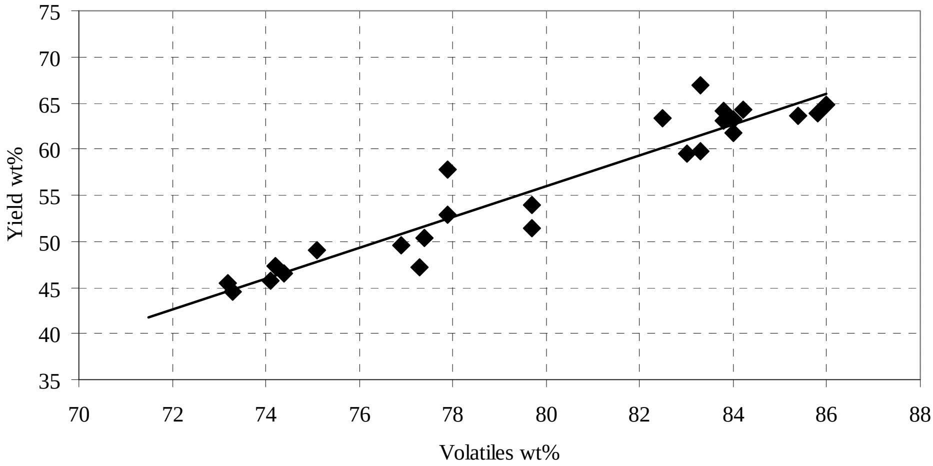

Figure 13. Yield of organic liquids in biomass pyrolysis as a function of the volatile matter of the feedstock, wt% based on dry feed (at defined and constant pyrolysis process parameters).

The main product gases, carbon monoxide and carbon dioxide, can be followed by an on-line gas chromatograph.

The main parameters of liquid quality to be followed are water and solids content. An increase in water may indicate a change in the feedstock moisture or processing conditions, or the presence of catalytic reactions. An increase in the solids of the liquid may indicate a failure in the cyclone operation or a blockage. For laboratory measurements, it is recommended that liquid samples from condensers be taken at fixed intervals.

On-line analysers are available for the determination of water and solids. Some of these may also be applicable for analysing fast pyrolysis bio-oils after testing. Water analyses by on-line coulometric Karl Fischer titration (Lehto et al. 2009) and by MCA (microwave-based analyzer)-method (Autio et al. 2011) are under test by Metso. For solids, follow-up online particle measurements are available that can be used as indicative tools for rapid changes in solid concentration. An on-line particle counter will be tested at the VTT in a 20 kg/h unit (Figure 14). Both of these on-line methods need a sample dilution unit.

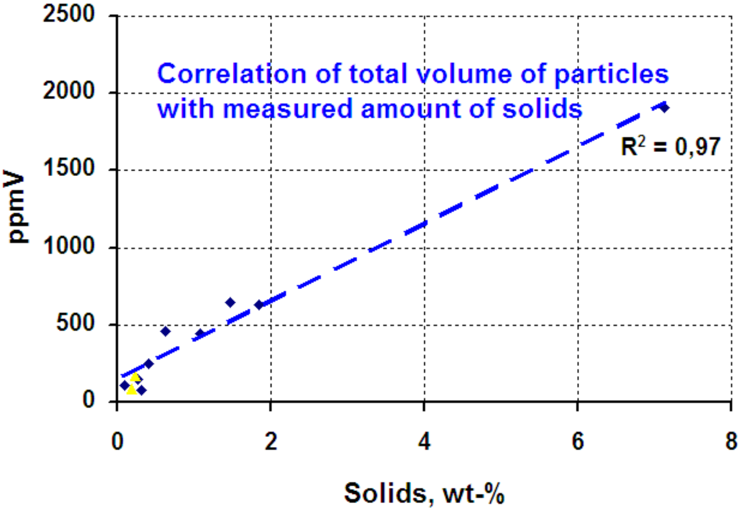

Figure 14. Correlation of the total volume of particles with measured amounts of solids.

Chemical characterisation depends on need of the user. For quality follow-up, the amount of water and water-insolubles typically provides enough information on the product composition for quality control when used in conjunction with the other tests described in this document. Additional information is easily obtained by analysing the water-soluble fraction for acids by Capillary Electrophoresis (CE) or TAN (total acid number) and for “sugars” (total amount of carbohydrates) by BRIX using the density meter (Oasmaa & Kuoppala 2008), however interference by other chemicals using the BRIX method needs to be avoided. TAN may be used on-line similar to KF titration.

11. Fuel oil specifications

Specifications are needed to standardise pyrolysis liquid quality on the market and promote its acceptance as a fuel. The methodology should be as similar to that of mineral oils as possible. Specifications for standard fuel oils have been laid down by ASTM and similar organisations in their respective countries. Elliott (1983) has suggested specification standards for several fast pyrolysis liquids in the International Energy Agency Biomass Liquefaction Test Facility (IEA BLTF) project. The classification was based on the ASTM standards D-396 for fuel oils, D-975 for diesel fuels and D-2880 for gas turbine fuels. A decade later, similar kinds of classifications (Peacocke et al. 2003) were proposed by the IEA PYRA (Pyrolysis Activity) project.

In 2002 in the EU, the CEN’s Technical Board created the working group CEN/BT/WG 149 “Liquid and Gaseous Alternative fuels” (Lundström & Olaru 2002). In 2005, the results of WG 149 were included in the CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological ”origin”, work plan including standardisation of fast pyrolysis liquid in the long term.

In 2007, a pyrolysis liquid standard initiative for ASTM within the D02 Petroleum Products and Lubricants Committee was initiated. The ASTM Initiative received Work Item Number 15564 within D02.E0.1 (Burner Fuels subcommittee) for the development of a burner fuel standard for Pyrolysis Liquid Biofuel.

Ensyn is now leading the ASTM standard development effort for fast pyrolysis liquid under the title of Pyrolysis Liquid Biofuel. After several draft iterations and votes, the standard has passed balloting in the D02-E0 Burner Fuels subcommittee and the D02 main committee, and the ASTM burner fuel standard (Table 10) has been approved and was established as D7544 in September 2009. In order to achieve approval, the solids separation method required laboratory validation involving tests of two bio-oils at two laboratories over a ten-day period. Subsequent standards for fast pyrolysis liquids (bio-oil) used as turbine fuel and diesel fuel will be the subjects of future evaluations, potentially leading to other standard developments. The initiation of the CEN standardisation in the EU is under discussion.

There is an IEA Bioenergy Task 34 on Pyrolysis for the 2010–2012 triennium. One of the main issues for the participants is standards development and registration efforts for pyrolysis liquid. As a group, the participants will contribute to efforts in standards development and registration. The US will be the Operating Agent and D.C. Elliott (PNNL) will serve as task leader.

Table 10. ASTM burner fuel standard D7544 for Pyrolysis Liquid Biofuels.

Property	Test Method	Specification	Units
Gross Heat of Combustion	D240	15 min	MJ/kg
Water Content	E203	30 max	mass %
Pyrolysis Solids Content	Annex A1	2.5 max	mass %
Kinematic Viscosity at 40 °C	D445[A]	125 max	mm^2/s
Density at 20 °C	D4052	1.1 – 1.3	kg/dm^3
Sulfur Content	D4294	0.05 max	mass %
Ash Content	D482	0.25 max	mass %
pH	E70-07	Report	
Flash Point	D93 Procedure B	45 min	°C
Pour Point	D97	- 9 max	°C

[A] without filtering, Annex A1 = ASTM D7579

12. Health, safety and transport

12.1 REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals)

In the EU, a new chemical regulation system REACH (Registration, Evaluation, and Authorisation of Chemicals) is being implemented. The European Chemicals Agency (ECHA) will manage the registration, evaluation, authorisation and restriction processes for chemical substances to ensure consistency across the EU. The regulation applies to substances manufactured in or imported into the EU in annual quantities of one tonne or more per company, unless the regulation indicates otherwise. REACH requires chemical substances on their own, in preparations and intentionally released from articles to be registered with the European Chemicals Agency (ECHA). The chemicals currently on the EU market that meet the definition of phase-in substances had to be preregistered in 2008. A SIEF (Substance Information Exchange Forum) will be formed for each pre-registered substance with the same identity. SIEF members need to nominate a "Lead Registrant". They will share and assess data and prepare common parts of the registration (joint submission). Compensation for sharing data is agreed among the respective SIEF members.

The deadlines for registrations depend on the production amount. Registration has to be made before 30 November 2010 if annual production is above 1000 tonnes and before 31 May 2013 if production is between 100 and 1000 tonnes.

In the EU Biotox project, completed in 2005, led by CIRAD (France) and sponsored by the European Commission, DG TREN toxicological, ecotoxicological and physico-chemical properties as well as Material and Safety Data Sheets (MSDS) were created for registration of fast pyrolysis bio-oils under CAS number 94114-43-9.

As this old CAS number applies to slow pyrolysis liquids, especially in the USA, a new CAS number 1207435-39-9 has been applied for by Elliott in IEA Bioenergy Task 34 on the pyrolysis project specifically for fast pyrolysis bio-oil. It is officially an “RN” meaning that it is a defined chemical mixture, not a true compound. The data created in the Biotox project will be processed and the information on fast pyrolysis liquids transferred under this new CAS number. Additional data for the REACH registration include modifications to the present MSDS and preparation of a chemical safety report (CSR). The CSR documents the results of the entire chemical safety assessment (CSA). The CSA is the documentation of the registrant’s chemical safety assessment (CSA) for his substance (or of relevant substances if the chemical safety report has been developed for a category of substances having similar properties). This chemical safety report contains a detailed summary of information on the environmental and human health hazard properties of the substance together with an assessment of exposure and risk for which such an assessment is required.

PPORD (product and process oriented research and development) is defined as any scientific development related to product development or the further development of a substance on its own, in preparations or in articles, in the course of which pilot plant or production trials are used to develop the production process and/or to test the fields of application of the substance. PPORD may be applied to a fast pyrolysis bio-oil if it is registered as a new substance. It allows up to five years for registration.

12.2 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 with regard to the duration of the test and the extent to which the animals are critically evaluated for general toxicity. The tests are defined as acute, prolonged and chronic toxicity tests.

The second category of tests consists of 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 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	effects on reproduction
Mutagenic	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.

The health risks posed by fast pyrolysis liquids have not been clearly elucidated, so far, although reports (Diebold 1999) would suggest that there is a limited degree of mutagenicity and teratogenicity from the liquids, depending on the 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 should be avoided. Skin contact should also be prevented by the use of protective gloves, clothing and safety glasses.

The most recent work has been performed as part of the EU-funded project BIOTOX (NNE5-2001–00744-BIOTOX) for the final report and proposed MSDS and guidance on transport and handling of pyrolysis liquids). This work included both fast and slow pyrolysis liquids. Following conclusions were drawn:

- All pyrolysis liquids are considered to be mutagenic. Extensive toxicological testing would result in the following conclusion, however: not mutagenic via the *In Vivo MAS test*, but shown to be lightly mutagenic via the *In Vitro MNV test.*
- Ecotoxicological testing showed variations in the degree of toxicity with the vast majority of the samples tested (20 out of 21) exhibiting none or weak eco-toxicological effects.
- All the samples were biodegradable with rates from 32 to 50% within 30 days.
- The oral LD_{50} of one selected pyrolysis liquid sample was calculated at over 2000mg/kg in rats.
- The test liquid would be classed as a moderate sensitiser based on the EC3 value obtained of 3.19%.
- Not toxic by oral route (B1 tris test) and 7 days oral gavage (B7 test).

In the on-going (2010-12) IEA Pyrolysis project one aim is to separate the data of fast and slow pyrolysis liquids and let a toxicological expert draw more comprehensive conclusions for fast pyrolysis liquids. As a result a new MSDS will be written.

12.3 Material and Safety Data Sheets (MSDS)

During the testing and utilisation of pyrolysis liquids, the liquids must be handled, stored, transferred and sampled. MSDSs 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) have their own MSDS for pyrolysis liquids. Czernik (Bridgwater et al. 1999), together with the IEA Bioenergy Pyrolysis Activity Group 1999, prepared an MSDS based on all available data. The latest MSDS prepared in the EU Biotox project is presented in Appendix F. 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).

12.4 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. The appropriate national and international regulations need to be met during transport and may need to comply with more than one mode of transport. It is likely that fast pyrolysis liquids will be classified as “corrosive” and/or as “dangerous” and/or “hazardous” substances in transportation. The prior suggested class from the previous guide [UN 1993] has therefore been updated following on from the results of the BIOTOX contract (EC Contract No. NNE5-2000-00744) and to comply with updates in the UN Approved Carriage List.

It should be noted that additional codes will be required to reflect the degree of toxicity and corrosivity of the liquids, and the user or handler must consult the latest (International Air Transport Association), IMDG (International Maritime Dangerous Goods), IMO (International Maritime Organisation), AND and AND (The European Provisions concerning the International Carriage of Dangerous Goods by Inland Waterways) and ADR (EU Agreement on the Carriage of Dangerous Goods by Road) guides guides for current regulations and classifications. A set of Material Safety Data Sheets (MSDS) must also accompany any samples.

Pyrolysis liquids are not listed on the UN approved carriage list for dangerous or hazardous goods; however, there are several classifications for not otherwise specified [N.O.S.] classification which may be appropriate, depending on the composition and properties of the liquid. The four most appropriate N.O.S codes for biomass derived pyrolysis liquids are UN 1992, UN1993, UN2924 and UN3286, the selection of which depends on the three key properties: flash point, corrosivity and toxicity and the transport category (1, 2 or 3: from highest to lowest flammability).

Table 11. Possible UN Classification Codes [N.O.S.] applicable to a variety of pyrolysis liquids.

