Thermonet –PyNe SG Report

Characterisation, Analysis, Norms & Standards

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The Subject Group Report is divided into 3 parts:

1. End-User Requirements and Specifications
2. Development of Test Methods
3. Pyrolysis Liquid Analyses Round robin

Part 1 End-User Requirements and Specifications

1 INTRODUCTION

The work described here was conducted as part of an EU funded ALTENER II project (contract no. 4.1030/C/00-015/2000), with the primary objective of determining norms and standards for biomass derived fast pyrolysis liquids. The work was continued in the IEA-EU PyNe Network. In addition, results from other studies were included. The following tasks were executed:

1. Review fast pyrolysis technologies and describe processes at pre-commercial and commercial scale, suitable for heat and power production in the near (1-4 years) to medium term (5-10 years). Review incentives to develop pyrolysis technologies at national and EU level.
2. Derive norms and standards for biomass fast pyrolysis liquids. Review end user requirements and specifications for biomass fast pyrolysis liquids to obtain specifications and standards in liquid fuel quality.
3. Sector and market strategies for the production of power from pyrolysis liquids.
4. Long-term cost/benefit analyses comparing biomass fast pyrolysis to traditional forms of energy and other alternative renewable energy sources and comparing the overall conversion efficiencies to electricity.
5. Quantification of benefits obtained in improving the producer-converter-user interface and improvement of the energy/environmental balance in pyrolysis liquids production.

Task 1 has been discussed in recent publications (Czernik & Bridgwater 2004, Bridgwater and Peacocke 2001) and hence it is only briefly dealt here. This publication mainly focuses on describing the results from task 2. Relevant results from other tasks will be incorporated as appropriate. Pyrolysis liquids offer some distinct advantages over gasification and combustion for power production:

- High energy density (>2.5-3.5 times the energy density of softwood, LHV basis),
- More easily transported and handled than the raw biomass or producer gas. Transportation of liquids is more cost effective than for raw biomass.

- The possibility to decouple solid biofuel handling from utilisation. Storability of liquid fuels for intermittent use (comparison to gaseous fuels).
- Use of pyrolysis liquid in existing boilers with modest retrofitting. Less emissions in boiler use compared to solid fuels due to better control of the combustion process.
- Intermittent power plant operation feasible (comparison to gasification and combustion power plants). Pyrolysis liquid is the least cost liquid biofuel for stationary use, and its net CO_2-balance is better than that of other bio-fuels.
- Light fuel oil may be replaced, which releases middle distillates to be used for transportation (comparison to biodiesel).
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For introducing pyrolysis liquids into widespread markets, nationally and internationally accepted liquid fuel standards and norms are needed. At present, there are no national or internationally recognized standards of fuel specifications for biomass-derived fast pyrolysis liquids. The reasons for the lack of specifications are the lack of large (> 100 t) quantities of pyrolysis liquid for long-duration field-tests, few commercially operational plants, and few commercial end users. Problems with variation in fuel oil quality of pyrolysis liquids need to be overcome.

Based on the preliminary diesel engine (Solantausta et al. 1993, 1994, 1995) and boiler tests (Hallgren 1996), an engine manufacturer, Wärtsilä NSD Oy (Finland), a potential bio-oil user, Birka Energi (Sweden, former Stockholm Energi AB), and a liquid producer Ensyn Ltd. (Canada) set the requirements that are presented in Table 1. This formed the basis for further discussions with Oilon Oy (Finland) and Fortum Oy (Finland), who also input their boiler experiences to the liquid specifications. Orenda (Canada) specified the critical properties of bio fuels (Table 2) based on their gas-turbine experience (Button 2003). Considering pyrolysis liquids some comments to the guidelines in Table 2 are:

Presented thermal stability (9. ii) cannot be obtained without a significant addition of alcohol. The average increase in viscosity (measured at 40 °C) for pure pyrolysis liquid in the test 24 hours @ 80 °C is 100 %.