N. No	Name and description	Transport category
1992	FLAMMABLE LIQUID, TOXIC, N.O.S.	1
1992	FLAMMABLE LIQUID, TOXIC, N.O.S.	2
1992	FLAMMABLE LIQUID, TOXIC, N.O.S.	3
1993	FLAMMABLE LIQUID, N.O.S. [vapour pressure @50ºC > 175 kPa]	1
1993	FLAMMABLE LIQUID, N.O.S. [vapour pressure @50ºC < 100 kPa, < 175 kPa]	1
1993	FLAMMABLE LIQUID, N.O.S. [vapour pressure @50ºC < 100 kPa, < 175 kPa]	2
1993	FLAMMABLE LIQUID, N.O.S. [vapour pressure @50ºC< 110 kPa]	2
1993	FLAMMABLE LIQUID, N.O.S.	3
2924	FLAMMABLE LIQUID, CORROSIVE, N.O.S.	1
2924	FLAMMABLE LIQUID, CORROSIVE, N.O.S.	2
2924	FLAMMABLE LIQUID, CORROSIVE, N.O.S.	3
3286	FLAMMABLE LIQUID, TOXIC, CORROSIVE, N.O.S.	1
3286	FLAMMABLE LIQUID, TOXIC, CORROSIVE, N.O.S.	2

"Recommendations on the Transport of Dangerous Goods – Model Regulations" – "The Orange Book" 16th revised edition, ISBN: 9789211391367 [see also: http://www.unece.org/trans/danger/danger.htm].

13. Fuel oil use of pyrolysis liquids

13.1 Use of pyrolysis liquids for heat or CHP

There is encouraging operational experience of fast pyrolysis liquids in boilers (Czernik & Bridgwater 2004, Oasmaa et al. 2005) that brings confidence to the implementation of heat and CHP plants. Technical difficulties concerning the use of the liquids remain, however, due to the small amount of long-term research and the insufficient number of commercial pyrolysis plants producing liquids for long-duration testing. With regard to the quality of fuel oil from pyrolysis liquids, some properties can be changed by improving the quality of the fuel. Adaptations are still required to the hardware for others.

Biomass fast pyrolysis technologies have seen slow growth in the past decade, primarily due to the low costs of crude oil and low base electricity prices in most of Europe and North America. The demand for a renewable liquid fuel for heat and power generation has therefore decreased and other competing technologies have come to the fore, namely for transport fuels, which have a higher market value, e.g., biodiesel. There is a range of incentives in the EU, at international and national level, for renewable energy technologies, although the level and form of support vary significantly. In some cases, no distinction is made between the levels of technological development in renewable energy technologies, with all of them being classed as commercially available, which is not the case. Some harmonisation of support measures is required to improve the technological development. There are not enough empirical data to allow full norms and standards for biomass-derived fast pyrolysis liquids to be determined at this time. There is a real need for bulk quantities of liquids to be supplied to boiler and power generation equipment developers to enable standards for liquids to be fully assessed and specified.

The initial market for biomass-derived fast pyrolysis liquids may lie in the replacement of domestic heating fuel. There is an opportunity for liquids to enter the power generation market for domestic applications albeit only in selected countries. Further long-term test work on pyrolysis liquids is required to establish performance and operability data for engines and turbines. Pyrolysis liquids can compete on energy cost terms with other renewable fuels but only in certain niche applications. One critical aspect is the price and availability of biomass fuel, as seen in Fortum's case. The overall energy balance of biomass fast pyrolysis can give 70% efficiency to liquids, with low environmental emissions. This is one of the major advantages of biomass fast pyrolysis and means that abatement costs for such systems are low. In conclusion, there is potential for pyrolysis liquids. Further work is required, however, to establish their long-term performance.

13.2 Use of pyrolysis liquids for power

Power production from biomass-derived pyrolysis liquids has been under development in the past few years (from the review by Chiaramonti et al. 2007). If technically successful, this would make decentralised bio-energy production possible. Several technologies and system components have been developed by academia, R&D organisations and industrial companies in many countries. Significant experience has been gained and many useful results published.

Taking into account the particular properties of biomass fast pyrolysis liquid, pyrolysis liquid should first be considered in power generation systems that use relatively steady injection conditions, such as gas turbines or boilers, and only afterwards in diesel engines in which injection is operated at high frequency and fuel is subject to significant thermal shear stresses. Moreover, the use of pyrolysis liquid in GT-combined cycles would allow greater efficiencies. On the other hand, diesel engines represent a very mature, widely available and proven technology that can easily be downscaled. A large maintenance infrastructure already exists worldwide, facilitating the operation and servicing of the engine.

In the context of gas turbines, Magellan Orenda has carried out long-term research into the modified GT 2500 gas turbine, which is the only product in this sector that is currently available. The Orenda turbine (a rather small one when compared with industrial GTs) has been successfully modified (nozzle re-design, new materials, new fuel feeding systems, on-line hot section cleaning system) to accept biomass fast pyrolysis liquid and to achieve low pollutant emissions. The main R&D needs are now related to the demonstration of long-term performance and reliability of the modified GT system, materials and component resistance (combustor, injectors, nozzle and turbine) to hot corrosion and deposits, operating and maintenance costs.

If other types and sizes of GTs are considered in combination with pyrolysis liquid, detailed work will have to be carried out to adapt each specific technology to this fuel, as pyrolysis liquid in standard GT cannot be used with only minor modifications to the technology.

Another important R&D area is represented by Micro Gas Turbines, which have recently been developed on a commercial scale and are widely available. These are usually single-stage turbomachines employing a centripetal turbine. Addressing small-scale decentralised power generation would modify the economics of the system and possibly further improve the possibility of cogeneration and market penetration.

The use of pyrolysis liquid in diesel-engines is probably the most technically challenging alternative. Various diesel engines of very different sizes have been tested with pure or derived (mixed, emulsified, etc.) pyrolysis liquids. Fuel oil quality and material issues are the most critical aspects to be addressed, as the typical high frequency of the injection process in diesel engines makes pyrolysis liquid use difficult. No long-term demonstration has been achieved so far. All these experimental activities except one reported a major problem in injector and pump components.

Ideally, pyrolysis liquid should be thermally more stable to tolerate liquid recycling. The lacquering tendency also has to be eliminated. The material of the injection nozzle is probably the most important element for successful and reliable operation, though the fuel pump also needs to be carefully adapted. The high density and low heating value of pyrolysis liquid requires careful re-design of the fuel feeding system.

With reference to emulsions and blending with high-cetane oxygenated compounds, these solutions were found to improve the ignition properties of the fuel, which burns quite well once ignited. The use of emulsions seems to accelerate the erosion-corrosion phenomenon in high-pressure, high-speed components such as the injector (hole of the nozzles, needle). In both cases (emulsification and blending), a high percentage of pyrolysis liquid generates deposit build-ups on the injector.

Promising developments have been achieved using pyrolysis liquid diesel oil mixtures (not emulsions) in diesel engines. Stirling engines could also use biomass pyrolysis liquid successfully, but the current stage of development of this technology represents a major obstacle to wider applications.

Finally, with regard to pyrolysis liquid co-firing, no major technical problems exist today. The main obstacle seems to be economical rather than technological, as pyrolysis liquid use can be implemented through material modifications and minor technological adaptations to an existing power plant. The supply cost of pyrolysis liquids is the critical issue for achieving market penetration: estimates by Wagenaar et al. (2002) indicate that the pyrolysis liquids cost needs to be in the range of 4–6 €/GJ to be competitive in NG large power stations. Activities were planned in the Harculo NG power station operated by Electrabel using the BTG pyrolysis liquid produced in a 2t/h plant in Malaysia. No liquids were ever shipped, however, due to a drop in the prices offered for co-firing renewable liquid fuels. The status of development of the alternatives is summarised in Table 12.

Table 12. Status of pyrolysis liquid-based power generation technologies.

	Gas turbine	**Diesel engine**	**Co-firing (NG, coal)**	**Stirling**
Development stage	2,500 kWe modified system ready for commercial demonstration No other modified GT plants available	Several engines tested: reliable system not yet developed Various activities ongoing	NG co-firing successfully tested	Short-term testing carried out in a very small unit
Major modifications, critical issues	Nozzles, materials, in-line cleaning system, feeding line	Injector and fuel pump material Emissions	Oil gun material, pump and feeding line	Pump and injector
R&D needs	Long-term commercial demonstration Modification of other GT turbomachines Demonstration of combined cycles	Development of: effective/reliable pumping and injections systems; good combustion to avoid deposits on the hot parts (cylinder, piston, injector); materials	Long-term commercial demonstration	Reliable small-scale Stirling engine to be developed and demonstrated long term with standard fuels before carrying out further tests on PO
Further developments	Application of pyrolysis liquids to MGT	Use of emulsions and blends for ignition, fuel handling and injection improvement	Further pyrolysis liquids cost reduction to make NG (first) and coal (second) co-firing economically possible	As above

14. Recommendations

Pyrolysis liquids exhibit unusual properties, which are not apparent in conventional hydrocarbon liquids. Based on the wide range of properties assessed and evaluated, the following modifications to the standard methods are recommended.

Table 13. Analytical methods for biomass pyrolysis liquids.

Analysis	**Method**	**Comment**	**Sample size**
Water, wt%	ASTM E 203	1	1 g
Solids, wt%	ASTM D7579	2	30 g
Particle size distribution	Optical methods	3	1 g
Carbon residue, 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%	Ion Chromatography	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)	DIN 51900	14	1 ml
effective (LHV)			
Flash point, °C	ASTM D 93	15	150 ml
Acidity	pH meter	16	50 ml
Total Acid Number (TAN)	ASTM D664		
Water insolubles, wt%	Water addition	17	5 ml
Stability	80°C 24 hours	18	200 ml

Sample size = minimum amount of pyrolysis liquid needed to carry out the analysis, including duplicates.

Comments for Table 13:

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

Note 2: Extractive-rich samples, such as forest residue liquids, foam easily. Gentle mixing, like rolling the sample bottle carefully, is recommended.

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 B.*
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 C).*
3. *Microscopy with the photo analysis programme or optical methods using high-speed cameras or light rays with programmes.*
4. *Controlled evaporation of water to avoid foaming.*
5. *Controlled evaporation of water to avoid foaming.*
6. *Proper homogenisation. For forest residue liquids, careful rolling of the sample bottle. Sample size as large as possible. Triplicates.Proper standard containing all elements measured at similar concentrations.*
7. *Sample pretreatment by halogene combustion.*
8. *Wet combustion as a pretreatment method.*
9. *Wet combustion 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 the 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 pyrolysis liquids. No prefiltration of the sample if visually*

homogenous. Elimination of air bubbles before sampling. Equilibration time 15 minutes. Maximum allowed difference of duplicates 5%.

12. *Precise temperature measurement. Cover 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 a calorimetric heating value and hydrogen analysis.*
15. *Elimination of air bubbles before sampling.*
16. *pH gives the level of acidity. Frequent calibration of the pH meter. TAN gives more accurate values for acidity. Tight window to be chosen. Derivatisation curve should be used.*
17. *Addition of 5g pyrolysis liquid into water, see Appendix E.*
18. *45 ml pyrolysis liquid in 50 ml tight glass bottles, heating in a heating oven (see Appendix D). Measuring of increase in viscosity and water. Viscosity determination at 40°C according to ASTM D 445.*

Other analyses from literature that were not tested in this study are presented in Table 14. The properties of pyrolysis liquids are summarised in Table 15.

Table 14. 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 15. Properties of wood pyrolysis liquids. Generic values.

Property	**Range (wet basis)**
Density (15°C), kg/dm^3	1.11–1.30
Lower heating value, MJ/kg	13–18
Viscosity-kinematic, cSt	15–40 @ 40°C
Thermal conductivity, W/mK	0.35–0.43
Specific heat capacity, J/gK	2.6–3.8 @ 25–60°C
Pour point, °C	¯9–36
Coke residue, wt%	14–23
Flash point, °C	40–110
Ignition limit, °C	110–120
Ignition temperature, °C	600–700
Water, wt%	20–30
Solids, wt%	< 1
Vapour pressure, kPa	5.2 @ 33.5°C
Surface tension, mN/m	29
Carbon, wt% (dry)	50–60
Hydrogen, wt% (dry)	6–7
Nitrogen, wt% (dry)	< 0.4
Oxygen, wt% (dry)	35–40
S, ppm	< 500
Cl, ppm	< 75
Ash, wt%	< 0.3
pH	2–3
K+Na, ppm	< 500

The use of biomass-derived pyrolysis liquids in heating and electricity generation applications is becoming increasingly important. 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 at avoiding some of the more common problems associated with the liquids and improve their usability in a range of applications.

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Appendix A: Homogenisation and sampling

A.1 Homogenisation

A small (containers < 10 l) sample vessel is homogenised in a laboratory mixer (about one hour at room temperature). Large containers can be homogenised most efficiently with a top-mounted propeller stirrer (Figure A1). 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, warm water (30–40°C) circulation may be used on the container discharge. The pyrolysis liquid is pumped from the bottom of the container and circulated for about one day.

The homogeneity of the liquid is ensured by analysing the water and solids content from the upper and lower parts 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 and unhomogenous liquids, a propeller mixer is recommended.

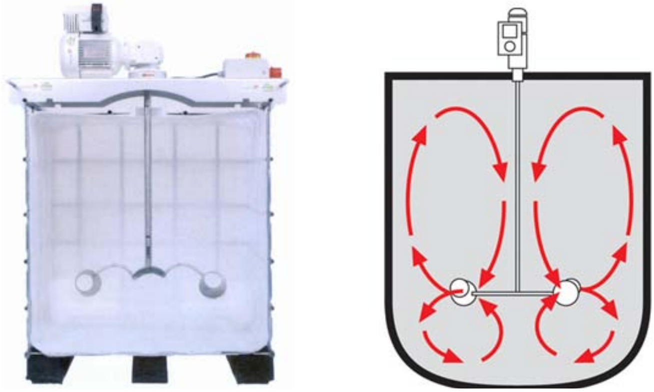


Figure A1. A proper mixing device (Inotec VISCO JET VJ350) for pyrolysis liquid in a 1 m^3 tote.

A.2 Sampling and homogeneity verification

Material suitable for sample bottles/containers

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

Sampling

Samples can be taken with a wide mouth piston pump or using a large syringe from the upper (10–20 vol% below the surface) and lower (10–20 vol% above the bottom) parts of the liquid.

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 A.3–A.4). The top surface and bottom (solids) may be different from the rest of the liquid, which is acceptable.

Seven-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 B) from the top, middle and bottom layers. If the difference in water from the top and bottom is less than 5%, the sample is accepted. See A.3. If the difference in water from the top and bottom is more than 5%, the sample is abandoned. See A.4.

A.3 Homogeneity determination

Good-quality liquid

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

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

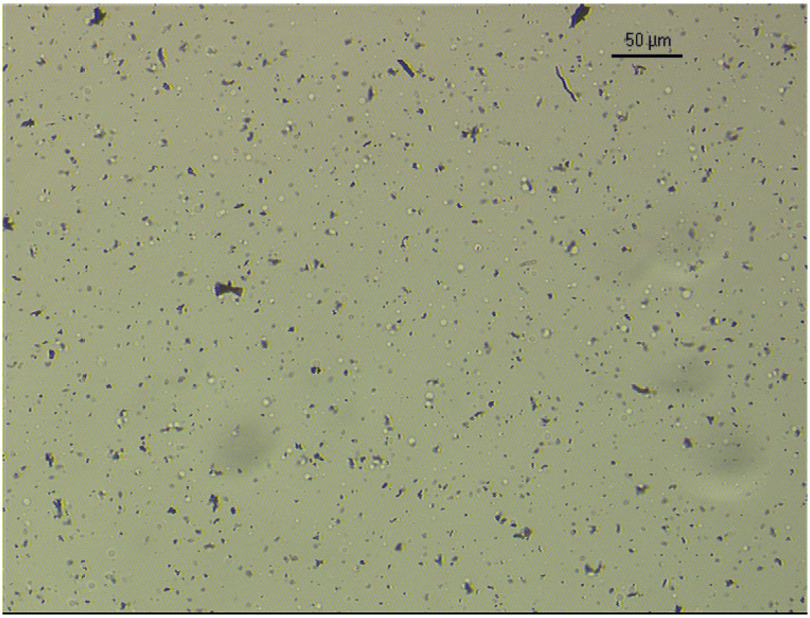


Figure A2. A homogenous pyrolysis liquid by Leica DM LS microscopy.

Water, wt%	
Before mixing	*After mixing containers*
Top	20.9 21.1
Middle	21.1
Bottom	20.7

A.4 Homogeneity determination

Inhomogenous liquid

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

Poor quality liquid

Clear phase separation can be observed visually and the liquid is then abandoned. Phase separation can be observed by microscopy. Samples are taken from the top, middle and bottom layers of the unhomogenised pyrolysis liquid.

The 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.

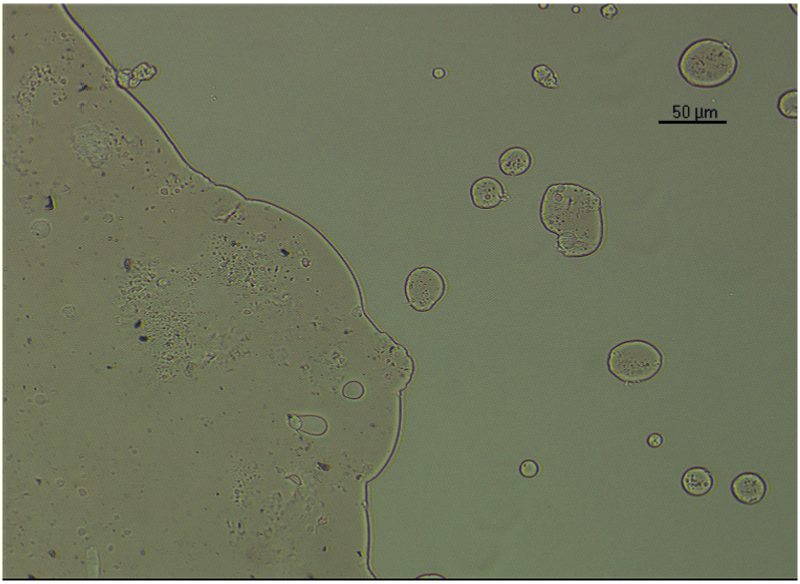
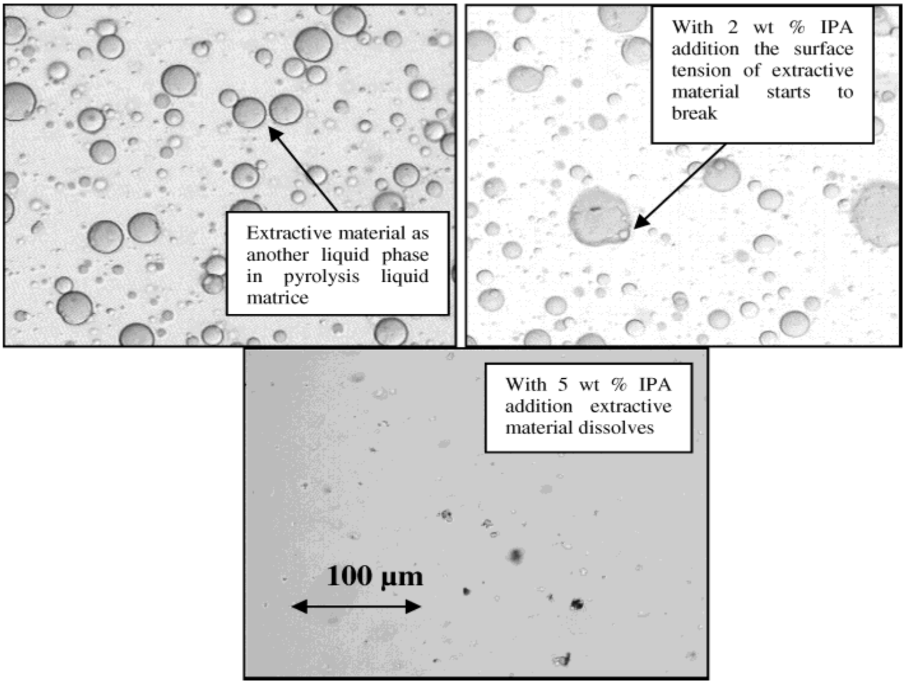


Figure A3. A phase-separated pyrolysis liquid by Leica DM LS microscopy.

Water, wt%	
Before mixing	*After mixing containers*
Top	31.1 28.3
Middle	32.4
Bottom	20.3

A.5 Homogenisation of unhomogenous pyrolysis liquid by solvent addition

Pyrolysis liquids may be homogenised by the addition of a polar solvent like alcohol



Extractive material as another liquid phase in pyrolysis liquid matrice

With 2 wt % IPA addition the surface tension of extractive material starts to break

With 5 wt % IPA addition extractive material dissolves

Figure A4. Dissolution of extractives in the pyrolysis liquid matrix. Note: Some of the extractives are not dissolved in alcohols.

Appendix B: Determination of water content

B.1 Method

Karl Fischer titration ASTM E 203

Water addition test

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

Table B1. Water addition test results.

No.	Forest residue [g]	Water added [g]	Total	Water calculated [wt%]	Water analysed [wt%]	Actual Difference [wt%]
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	2 phase	

Forest residue = VTT PDU 5/07, bottom phase.

Table B2. Problem solving in Karl Fischer titration.

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

Appendix C: Determination of solids content

Solids content ASTM D7579

Solvent

Methanol-dichloromethane (1:1) also dissolves 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 90 ml of solvent.
3. The solution is filtrated through a 1 µm pore size filter (e.g., Whatman/Class micro fibre filters GF/B 47 mm Cat No: 1821-047). The filter paper is soaked on to the filter by the solvent used. If the filtration time is very long, due to a 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 30 minutes.
6. The solid content is calculated based on the original pyrolysis liquid sample.

Filtration apparatus

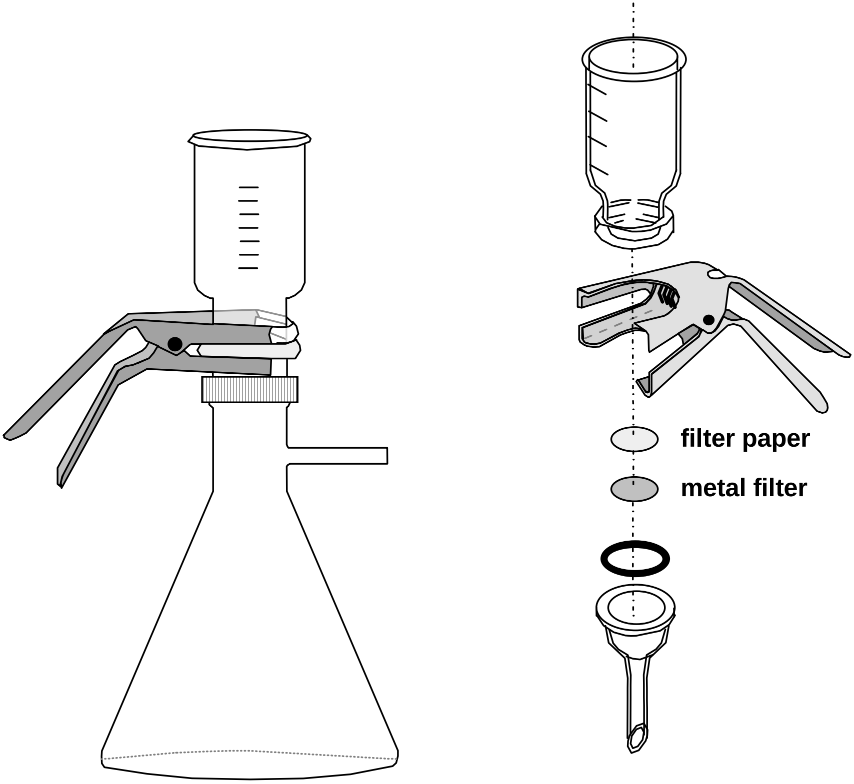


Figure C1. Millipore filtration system.

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

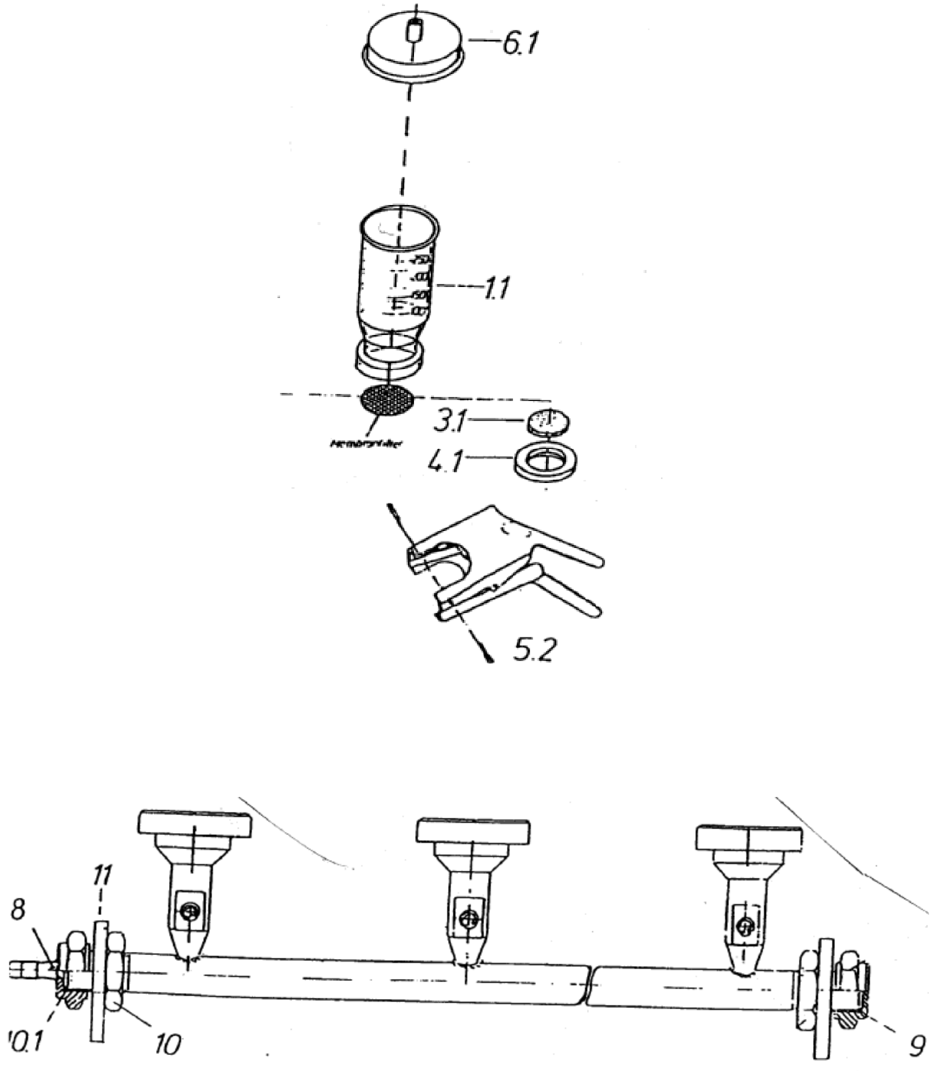


Figure C2. Six-place filtration system.