Based on present knowledge the pH (8.) cannot be raised above 4 without causing a phase-separation. Some amines raise the pH above 4, but the introduction of N into the liquid would be unbeneficial for fuel use.

The meaning of Ramsbottom Carbon (11.) for pyrolysis liquids is unclear and this value cannot be much influenced.

Table 1 Specifications set by Ensyn, Wärtsilä, and Birka in early 90ies.

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

Table 2 Preliminary BioFuel Property Guidelines for the OGT2500

ID	Fuel Parameter	**Test Method**	**Units**	Guidelines
1.	Low Heating Value	ASTM D240/5291	MJ/kg	15-25
2.	Pour Point. Max	ASTM D97	˚C	15
3.	Kinematic Viscosity at 80˚C	ASTM D445 mod.	cSt	4-7
4.	Surface Tension at 80˚C, Max	D971 mod.	MN/m	30
5.	Specific Analysis, max Na+K Ca V Pb Cl S Ash	 AA[a] or ICP “ “ “ ASTM D240 ASTM D4294 ASTM D482	 ppm_w ppm_w ppm_w ppm_w ppm_w wt% wt%	 5 5 3 5 1 .02 0.05
6.	Density @ 80˚C, max	ASTM D4052	G/ml	1.20
7.	Solids Content greater than 0.1µm, max (Note: 90% solids should be less than 5.0µm in size)	ASTM D2276 (Millipore Membrane Filtration)	Wt%	0.25
8.	pH	Accumet 925 pH meter	pH	2.5-7.0
9.	Thermal Stability: Exposure for 24 hrs @ 80˚C Parameters @ 80˚C: i) Solids creation, max ii) Viscosity, max iii) Phase stability	NA	wt%	i) 0.1 wt% increase in solids content. ii) 5% increase in viscosity iii) no phase separation permitted.
10.	Water content	ASTM D95 followed by D1744	wt%	15-25
11.	Ramsbottom Carbon Residue on 10% Distillation residue, max	ASTM D5245	wt%	10

2 FUEL OIL PRODUCTION

Over the past 20 years, developments in fast pyrolysis technologies have lead to the construction and operation of plants ranging from laboratory scale to commercial/demonstration scale. A summary of current plants in operation is given in Table 3. Ensyn/Red Arrow plants produce primarily chemicals, but rest of the liquids are burnt for energy. Ensyn has also supplied large quantities of pyrolysis liquid to fuel oil use (Oasmaa et al. 1997 and 2001). Dynamotive has recently provided the fuel for Orenda's long-duration gas-turbine tests (Button 2004) and is constructing the worlds first pyrolysis oil fuelled power co-generation facility (100 t/day) to produce power and heat with an Orenda turbine. Costruction should be completed late June 2004. The feed will be wood residues from Erie Flooring and Wood Products. VTT has continuously produced liquid fuel for boiler tests (Gust 2001) and fuel oil quality studies (Oasmaa et al. 1997, Oasmaa & Peacocke 2001). Fortum Oy and Vapo Oy constructed a 500 kg/h pyrolysis plant 2001, but they stopped the development work in late 2003 due to combination of factors including: poor availability of feedstocks and a price increase of about 30%, change in taxes in Sweden on fossil fuels in CHP plants reducing the competitiveness of Forestera, higher combustion system costs than anticipated due to the high costs of industrial pumps and the poor results from using cheaper pumps, the higher than anticipated shipping costs and the focus of Fortum development work on traffic fuels.

Table 3 Operational fast pyrolysis plants (> 20 kg/h) in 2004 for the production of liquid fuels.