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	17.7	0.12	0.12
	Ethanol (EtOH)	14.8577	30.2	0.20	0.20
	MeOH-Methylene chloride (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)	15.162	70.70	0.47	0.47
	IPA-20 vol-% MeCl2	15.5704	59.1	0.38	0.38
	IPA-hexane (1:1)			Not soluble	
	Methanol-20 vol-% hexane	14.9014	16.5	0.11	0.11
	Methanol-hexane (2:1)	16.5295	15.5	0.09	0.09
	Acetone	15.2881	144.2	0.94	0.94
	Dioxane-Acetone (1:1)	15.0626	63.3	0.42	0.42
	Dioxane-20 vol-% IPA	15.1776	62	0.41	0.41
	Industol*	15.916	30	0.19	0.19
	Industol-20 vol-% Dioxane	15.7802	25.5	0.16	0.16
	Methoxy propanol	15.9512	40.6	0.25	0.25
	Methoxy propanol-20 vol-% Dioxane	15.8626	36.5	0.23	0.23

Testing of solids content of forest residue liquids

Whole liquid*

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	0.21	**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	0.39	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	0.71	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	

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

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-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	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	0.90	
		2.47	22.7	0.92	
		1.912	18.4	0.96	
		1.1592	13.4	1.16	
		0.8016	9	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	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	

Appendix D: Stability test method

The pyrolysis liquid sample is mixed properly and left to stand until the air bubbles are removed. Next, 45 ml of the sample is poured into 50 ml tight glass bottles. The new bottles are treated at 80°C for a few hours before use to remove moisture. The bottles are firmly closed and pre-weighed before being placed in a heating oven at 80°C (± 1°C) for exactly 24 hours. It is recommended that the same heating oven and preferably the same number of bottles are used every time. At VTT maximum five bottles are placed in an about 10 dm^3 heating oven. A reference sample of known pyrolysis liquid is included in the series. The bottles are re-tightened after 10 minutes. After a certain time, the closed sample bottles are cooled at room temperature for 1.5 hours, weighed and analysed. 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.

$$\Delta \text{ viscosity @ 40°C } [\%] = \frac{\nu_2 - \nu_1}{\nu_1}$$

$$\Delta \text{ water } [\%] = \frac{\omega_2 - \omega_1}{\omega_1}$$

$\nu 1$ = 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 for use in internal comparisons of liquid stability for pyrolysis liquids from one process. The test is more reliable if the initial viscosities of the tested samples are similar.

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

Note 3: The reference sample is a good quality pyrolysis liquid that has been freshly divided into sample bottles and stored in a freezer below –9°C.

Appendix E: Solvent fractionation method

Solubility-based scheme for pyrolysis oils – short method – work instruction, VTT, 3.4.2008

E1. Summary

This method is suitable for determining the composition of biomass-based pyrolysis liquids divided into compound groups. The method can be used to monitor differences in the composition of various biomass-based pyrolysis liquids and follow changes occurring in the liquids during storage. The method is based on water extraction.

Pyrolysis liquid is divided into water-soluble and water-insoluble fractions. “Sugars” are determined as ether-insoluble substances of water-soluble fractions. The water content of the pyrolysis liquid is analysed by Karl Fischer titration.

> Water-solubles = water + “sugars” + acids + aldehydes & ketones (as a difference)

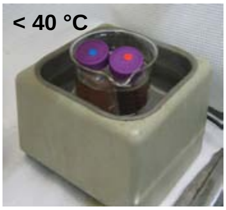
The water-insoluble material consists mainly of lignin material (owing to a wide molecular weight distribution), extractives and solids. In aged liquids, this fraction also includes high-molecular-weight reaction products. The amount of extractives (neutral substances) is analysed by n-hexane extraction (evaporation residue of n-hexane-soluble materials) of the original pyrolysis liquid.

> Water-insolubles = lignin-based material + extractives + solids + reaction products due to ageing

The main steps of the scheme are shown in the figures below. Note: Step 3 filtration can be replaced by centrifugation as described in the following work instructions.

Water extraction – WIS (water insolubles)

1. Add 30 ml water into 3 g oil in a centrifuge tube (homogenous, representative sample!)

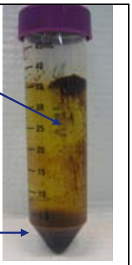


< 40 °C

2. Place the mixture in ultra sonic bath for 30 min

3. Centrifuge the mixture

4. Filter the clear phase



Water-solubles

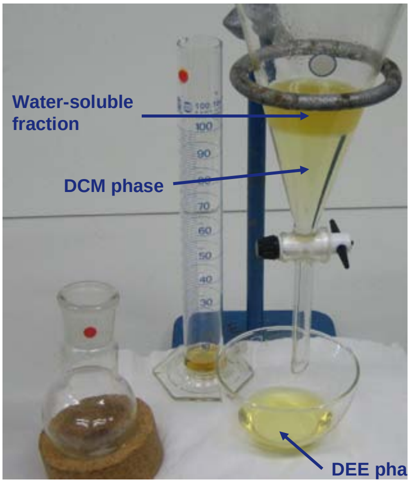
Water-insolubles

5. Wash the tube and precipitate with 15 ml water

Water-solubles

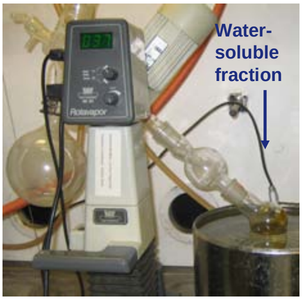
6. Dry the bottle and solids in a heating oven < 40 °C over night

Ether-extraction of aqueous phase – EIS ('sugars')



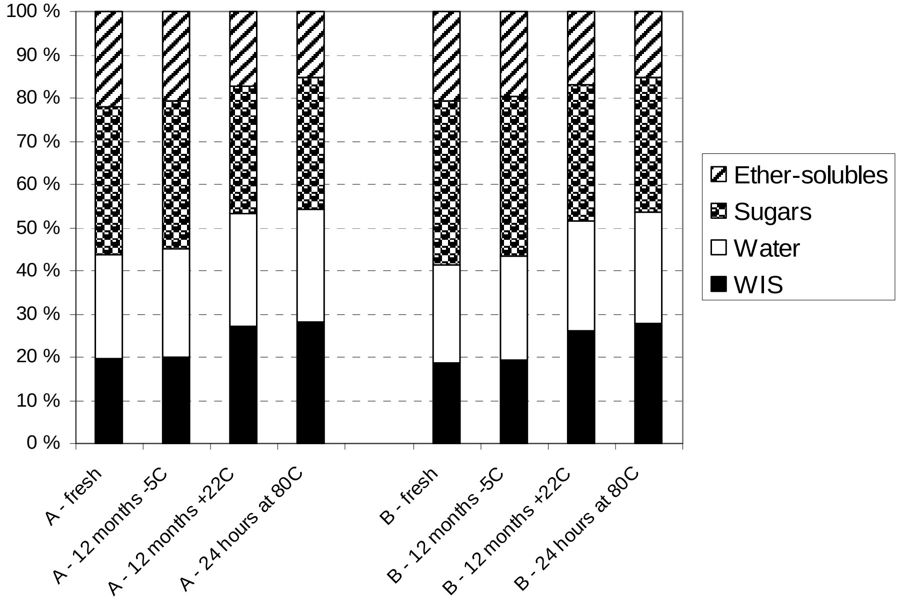
1. Add 1:1 (about 45 ml) diethyl ether (DEE) into the water-soluble fraction
2. Extract the mixture in a funnel abt. 10 min
3. Let the solution to settle
4. Separate the aqueous phase from the bottom
5. Extract the aqueous phase with 50 ml dichloromethane (DCM)
6. Remove the DCM from the bottom and combine it with DEE fraction (-> ES)
7. Evaporate the aqueous phase in a rotavapor below 40 °C

ES = 100 – WIS – water - EIS



If necessary, solids and extractives are analysed separately from the original pyrolysis liquid and volatile acids from the water soluble fraction by CE (Capillary Electrophoresis).

The different fractions of the solubility scheme are calculated as % by weight of the original liquid. Results are graphically presented in the form of a chart (see below). The results are given to one decimal place.



Composition of pyrolysis liquid based on a solvent-extraction scheme. A = fractions from the “short method”. In B, “sugars” have been determined by Brix (no ether extraction) directly from the water-soluble fraction.

E2. Working instructions

E2.1 Scope of application

This solubility-based determination method is suitable for group-level analysis of the composition of pyrolysis liquids in wood. The method can be used to monitor differences in composition of different pyrolysis liquids and changes occurring during storage.

E2.2 Principle

E2.2.1 Water-insoluble fraction

The water-insoluble material is separated from the pyrolysis liquid through water extraction. The water-insoluble material consists of lignin material, extract materials and solid matter.

The water-insoluble material is further extracted with methylene dichloride. The methylene dichloride-insoluble fraction (powder-like) consists of high-molecular-mass (HMM) lignin material (pyrolytic lignin material, average molecular weight about 1040 DA) and solids. Solids are determined directly from the pyrolysis liquid using a separate method and deducted from the resulting fraction.

The methylene dichloride-soluble fraction consists of extractive agents (e.g., fatty acids, resin acids, fatty alcohols, hydroxy fatty acids, sterols) and low-molecular-mass (LMM) lignin material (“guaiac wood oil”, average molecular weight about 400 DA).

E2.2.2 Water-soluble fraction

The water-soluble fraction consists of the sugar-containing material in the pyrolysis liquids as well as degradation products of cellulose (e.g., aldehydes, ketones), hemicellulose (e.g., volatile acids) and lignin (lignin monomers).

The water-soluble fraction is further extracted using diethyl ether and methylene dichloride. The majority of the GC-eluted compounds (aldehydes, ketones, lignin monomers, volatile acids) are dissolved in diethyl ether and methylene dichloride (continued extraction).

Sugar-containing material (levoglucosan, dimer and trimer anhydro-poly saccharides) is diethylether insoluble in aqueous phase. The water content of the pyrolysis liquid is analysed using Karl Fischer titration.

If necessary, the pyrolysis liquid is analysed directly for extractive agents by means of n-hexane extraction (evaporation residue of n-hexane-soluble materials). Volatile acids can be analysed by CE (Capillary Electrophoresis) from the water-soluble fraction.

E2.3 Equipment and accessories

- 2 x 50 ml centrifuge tubes + threaded caps (Dia 28.8 x Ht 114.1 mm, PP Polypropylene, EUROPEAN ARTICLE NO 525-0155 NALGENE)
- 2 x 50 ml measuring glasses
- 2 x funnels, diameter 5 cm
- 2 x filter papers, 589 blue ribbon, diameter 90 mm
- 2 x 200 ml separating funnels + ground glass stoppers
- 2 x 100 ml evaporating flasks
- Shaker
- Analysis scale
- Ultrasonic bath
- Centrifuge (EPPENDORF CENTRIFUGE 5804)
- Heating oven
- Evaporator (Buch rotavapor + Vacuum Controller)
- Water
- Diethyl ether, p.a
- Methylene dichloride, p.a
- Acetone, p.a
- Antifoam agent.

Note! See material safety data sheets for solvents, wear personal protective equipment and handle in a fume hood.

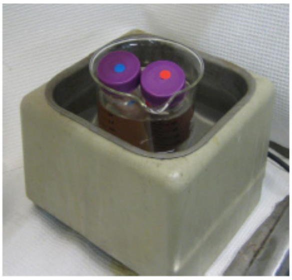
E2.4 Process

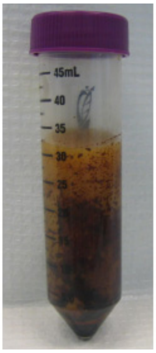
- Carry out parallel determinations.
- The sample must be mixed well before sampling.
- All devices are to be weighed separately while they are clean.
- Weights are recorded to three decimals.

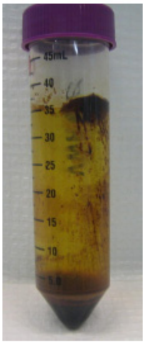
E2.4.1 Water-extraction (1:10)

- Weigh about 3 g of homogenic bottom phase into a 50 ml centrifuge tube (weighed tube and cap).
- Spread the sample evenly on the bottom and sides of the bottom section of the centrifuge tube to allow the sample maximum contact surface with the added water. The sample must remain below the water surface.

- Add approximately 30 ml of water (the sample-water ratio 1:10) and close the tube using the cap.
- Immerse the centrifuge tube in an ultrasonic bath (< 40°C) for approximately 30 minutes (max. 60 minutes). Shake the tube occasionally at the beginning of the process. The water extraction will form into an even mixture with the water-insoluble bituminous matter slowly separating at the bottom. The water extract is often highly emulsified however. The sample is treated in the centrifuge for about 30 minutes (4,500 rpm) so that the emulsion will break and it will be easier to filter.







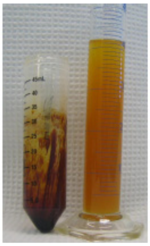
To note:

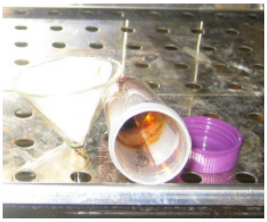
- The major source of error is the non-homogeneity of the sample: a cold/frozen sample is allowed to reach room temperature; it is mixed well (using a shaker) and the sample is taken immediately after shaking.
- If the water content of the sample is more than 30% by weight, the sample will tend to phase separate. A disposable pipette can be used in weighing, and the full volume be sprayed into the centrifuge tube immediately after mixing.
- Viscous samples (e.g., surface phase) can be heated (< 40°C) to improve the mixing qualities. A smaller sample (1–2 g) in relation to water (30 ml) can also be used. The water extraction / ultrasonic treatment can be repeated. After filtering the first water extract, the centrifuge tube and insoluble bituminous matter are heated in the heating oven (< 40°C) so that the solid matter can be spread over as wide an area as possible on the sides of the tube, after which heated water (< 40°C) is added, the ultrasonic treatment is repeated and the filtrate is combined with the previous filtrate.

- The ultrasonic treatment can be made longer (60 minutes) and the tube can be turned occasionally during treatment. The ultrasonic treatment may also be replaced by intensive shaking (overnight in the shaker) or shaking may be used in addition to the ultrasonic treatment.

E2.4.2 Filtering

- The funnel and pleated filter paper are weighed and the filter paper moistened using water.
- The water portion is poured out of the centrifuge tube as well as possible through the filter paper into a 50 ml measuring glass and the tube is flushed using about 15 ml of water. The ultrasonic and centrifugal treatments are repeated if necessary. The filtrate (approximately 45 ml) in the measuring glass may be slightly cloudy.
- The centrifuge tube and its precipitate, the cap and the filter paper and its precipitate are dried in the heating oven at 40°C overnight and weighed.
- Calculate the amount of water-insolubles.





To note:

- Drying the bitumen-type sediment in the centrifuge tube may cause the biggest error. There may be water inside the bitumen droplets. It is advisable to place the tube on its side at the beginning of the drying process with the aim of making the bitumen-type material flow onto one side, which helps the droplets of water to separate.
- The paper should not dry out during filtration. The sugar-containing material (syrupy material) in the water portion forms a sticky film on the paper surface. The syrupy material in the water portion also causes errors in weighing.

- The filtrate in the measuring glass may remain emulgated, but this will not cause a significant error. When allowed to stand, the filtrate clears and a small amount of sticky precipitate may be deposited on the bottom of the measuring glass. This precipitate will dissolve when processed further (ether-methylene dichloride extraction, ES ether-solubles).
- The water-insoluble fraction of the bottom phases of pyrolysis liquids is 10–25% by weight of the original product.

E2.4.3 Water-soluble matter

Diethyl extraction and continued methylene dichloride extraction of the water-soluble fraction. This fraction will not be recovered in the quick method. In the quick method, sugar-like material is analysed by BRIX directly from the water-soluble fraction.

- The water extract (about 45 ml) is poured from the measuring glass into a 200 ml separation funnel.
- Add approximately 45 ml of diethyl ether (1:1) using the same measuring glass (flushing).
- Shake the separation funnel well for approximately 10 minutes. The vaporised ether forms pressure in the separating funnel and is removed through the tap.
- Allow the diethyl ether to separate onto the surface (the fraction is clear and yellow in colour).
- Separate the water portion into a measuring glass (use the above-mentioned measuring glass).
- Extract the water portion again with 50 ml of methylene dichloride. Any pressure is removed through the funnel tap. The methylene dichloride extract is bright and nearly colourless. The brownish-yellow water fraction may be strongly emulgated, but this will not cause an error.
- The methylene dichloride is allowed to deposit on the bottom, after which it will be separated.
- The combined diethyl ether and methylene dichloride fraction is thrown out in the quick method and the soluble matter of ether is calculated as a difference.

- Treatment of the diethyl ether and methylene dichloride-insoluble part of the water-soluble fraction (“sugars”).
- After solution extractions, the separation funnel will include the water fraction (about 45 ml), which is drained into a weighed 100 ml evaporating flask.
- Rinse a 50 ml measuring glass and separating funnel using a small amount of acetone (approximately 15 ml), which will be combined with the water fraction in the evaporating flask.
- Add 2–3 drops of antifoam agent into the evaporating flask.
- The water fraction is evaporated as “dry” as possible using Rotavapor (< 40°C). The syrupy residue in the flask is very stiff and highly evaporative so that there will be no losses when evaporating.
- Dry the residue in an incubator (40°C) overnight, rotating the flask to allow any moisture to evaporate.
- The evaporation residue is weighed (EIS).

To note:

- Sugar-containing material in the moisture and water droplets may cause an error. The ether fraction can be poured into the separating dish via the mouth of the funnel, which makes it easier to separate the water droplets flowing from the walls and tap.
- The volume of volatile acids (acetic and formic acid, about 90% of the volatile acids, 3–7% by weight of the pyrolysis liquid) can be quantified using other methods, such as capillary electrophoresis.
- As the ether extract is mainly composed of the CG-eluted compounds in the pyrolysis liquid, they may be quantified using other methods such as GC-FID.
- A major error may occur during the residue drying process. Some moisture remains in the syrupy residue. Evaporation must be started slowly as the water portion may suddenly froth. Towards the end of the evaporation process, the residue may also splash. The temperature in the water bath must not exceed 40°C because at higher temperatures the sugar-containing material starts to decompose (acidic hydrolysis).

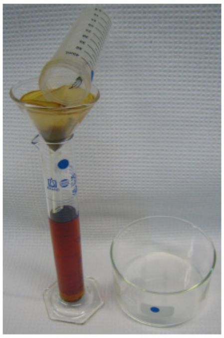
- With pyrolysis liquids, the amount of sugar-containing material in the bottom phases is 27–35% by weight of the original product. GC-eluted compounds (levoglucosan, cellobiose, hydroxy acids) only account for less than 5% by weight of the original product.

E2.4.4 Water-insoluble matter

Insoluble HMM (high-molecular mass) and soluble LMM (low-molecular mass) lignin matter and solids

- Add 50 ml of methylene dichloride (previously used 50 ml measuring glass) into the centrifuge tube and keep it in an ultrasonic bath for 30 minutes. The extract will form a brown mixture from which flaky matter will slowly separate on the bottom.
- After the ultrasonic treatment, the powdery precipitate is allowed to separate on the bottom of the centrifuge tube. A centrifugal treatment is not carried out.
- Pour the powdery precipitate and filtrate from the centrifuge tube onto the filter paper.
- 50 ml of methylene dichloride is added into the centrifuge tube again. The ultrasonic treatment is repeated if the precipitate in the tube is still bituminous.
- The centrifuge tube and the precipitate on the filter paper are washed using 50–100 ml of methylene dichloride.
- Dry the centrifuge tube, cap and filter paper + precipitate in the heating oven at 40ºC overnight and weigh them.
- Calculate the amount of water-insolubles (HMM + solids). The methylene dichloride-insoluble part of the water-insoluble material is brown and powdery.






To note:

- A major error may occur in the dissolving process (the methylene dichloride-insoluble part is powdery and must not contain any bitumen-type matter).
- The methylene dichloride-soluble fraction contains the LMM lignin matter in the pyrolysis liquid (MW approximately 400 DA) and extractive agents. The GC-eluded compounds consist of lignin monomers that are poorly water-soluble (guaiacols, syringols), lignin dimers (stilbenes) and extractive agents (fatty acids, resin acids, fatty alcohol, hydroxy fatty acids, sterols). GC-eluted compounds account for less than 10% by weight of the original product (bottom phases of pyrolysis liquid). LMM lignins account for 10–20% by weight of the original product.
- The insoluble part is fully powdery (pyrolytic lignin); if it contains bitumen-type material, the fraction was not fully dissolved.
- Polymerisation and condensation products also form in the fraction during storage; these products will also significantly increase the viscosity of the pyrolysis liquid.
- The fraction does not contain GC-eluted compounds and, with the exception of solids, the fraction dissolves in methanol.
- HMM material accounts for 1–15% by weight of the bottom phase of the pyrolysis liquid.
- The amount of solids is analysed from the original product by a separate method, if necessary.

E3. Presenting the results

Results are given to one decimal place and presented in the form of columns.

HMM lignin and solids

HMM lignin + solids (% by weight of original oil) = HMM + solids (g) * 100 / original sample (g).

Solids

Solids are determined from the original pyrolysis oil using a separate method, if necessary.

LMM lignin and extractives

LMM lignin + extractives (% by weight of original oil) = WIS (g) - (HMW + solids (g)) * 100 / original sample (g).

Extractives

Extractives are determined from the original pyrolysis oil using a separate method, if necessary.

Ether-insoluble matter (EIS, sugar-containing matter)

EIS (% by weight of original oil) = EIS evaporation residue (g) * 100 / original sample (g).

Ether-soluble matter

ES (% by weight of original oil) = 100 (% by weight) - water-insoluble material (% by weight) - EIS (% by weight) - water (% by weight).

Volatile acids

Volatile acids are determined from the water fraction of pyrolysis oil using a separate method (CE), if necessary.

Alcohols

Alcohols are determined from the water fraction of pyrolysis oil using a separate method (GC), if necessary. Error margins ± 10%.

References

Oasmaa, A. 2003. Fuel oil quality properties of wood-based pyrolysis liquids. Academic dissertation. Jyväskylä, Department of Chemistry, University of Jyväskylä. Research Report Series, Report; 99. 32 p. + app. 251 p. ISBN 951-39-1572-7.

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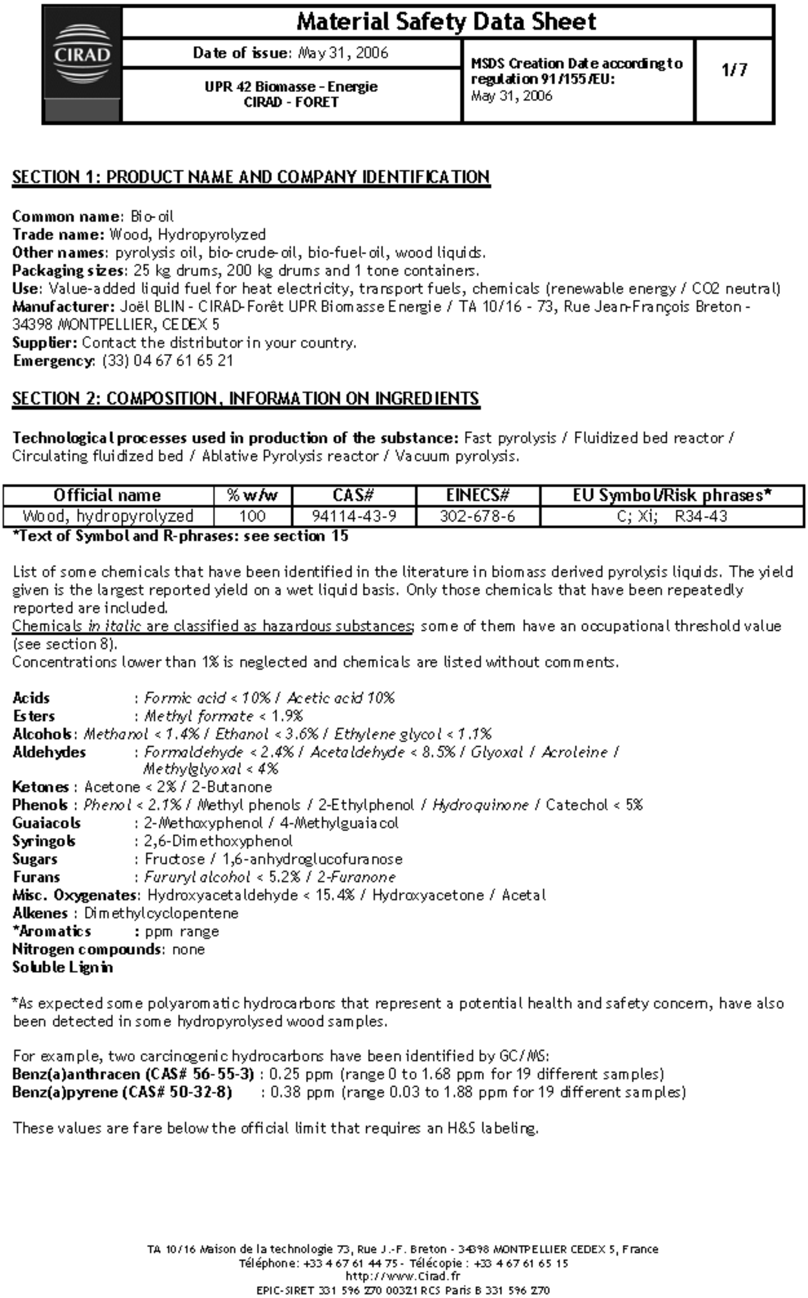
Appendix F: MSDS – Material health and safety data sheet for pyrolysis



CIRAD	**Material Safety Data Sheet**		
	Date of issue: May 31, 2006	**MSDS Creation Date according to regulation 91/155/EU:** May 31, 2006	**1/7**
	UPR 42 Biomasse - Energie **CIRAD - FORET**		

SECTION 1: PRODUCT NAME AND COMPANY IDENTIFICATION

Common name: Bio-oil
Trade name: Wood, Hydropyrolyzed
Other names: pyrolysis oil, bio-crude-oil, bio-fuel-oil, wood liquids.
Packaging sizes: 25 kg drums, 200 kg drums and 1 tone containers.
Use: Value-added liquid fuel for heat electricity, transport fuels, chemicals (renewable energy / CO2 neutral)
Manufacturer: Joël BLIN - CIRAD-Forêt UPR Biomasse Energie / TA 10/16 - 73, Rue Jean-François Breton - 34398 MONTPELLIER, CEDEX 5
Supplier: Contact the distributor in your country.
Emergency: (33) 04 67 61 65 21

SECTION 2: COMPOSITION, INFORMATION ON INGREDIENTS

Technological processes used in production of the substance: Fast pyrolysis / Fluidized bed reactor / Circulating fluidized bed / Ablative Pyrolysis reactor / Vacuum pyrolysis.