Organisation	Plant Capacity, kg/h	Liquid end-use
Ensyn Red Arrow	2000	Internal energy use
BTG, the Netherlands	250	Boiler tests
Dynamotive, Canada	400	Gas-turbine and boiler tests
PyTec, Germany	20	Gas-turbine tests?
VTT Processes, Finland	20	Boiler tests

Main problems in emerging of pyrolysis technologies from pilot to demonstration scale are that to make this economically viable you need to have access to large quantities of cheap biomass and government support. In Europe the biomass resource is a major problem. One of the challenges facing the industry is that pyrolysis liquids will have to compete with conventional fuel oils, which are well established and known to the end-user (utility, local grid, on-site use for heat and power, etc.). Some of the main problems in the large-scale application of pyrolysis liquids have been:

1. High solids content (> 0.5 wt%) and no universally agreed method for accurate determination of its components.
2. Inconsistent physical and chemical properties – viscosity, lower heating value, water content, number of phases and pH.
3. Irregular supply of pyrolysis liquids produced under consistent conditions
4. Lack of handling (transferring, pumping, storage) instructions and Health and Safety data
5. Lack of quality specifications. Poor fuel quality (relative to conventional fuel oils)
6. Low pH which is not acceptable in conventional fuel handling systems.

3 FUEL OIL QUALITY

Production of consistent high quality liquid has been demonstrated by Dynamotive in Canada and by Fortum in Finland. Properties of pyrolysis liquids produced in large scale (> 80 kg/h) units are presented in Table 4.

Table 4 Pyrolysis liquids properties from different feedstocks produced in pyrolysis units > 80 kg/h.

Analysis **Feedstock**	Dynamotive Pine/Spruce (Morris et al. 2000) 100% wood	Dynamotive Pine/Spruce (Morris et al. 2000) 53% wood 47% bark	Dynamotive Bagasse (Morris et al. 2000)	Forestera^{TM} Spruce (VTT data) 100% wood	Ensyn Mixed hardwood [1] (VTT data)	LFO#2
Moisture, wt %	2.4	3.5	2.1			
Particle size, mm	<1.2	<1.2	<1.2	<3		
Ash, wt%	0.42	2.6	2.9			
Bio-Oil						
Water, wt %	23.3	23.4	20.8	23.8	22	Max 0.05
Solids, wt %	<0.1	<0.1	<0.1	0.01	0.045	0
Ash, wt %	<0.02	<0.02	<0.02	<0.001	0.01	0
Nitrogen, wt %					0.2	
Sulphur, wt %					<0.01	0.5
Viscosity (20°C), cSt	73	78	57			
Viscosity (40°C), cSt				15	50@50ºC	3.4
Viscosity (80°C), cSt	4.3	4.4	4			
Density (15°C), kg/dm^3	1.20	1.19	1.20	1.19	1.18	0.876
Flash point, °C					55	Min 38
Pour point, °C					-25	Min. -6
HHV, MJ/kg	16.6	16.4	15.4		17	
LHV, MJ/kg						40
pH	2.3	2.4	2.6	2.4	2.5	
Distillability	Not distillable	Not distill.	Not distill.	Not distill.	Not distill.	Distillable
Water insolubles, wt%	25	25	24	21	50	100

[1] A part of the pyrolysis liquid has been removed for chemicals production hence the lignin content is a typically high. Analytical data is found in Oasmaa et al. (1997)

Feedstock is the main variable affecting the quality of pyrolysis liquid. Hence the properties and composition of feedstock should be followed. Considering fuel oil quality the main criterias are water (Figure 1), and solids (Solantausta et al. 2003). Both of them indicate change in feedstock properties or failures in process. The change in water indicates a change in feedstock moisture, process parameter, or an oxygen leak. Increase in solids can result from malfunctioning of cyclones. Quick response from these analyses is hence crucial for process control. In addition, liquid homogeneity should be observed during operation.