Official name	% w/w	CAS#	EINECS#	EU Symbol/Risk phrases*
Wood, hydropyrolyzed	100	94114-43-9	302-678-6	C; Xi; R34-43

***Text of Symbol and R-phrases: see section 15**

List of some chemicals that have been identified in the literature in biomass derived pyrolysis liquids. The yield given is the largest reported yield on a wet liquid basis. Only those chemicals that have been repeatedly reported are included.
Chemicals *in italic* are classified as hazardous substances; some of them have an occupational threshold value (see section 8).
Concentrations lower than 1% is neglected and chemicals are listed without comments.

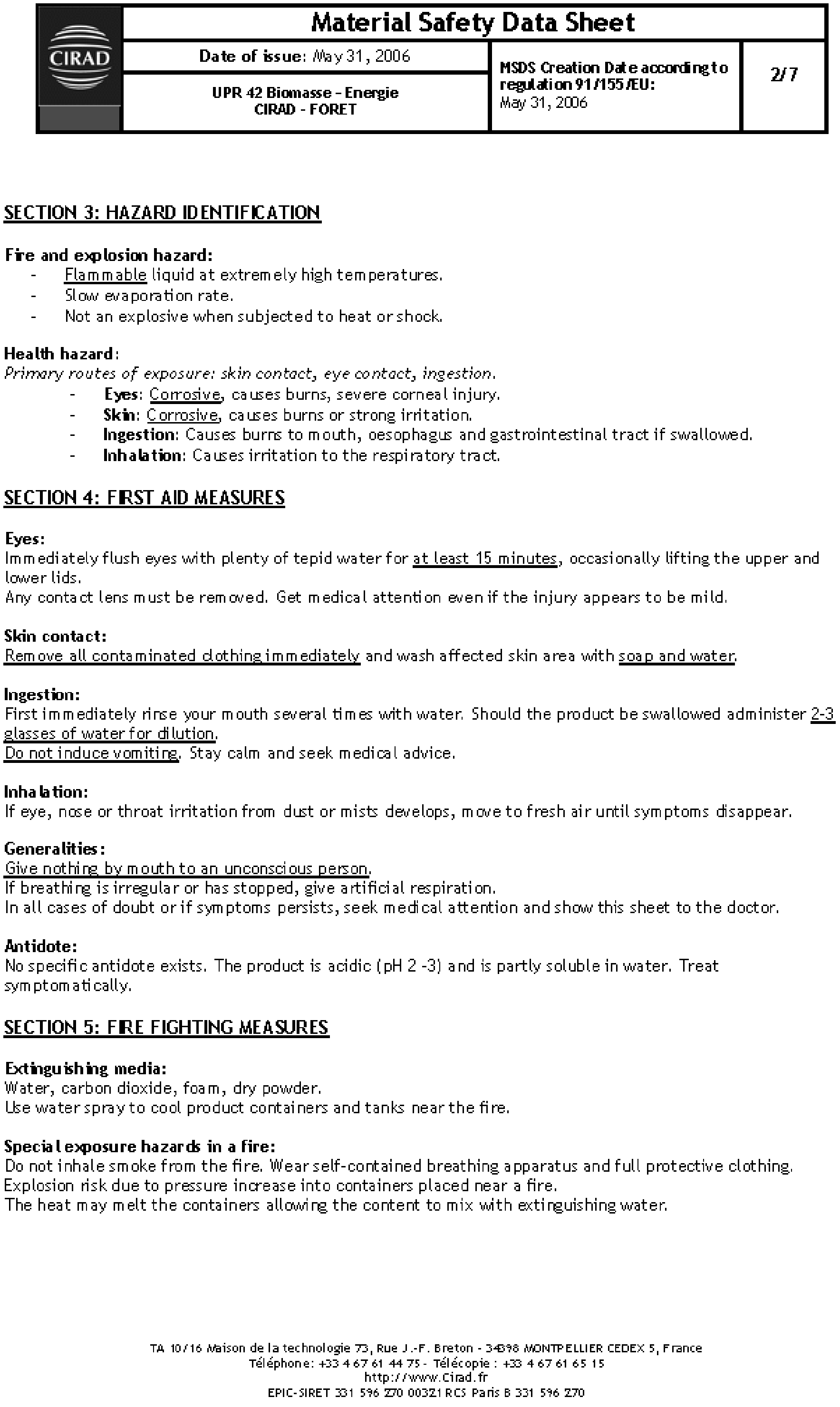
Acids : *Formic acid < 10% / Acetic acid 10%*
Esters : *Methyl formate* < 1.9%
Alcohols: *Methanol < 1.4% / Ethanol < 3.6% / Ethylene glycol < 1.1%*
Aldehydes : *Formaldehyde < 2.4% / Acetaldehyde < 8.5% / Glyoxal / Acroleine / Methylglyoxal < 4%*
Ketones : Acetone < 2% / 2-Butanone
Phenols : *Phenol* < 2.1% / Methyl phenols / 2-Ethylphenol / *Hydroquinone* / Catechol < 5%
Guaiacols : 2-Methoxyphenol / 4-Methylguaiacol
Syringols : 2,6-Dimethoxyphenol
Sugars : Fructose / 1,6-anhydroglucofuranose
Furans : *Fururyl alcohol* < 5.2% / *2-Furanone*
Misc. Oxygenates: Hydroxyacetaldehyde < 15.4% / Hydroxyacetone / Acetal
Alkenes : Dimethylcyclopentene
***Aromatics** : ppm range
Nitrogen compounds: none
Soluble Lignin

*As expected some polyaromatic hydrocarbons that represent a potential health and safety concern, have also been detected in some hydropyrolysed wood samples.

For example, two carcinogenic hydrocarbons have been identified by GC/MS:
Benz(a)anthracen (CAS# 56-55-3) : 0.25 ppm (range 0 to 1.68 ppm for 19 different samples)
Benz(a)pyrene (CAS# 50-32-8) : 0.38 ppm (range 0.03 to 1.88 ppm for 19 different samples)

These values are fare below the official limit that requires an H&S labeling.

Appendix F: MSDS – Material health and safety data sheet for pyrolysis



CIRAD	Material Safety Data Sheet		
	Date of issue: May 31, 2006	**MSDS Creation Date according to regulation 91/155/EU:** May 31, 2006	**2/7**
	UPR 42 Biomasse - Energie **CIRAD - FORET**		

SECTION 3: HAZARD IDENTIFICATION

Fire and explosion hazard:

- Flammable liquid at extremely high temperatures.
- Slow evaporation rate.
- Not an explosive when subjected to heat or shock.

Health hazard:

Primary routes of exposure: skin contact, eye contact, ingestion.

- **Eyes**: Corrosive, causes burns, severe corneal injury.
- **Skin**: Corrosive, causes burns or strong irritation.
- **Ingestion**: Causes burns to mouth, oesophagus and gastrointestinal tract if swallowed.
- **Inhalation**: Causes irritation to the respiratory tract.

SECTION 4: FIRST AID MEASURES

Eyes:

Immediately flush eyes with plenty of tepid water for at least 15 minutes, occasionally lifting the upper and lower lids.
Any contact lens must be removed. Get medical attention even if the injury appears to be mild.

Skin contact:

Remove all contaminated clothing immediately and wash affected skin area with soap and water.

Ingestion:

First immediately rinse your mouth several times with water. Should the product be swallowed administer 2-3 glasses of water for dilution.
Do not induce vomiting. Stay calm and seek medical advice.

Inhalation:

If eye, nose or throat irritation from dust or mists develops, move to fresh air until symptoms disappear.

Generalities:

Give nothing by mouth to an unconscious person.
If breathing is irregular or has stopped, give artificial respiration.
In all cases of doubt or if symptoms persists, seek medical attention and show this sheet to the doctor.

Antidote:

No specific antidote exists. The product is acidic (pH 2 -3) and is partly soluble in water. Treat symptomatically.

SECTION 5: FIRE FIGHTING MEASURES

Extinguishing media:

Water, carbon dioxide, foam, dry powder.
Use water spray to cool product containers and tanks near the fire.

Special exposure hazards in a fire:

Do not inhale smoke from the fire. Wear self-contained breathing apparatus and full protective clothing.
Explosion risk due to pressure increase into containers placed near a fire.
The heat may melt the containers allowing the content to mix with extinguishing water.

SECTION 6: ACCIDENTAL RELEASE MEASURES

Personal precautions: evacuate people upwind from the spill area.
Environmental precautions: do not allow the product to enter drains or surface water.

Methods for cleaning up:
To handle spills, the following preliminary advices are given.

- **Small quantities (< 1000 ml)**
  The suggested actions for such spillage are:
  Wear rubber gloves and suitable eye and face protection. If there is an inadequate ventilation, a suitable organic vapours filter mask or NIOSH approved respirator must be worn. Cover contaminated area with an inert adsorbent e.g. vermiculite, sawdust. Take up the used adsorbent and place it in a container for disposal or incineration.

- **Large quantities (> 1000 ml)**
  For spillage of significant quantities first evacuate rapidly workers present in the area and then take the same actions as described above.

SECTION 7: HANDLING AND STORAGE

Handling
Combustible.
Keep away from sources of ignition. Take precautionary measures (e.g. earthing) against electrostatic discharges.
When transferring the product and opening containers, avoid inhalation of vapours or gases. Ensure good ventilation when handling the product.
During tank cleaning operations follow special instructions provided by the manufacturer.

Storage
The product must be stored in containers suitable for combustible liquids and resistant to acids. Keep containers tightly closed at temperatures below 25°C in a well ventilated area. The product contains compounds that may either consume oxygen creating an under-pressure in the container; or may emit vapours that create an overpressure in the container.

Recommended storage materials: acid-proof steel, plastics (PETE, PP, HDPE). Filled containers may be gently heated to not more than 50°C before use for transfer of contents.

SECTION 8: EXPOSURE CONTROLS, PERSONAL PROTECTION

Engineering controls

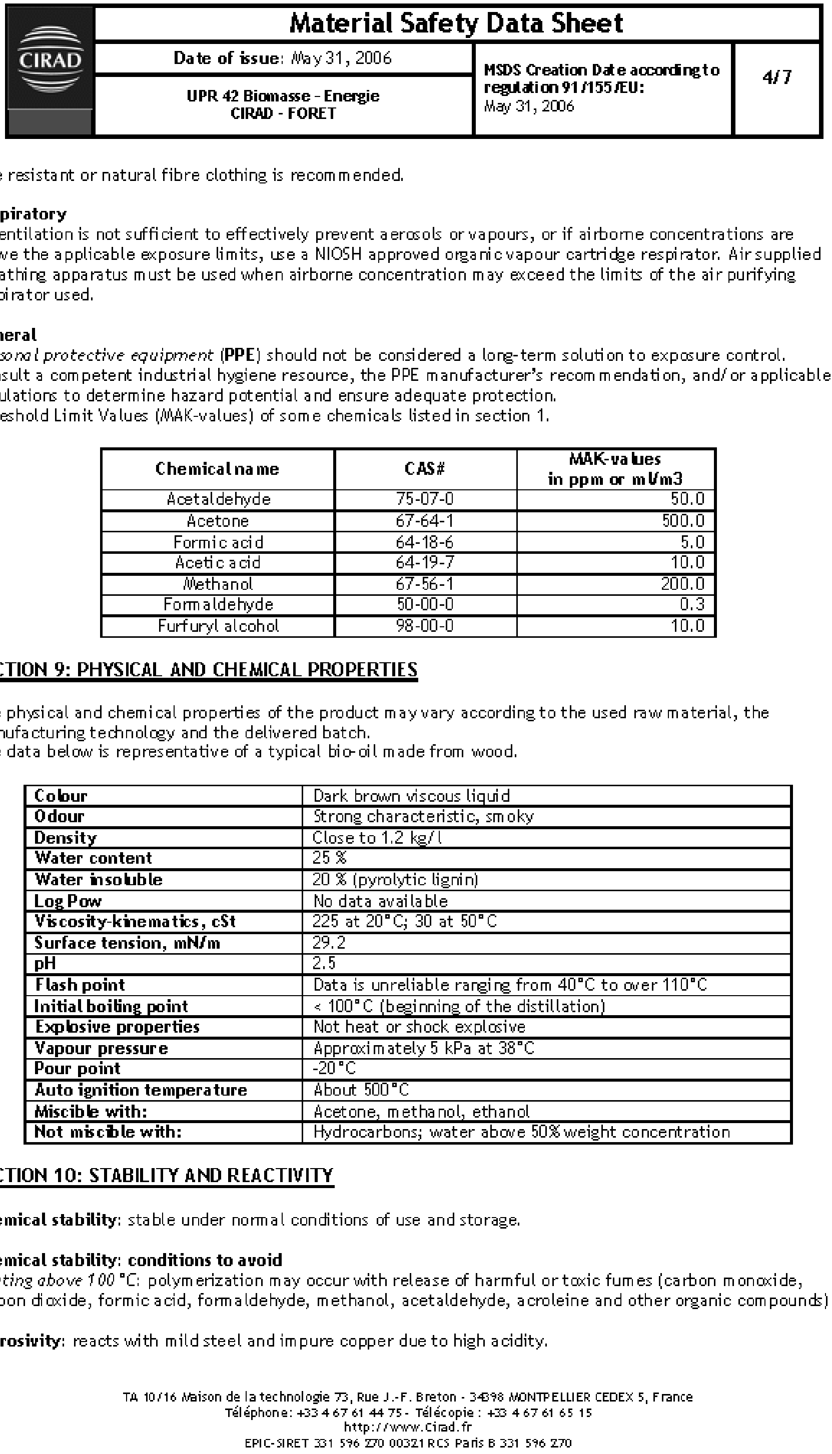
Provide local and general exhaust ventilation to effectively remove and prevent vapors and mists generated from the handling of this product. Ensure that eyewash station and safety showers are proximal to the workplace location.

Personal protective equipment:

Eyes/Face
Wear safety glasses, chemical goggles if splashing is possible, or to prevent eye irritation from heated vapours or mists.

Skin/Hands/Feet
Wear chemically resistant gloves (nitrile gloves or thermally insulated gloves when handling hot products) and footwear with good traction to avoid slipping.
If splashing or contact with hot material is possible, consider the need for use of an impervious overcoat.
Remove contaminated clothing and clean before reuse.

Appendix F: MSDS – Material health and safety data sheet for pyrolysis



Fire resistant or natural fibre clothing is recommended.

Respiratory
If ventilation is not sufficient to effectively prevent aerosols or vapours, or if airborne concentrations are above the applicable exposure limits, use a NIOSH approved organic vapour cartridge respirator. Air supplied breathing apparatus must be used when airborne concentration may exceed the limits of the air purifying respirator used.

General
Personal protective equipment (**PPE**) should not be considered a long-term solution to exposure control. Consult a competent industrial hygiene resource, the PPE manufacturer's recommendation, and/or applicable regulations to determine hazard potential and ensure adequate protection.
Threshold Limit Values (MAK-values) of some chemicals listed in section 1.

Chemical name	CAS#	MAK-values in ppm or ml/m3
Acetaldehyde	75-07-0	50.0
Acetone	67-64-1	500.0
Formic acid	64-18-6	5.0
Acetic acid	64-19-7	10.0
Methanol	67-56-1	200.0
Formaldehyde	50-00-0	0.3
Furfuryl alcohol	98-00-0	10.0

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

The physical and chemical properties of the product may vary according to the used raw material, the manufacturing technology and the delivered batch.
The data below is representative of a typical bio-oil made from wood.

Colour	Dark brown viscous liquid
Odour	Strong characteristic, smoky
Density	Close to 1.2 kg/l
Water content	25 %
Water insoluble	20 % (pyrolytic lignin)
Log Pow	No data available
Viscosity-kinematics, cSt	225 at 20°C; 30 at 50°C
Surface tension, mN/m	29.2
pH	2.5
Flash point	Data is unreliable ranging from 40°C to over 110°C
Initial boiling point	< 100°C (beginning of the distillation)
Explosive properties	Not heat or shock explosive
Vapour pressure	Approximately 5 kPa at 38°C
Pour point	-20°C
Auto ignition temperature	About 500°C
Miscible with:	Acetone, methanol, ethanol
Not miscible with:	Hydrocarbons; water above 50% weight concentration

SECTION 10: STABILITY AND REACTIVITY

Chemical stability: stable under normal conditions of use and storage.

Chemical stability: conditions to avoid
Heating above 100 °C: polymerization may occur with release of harmful or toxic fumes (carbon monoxide, carbon dioxide, formic acid, formaldehyde, methanol, acetaldehyde, acroleine and other organic compounds).

Corrosivity: reacts with mild steel and impure copper due to high acidity.

SECTION 11: TOXICOLOGICAL INFORMATION

The test results given below are based on one selected representative sample.

This sample has been obtained under well known operating conditions: temperature of 500°C; fluidized bed system; softwood.

- **LD50 (oral, rat)**: >2000 mg/kg/body weight
- **7-days oral, gavage, rats:** At 150 mg/kg/body weight, there were no clinical signs of toxicity, a slight reduction in the body weight gain of the females and no effect on food consumption. No macroscopic abnormalities were observed.
- **Acute dermal toxicity**: Test not performed as the product is corrosive.
- **Dermal Irritation** (rabbit): Corrosive
- **Eye Irritation** (not done for ethical reason): Corrosive
- **Inhalation**: Avoid inhalation as the product may contain hazardous substances depending on the manufacture process and temperature.
- **Skin sensitization** (LLNA, mice): Moderate sensitizer
- **Mutagenic tests:**
  1. *Ames test (Salmonella typhimurium):* Positive, the product is mutagenic in this test.
  2. *Bone marrow micronucleus test by oral route gavage in mice*: Negative
  3. *Micronucleus test in L5178 TK mouse lymphoma cells*: Light mutagenic activity
- **Teratogenicity**: No known or listed teratogenic effects.
- **Reproductive effects**: No information available.
- **Neurotoxicity**: No information available.
- The product contains traces of substances classified as **carcinogenic** (e.g. formaldehyde, acetaldehyde, and furfural).

SECTION 12: ECOLOGICAL INFORMATION

- **Biodegradation** (Modified Sturm Test): The product biodegrades rapidly at percentages between 32 and 50%. Low biodegradation under anaerobic conditions.
- **Algal growth test**: At low concentration the product has a small fertilizing effect. At higher concentration, algal growth is slightly inhibited. From 0 to 72 hours the NOEL was > 100 mg/l.
- **EC50 (Acute toxicity to Daphnia Magna)**: > 100 mg/l

The potential to contribute to eutrophisation should be small due to the very low nitrogen, and very low minerals content of the product.
The product is not likely to bioaccumulation as most of components are highly soluble in water and/or biodegrade rapidly.

Waste treatment organisms: Large quantities may increase the pH value.

SECTION 13: DISPOSAL CONSIDERATIONS

Product waste is classified as **hazardous waste.**

European waste catalogue number: 13 07 03* Other Fuels (including mixture)
Do not allow this product to reach drains or ground water.
Follow national and municipal regulations obtained from local authorities.

SECTION 14: TRANSPORT INFORMATION

The information given below is provided to assist in documentation. See also *Section 16, 1)*

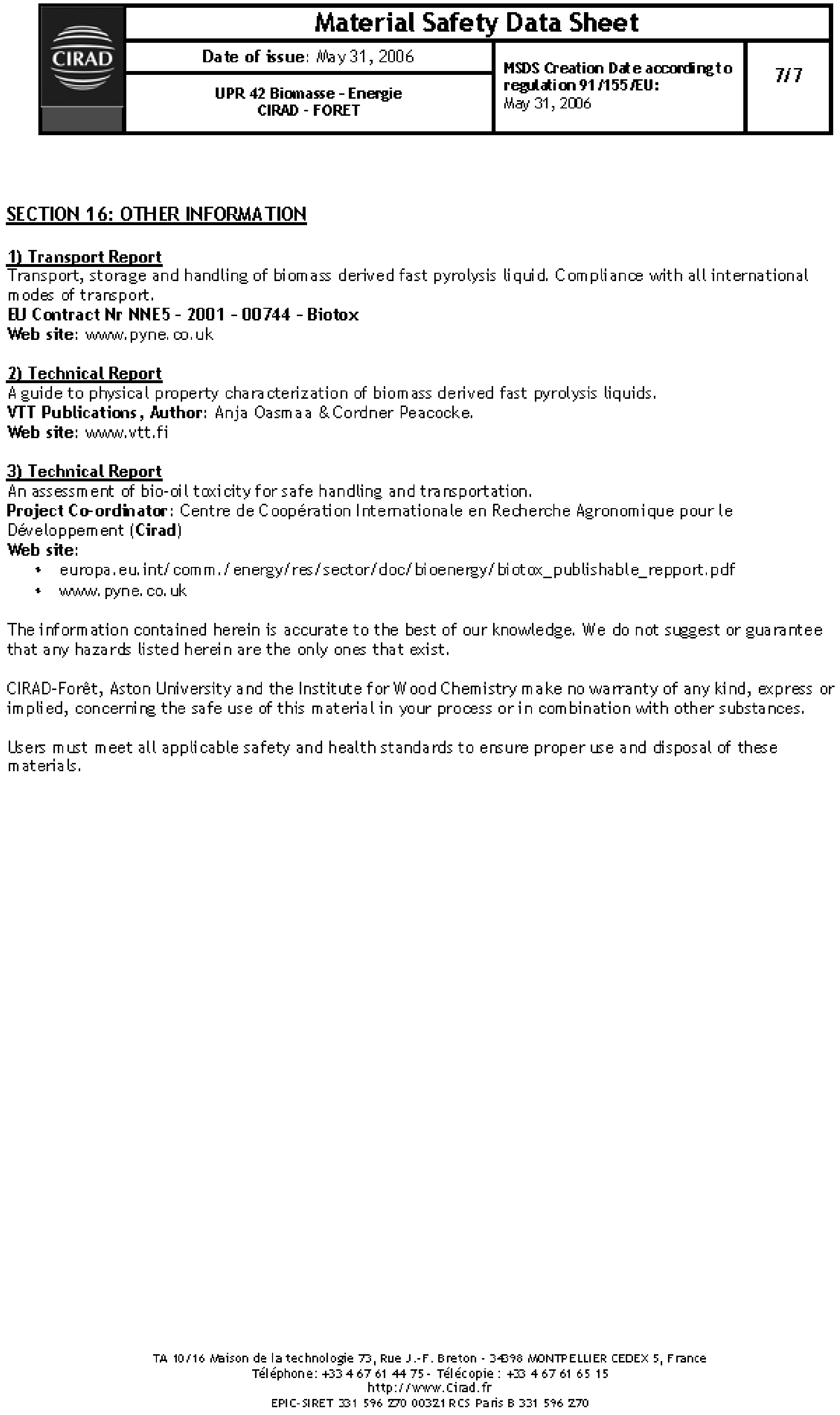
ADR/RID:	UN Number: Labels: Proper shipping name: Risk Code Packaging group:	UN 2924 6 + 8 + 11 FLAMMABLE LIQUID, CORROSIVE, N.O.S. Wood distillate 30 III
IMDG:	UN Number: Labels: Proper shipping name: EmS: Packaging group:	UN 2924 6 + 8 + 11 FLAMMABLE LIQUID, CORROSIVE, N.O.S Wood distillate 3-07 III
IATA:	UN Number: Labels: Proper shipping name: Class: Packaging group:	UN 2924 6 + 8 + 11 FLAMMABLE LIQUID, CORROSIVE, N.O.S. Wood distillate 3 III

SECTION 15: REGULATORY INFORMATION

European labeling: Wood, hydropyrolysed.

Symbol C: Corrosive

R 34: Causes burns.
R 43: May cause sensitization by skin contact.
S 26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S 23: Do not breathes vapours.
S 37/39: Wear suitable gloves and eye protection.
S 45: In case of accident or if you feel unwell, seek medical advice immediately and show the product label or MSDS.



CIRAD	**Material Safety Data Sheet**		
	Date of issue: May 31, 2006	**MSDS Creation Date according to regulation 91/155/EU:** May 31, 2006	7/7
	UPR 42 Biomasse - Energie **CIRAD - FORET**		

SECTION 16: OTHER INFORMATION

1) Transport Report
Transport, storage and handling of biomass derived fast pyrolysis liquid. Compliance with all international modes of transport.
EU Contract Nr NNE5 - 2001 - 00744 - Biotox
Web site: www.pyne.co.uk

2) Technical Report
A guide to physical property characterization of biomass derived fast pyrolysis liquids.
VTT Publications, Author: Anja Oasmaa & Cordner Peacocke.
Web site: www.vtt.fi

3) Technical Report
An assessment of bio-oil toxicity for safe handling and transportation.
Project Co-ordinator: Centre de Coopération Internationale en Recherche Agronomique pour le Développement (**Cirad**)
Web site:

- europa.eu.int/comm./energy/res/sector/doc/bioenergy/biotox_publishable_repport.pdf
- www.pyne.co.uk

The information contained herein is accurate to the best of our knowledge. We do not suggest or guarantee that any hazards listed herein are the only ones that exist.

CIRAD-Forêt, Aston University and the Institute for Wood Chemistry make no warranty of any kind, express or implied, concerning the safe use of this material in your process or in combination with other substances.

Users must meet all applicable safety and health standards to ensure proper use and disposal of these materials.

Appendix G: Properties of pyrolysis liquids

Table G1.

Organisation	**VTT**	**VTT**	**VTT**	**NREL**	**NREL**	**Ensyn**	**Bio-Alternative**	**Bio-Alternative**	**N/A**	**Dynamotive**	**Dynamotive**
Technology				Vortex (HGF**)	Fluid bed	RTP	Fixed bed	Fixed bed	Fluid bed	Fluid bed	Fluid bed
Reference				5		5	1	1	2	3	3
Feedstock	Pine	Straw	Forest residue*	Poplar	Switchgrass	Mixed hardwood	Fir	Beech	Rice husk	Pine/Spruce 100% wood	Pine/Spruce 53% wood 47% bark
Water, wt%	16.6	19.9	24.1	18.9	n.d.	22	4.5	14.0	28.0	23.3	23.4
pH	2.6	3.7	2.9	2.8	n.d.	2.5		2.7	3.2	2.3	2.4
Density (at 15°C), kg/dm^3	1.24	1.19	1.22	1.2	n.d	1.18		1.216	1.14 @ 30°C	1.20	1.19
Elemental analysis (wt%, dry)									wt%, wet		
C	55.8	55.3	56.6	57.3	55.8	56.4	58.12	55.10	39.92		
H	5.8	6.6	6.2	6.3	6.9	6.2	6.55	7.20	8.15		
O (by diff.)	38.2	37.7	36.9	36.2	36.3	37.1	34.81	35.10			
N	0.1	0.4	0.1	0.18	0.79	0.2	0.52	2.00	0.61		
S	0.02	0.05	0.03	0.02	0.03	< 0.01		0.6	0.03		
Ash (solids)	0.03	0.14	0.08	< 0.01	n.d.	0.1	< 0.05		0.25	< 0.02	< 0.02
K+Na, ppm	20	2	60	10	128	460					
Cl, ppm	30	330	< 100	8	1900	3					
Solids (wt%)									0.5	< 0.1	< 0.1

Organisation	**VTT**	**VTT**	**VTT**	**NREL**	**NREL**	**Ensyn**	**Bio-Alternative**	**Bio-Alternative**	**N/A**	**Dynamotive**	**Dynamotive**
Technology				Vortex (HGF**)	Fluid bed	RTP	Fixed bed	Fixed bed	Fluid bed	Fluid bed	Fluid bed
HHV, MJ/kg	19.1	18.5	17.4	18.7		17.0			16.5	16.6	16.4
HHV (dry), MJ/kg	22.9	23.1	23.0	22.3	23.8	23.1					
LHV				17.0			22.2	20.9			
Viscosity, cP				18 @ 40°C		45 @ 40°C	250 @ 60°C	10 @ 70°C			
Viscosity, cSt											
20°C	n.d.	55	152	128		233 @ 25°C 134 @ 40°C			13.2 @ 40°C	73	78
50°C	31	11	29 (40°C)	13.5		50				4.3 @ 80°C	4.4 @ 80°C
Flash point, °C	n.d.	56	42	64		55			68		
Pour point, °C	-19	-36	-12	-36		-25					
Solubility, wt% insolubles in											
Ethanol	0.3	0.3	0.1	0.045		0.045					
Methanol/dichloro-methane	n.d.	n.d.	0.02	n.d.		n.d.					
Cp (J/kgK)									2788		
K (W/mK)									0.39		
Surface tension (mN/m)									35.3 @ 30°C		

Cp – specific heat capacity, K – liquids thermal conductivity, n.d. = not determined, *Bottom phase (90 wt% of total liquid), **H.G.F. = Hot gas filtered

Table G2.

Organisation	**Dynamotive**					**Pyrovac**		**Waterloo**	**Waterloo**	**Waterloo**	**Laval**		
Technology	Fluid bed	Auger	Auger	Auger	Auger	Vacuum pyrolysis	Fluid bed	Fluid bed	Fluid bed	Fluid bed	Vacuum pyrolysis		
Reference	3	4	4	4	4	5	24	5	5	5	6		
Feedstock	Bagasse	Pine	Oak	Pine bark	Oak bark	Fir/spruce bark	Japanese larch	Poplar	Spruce	Red maple	Softwood bark		
Physical property											Upper layer	Bottom layer	Whole bio-oil
Water, wt%	20.8	16.0	22.5	19.8	22.0	23	28.0	18.70	22.40	18.00	< 3.5	14.6	
pH	2.6	3.1	3.1	3.2	3.2	3	2.1	2.40	2.10	2.40	3.03	2.98	3.00
Density (at 15°C), kg/dm^3	1.20	1.19	1.20	1.17	1.20	1.14		1.20	1.22	1.19	1.089	1.222	1.188
Elemental analysis (wt%, dry)		wt% wet	wt% wet	wt% wet	wt% wet	wt% wet							
C		52.6	47.19	53.99	45.47	55.4	57.0	54.70	54.00	54.70	74.13	61.26	62.59
H		7.53	4.51	6.97	6.05	8.4	7.0	6.90	6.80	6.40	8.50	6.49	7.02
O (by diff.)		39.52	47.97	38.21	47.75	35.3	34.2	38.40	39.20	38.90	17.00	31.29	29.02
N		0.09	0.12	0.37	0.32	0.6	1.8				0.25	0.60	1.05
S		0.0197	0.022	0.035	0.28	< 0.01					0.05	0.07	0.07
Ash (solids)	< 0.02	0.20	0.184	0.428	0.08	0.3					0.07	0.29	0.25
K+Na, ppm						23	< 0.1 + 4.2				4.9 + 5.1	32+15.7	
Solids (wt%)	< 0.1	0.19	0.80	2.10	1.83		< 0.005				1.30	0.61	0.71
HHV, MJ/kg	15.4	21.9	18.7	18.3	19.0	23.0		23.20	22.70	22.40			

Organisation	**Dynamotive**					**Pyrovac**		**Waterloo**	**Waterloo**	**Waterloo**	**Laval**		
Technology	Fluid bed	Auger	Auger	Auger	Auger	Vacuum pyrolysis	Fluid bed	Fluid bed	Fluid bed	Fluid bed	Vacuum pyrolysis		
HHV (dry), MJ/kg							22.2				34.3	26.4	27.9
Viscosity, cP													
25°C		200	206	7253	7289								
50°C		154	171	2529	5047								
80°C		92	38	70	131								
Viscosity, cSt													
20°C	57												
50°C	4.0 @ 80°C	60.9	41.6	n.d.	n.d.	5.6					88	66	62
Flash point, °C						> 95							
Solubility, wt% insolubles in													
Methanol/dichloro-methane											0.28	0.58	0.55
Cp (J/kgK)											1400	2300	2100
Surface tension (mN/m)											22.3 @ 80°C	22.6	23.5

Cp – specific heat capacity, K – liquids thermal conductivity

Table G3.

Organisation	**Laval**		**Laval**	**Laval**								**BTG**
Technology	Vacuum pyrolysis		Vacuum pyrolysis	Vacuum pyrolysis	Packed bed vacuum pyrolysis	Fixed bed static	Fixed bed	Fixed bed	Fluid bed		Fixed bed	Rotating cone
Reference	6		7	8	9	10	11	12	13		14	23
Feedstock	Hardwood rich in fibres		Sugarcane bagasse	Softwood bark	Cashew nut shells	Rapeseed	Soybean oil cake	Safflower seed press cake	Microalgae *C. protothecoides*	Microalgae *M. aeruginosa*	Motorcycle tyre waste	Pine
Physical property	Waxy layer	Bottom layer										
Water, wt%	< 3.5	13.0	13.8	5.3	3		0	0			n/a	33.7
pH	-	2.34				0					4.40	2.9
Density (at 15r), kg/dm^3	0.914	1.209	1.211 @ 20°C	1.07 @ 20°C	0.987 @ 28°C	0.918 @ 30°C	1.107	1.08			0.957	1.2
Elemental analysis (wt%, dry)	wt% dry	wt% dry	wt% dry		wt% dry	?	?	?	?		?	
C	81.21	56.8	54.6	77.56	79.9	74.0	67.9	67.0	62.1	61.0	85.9	53.7
H	11.89	6.53	6.5	8.69	11.8	10.3	7.8	6.29	8.76	8.23	9.15	6.0
O (by diff.)	7	36	38	13.13	8	11.7	13.5	22.15	19	21	3	40
N	0.03	0.19	0.73	0.59	< 0.2	3.9	10.8	4.58	9.74	9.83	0.65	0.3
S	0.07	0.02	< 0.10		n.d.						1.25	
Ash (solids)	0.005	0.12	0.05		0.01						0.22	0.03
K+Na, ppm		2.54+9.3	5.3+21.5	6+2								
Solids (wt%)	-	0.246	0.38	0.34	0							

Organisation	**Laval**		**Laval**	**Laval**								**BTG**
Technology	Vacuum pyrolysis		Vacuum pyrolysis	Vacuum pyrolysis	Packed bed vacuum pyrolysis	Fixed bed static	Fixed bed	Fixed bed	Fluid bed		Fixed bed	Rotating cone
HHV (wet, MJ/kg)			22.4		40	38.4	33.60	36.0	30	29		
HHV (dry, MJ/kg)	42.4	24.3										
LHV (wet, MJ/kg)				32.4								13.9
Viscosity, cP												
25 C					164 @ 30°C				100 @ 40°C			79 @ 21°C
50°C		24			38.5 @ 60°C							
Viscosity, cSt												
20°C			116.5		166 @ 30°C						4.75 @ 30°C	
50°C	-	19.85	16.4		39 @ 60°C	43	72.38	225				
Flash point, °C			> 90	> 90	164	83	63	58			≤ 32	
Pour point, °C				3							-6	
Solubility, wt% insolubles in												
Ethanol		0.095										
K (mN/m) [1]	-	24.0 @ 80°C		35.3 @ 20°C								
				33.2 @ 40°C								
				31.0 @ 60°C								

Cp – specific heat capacity, K – liquids thermal conductivity

Table G4.

Organisation		**UNICAMP**	**Fortum**			**CNRS**							
Technology	Fixed bed	Fluid bed	Fluid bed	Fixed bed	Fixed bed	Cyclone reactor	Fluid bed	Fluid bed	Fluid bed	Fluid bed		Fluid bed	
Reference	15	18	19	15	15	16	17	20	21	22		22	
Feedstock	Scrap tyre	Elephant grass	Pine	Waste paper	Waste plastic	Oak & beech sawdust	Rice husk	oil palm shell	Pinus radiata	Rice straw		Bamboo	
Physical property		heavy phase				Heavy oil				upper phase	lower phase	upper phase	lower phase
Water, wt%	(ASTM) 0.1	13.2	26.1			12	25.2	10 #	28.8	63	8	48	35
pH	4.25	2.2	2.5–3	1.5	5.5	2.6	2.8	2.7	2.3	3.0	2.73		
Density (at 15°C), kg/dm^3	0.965	1.15 @ 20°C	1.22 @ 20°C	1.205	0.905	1.27	1.19	1.2					
Elemental analysis (wt%, dry)	?assumed			?assumed	?assumed	wet (calculated)	?assumed						
C	80	80.6	57.1	40.80	72.20	52.24	41.7	61.7	64.5	18.7	56.7	30.5	47.7
H	6.33	6.5	6.4	6.29	14.04	6.36	7.7	6.0	4.8	4.7	4.7	4.6	6.4
O (by diff.)	13.67	10.7	36.4	52.91	13.76	41.04	50.3	31.8	28.8	76.3	36.1	64.6	43.6
N	0	2.0	0.1	0	0	0.36	0.3	0.5	2.0	0.1	2.1	0.1	2.3
S	0	0.2		0	0		0.2	0.02		0.07	0.38	0.12	0.02
Ash (solids)	0.06	0.55	0.035	0.35	0.1				n.d.			< 0.1	
K+Na, ppm									0.3 + 4.1	25 + 46		6 + 16	
Cl, ppm													
Solids (wt%)			0.2			0.39			< 0.005			< 0.1	
HHV, MJ/kg	41.5	31.4		13.19	43.5			22.1	22.0	2.9	18.6	7.6	17.4

Organisation		**UNICAMP**	**Fortum**			**CNRS**							
Technology	Fixed bed	Fluid bed	Fluid bed	Fixed bed	Fixed bed	Cyclone reactor	Fluid bed	Fluid bed	Fluid bed	Fluid bed		Fluid bed	
HHV (dry), MJ/kg													
LHV							17.42						
Viscosity, cP		575 @ 37°C				150 @ 20°C							
25$^{\circ\mathrm{C}}$		115 @ 65°C				47 @ 40°C							
50$^{\circ\mathrm{C}}$													
80$^{\circ\mathrm{C}}$	4.9 @ 35°C	500 @ 37°C	25 @ 40°C	2 @ 35°C	7.5 @ 35°C		128						
Viscosity, cSt		100 @ 65°C					< 40 @ 60°C						
20°C	32	70		200	48								
50°C	-25	9		-8	-14			14.6					
Flash point, °C								54					
Pour point, °C								< -10					
Solubility, wt% insolubles in													
Ethanol													
Methanol/dichloro-methane													
Cp (J/kgK)													
K (W/mK)													
Surface tension (mN/m)													

Notes: # ASTM 4928-89 and IP 386/90, Cp – specific heat capacity, K – liquids thermal conductivity

Table G5. Liquid fuels comparison.

	Ethanol	**Methanol**	**DME (di-methyl ether)**	**Biodiesel**	**FT Diesel**	**Vegetable oil (canola)**	**Low Sulphur Diesel**	**Beef Tallow**	**Methyl tertiary butyl ether (MTBE)**	**# 2 fuel oil**	**Butanol**
Density (at 15°C), kg/dm^3	0.789	0.794	0.665	0.888	0.797	0.93	0.847	0.92	0.743	0.93	0.810
HHV (MJ/kg) [1]	29.8	22.9	31.7	40.2	45.5	39.7	45.6	43.5	38.0	44.2	37.3
LHV (MJ/kg)	27.0	20.1	28.9	37.5	43.2	36.9	42.6	40.0	35.1	41.1	34.4
Viscosity, cP (@ 20°C)	1.07	0.54	0.32	3.1–4.4 [2]	1.9–3.6	30.0	1.6	40.0	0.3 [3]	2.8–6.9	3 [3]
Flash point, °C	13	11	-45	> 130		220	> 62	> 130	-28	38	29

Notes: [1] HHV at 25°C, [2] as per BS EN 14214:2003 at 40°C, [3] at 25°C.

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Title
Properties and fuel use of biomass-derived fast pyrolysis liquids. A guide

This report is a valuable resource for those involved in biomass fast pyrolysis for fuel oil production. The report provides details of the analysis of the fuel properties of the bio-oil products from fast pyrolysis of biomass and also includes what is known about utilization of the products as fuels. This report is the latest update of the previous analytical methods reports from VTT (#306 from 1997 and #450 from 2001). The report begins with a short introduction to the technology for bio-oil production and the chemical composition of the liquid products. It addresses the key complication for testing (and using) bio-oil, the recovery of a representative sample. The analytical methods are then presented with both chapters describing the details and results in the main report and related appendices with the actual method procedures provided for several of the analyses. The fuel oil properties described range from compositional methods, such as elements, water and solids, to various relevant physical properties, such as density, viscosity, lubricity, and a number of chemical-based properties, such as carbon residue, flash point, heating value, acidity and thermal stability. Consideration of fuel oil specifications, quality control and environmental and safety issues is also addressed. The report contains a representative Material Safety Data Sheet (MSDS) as an appendix. Finally, the report contains an invaluable collection of data from the literature describing 50 different bio-oil products from the around the world including a wide range of biomass feedstock types and numerous reactor configurations.

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