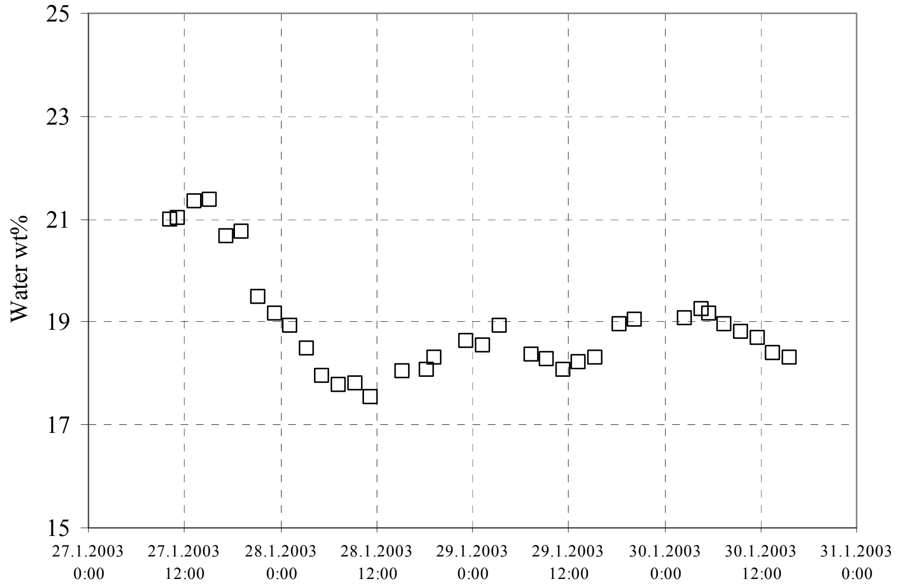


Figure 1 Follow-up of water content during pyrolysis experiment. After the replacement of the seed oil the water content evens to 18-19 wt%.

Water content is recommended to be measured by Karl-Fischer titration according to the standard ASTM E 203. In order to verify use of another sample solvent or reagent use of water addition method for calibration is recommended. In solids determination ethanol is suggested to be used for white wood liquids from softwood or hardwood. For extractive-rich liquids like forest residue and bark methanol-dichloromethane (1:1) should be used. Microscopic determination gives information on possible phase-separation or presence of solid material, e.g. extractives, inorganics, in the liquid. The homogeneity of the liquid can be verified by microscopic determination and/or by sampling from different depths and analysing the moisture content by KF titration (Oasmaa & Peacocke 2001). Criteria for poor-quality liquid product are: water content above 30 wt-% and/or duplicates differ more than 1 wt-%. Criteria for good-quality liquid product are: below 0.1 wt-% solids.

Presently, both water and solids are carried out in laboratory as separate analyses, but on-line methods are developed (Isoaho 2004, Oasmaa 2004). Water content has good correlations with density and heating value. Hence, a density meter based on Coriolis has been tested at VTT. The results are promising, but more work is needed. For more detailed quality description following analyses are suggested to be carried out: microscopic determinations, stability, inorganics in solids, water-insoluble material, extractives.

4 FUEL OIL APPLICATIONS

The majority of efforts in applications have been on pyrolysis liquids produced by Union Fenosa (1992-1996 – approx 40 t), Ensyn (1991-2003 approx 500 t), BTG (1999-2004 approx 50 t), Fortum (2002-2003 – approx 8 t), and Dynamotive (2004 – approx ? t), as these have been the only companies producing significant (tonne) quantities for supply tested by various organisations. Problems in use have arisen too often due to inconsistent liquids quality. Hence, it is necessary to have a quality control system at the liquid production site. It is expected that increasing the availability of liquids in significant quantities will lead to more boiler, engine and turbine manufacturers offering to test liquids for combustion applications.

4.1 Boiler application

Boiler work has been carried out predominantly in the EU by Fortum Oy (Finland), VTT/Oilon (Finland) and Birka Energi (Sweden). The most interesting application test (*do we include this one???*) of BTG (Netherlands) is the one of co-firing of 15 tons of bio-oil (> 1 % bio-oil of the feed) in the gas-fired power station in Harculo, The Netherlands (Venderbosch et al. 2002). The only commercial system since for over 10 years where pyrolysis liquid is used for heat generation is at the Ensyn Red Arrow Products pyrolysis plant in USA (ref). A 5 MWth swirl burner is used for combustion of pyrolysis liquid fractions and char and gas from the plant with average emissions of 17 % CO, 1.2 % NOx, and 0.2 % formaldehyde of the permitted levels (Czernik & Bridgwater 2004). Some work has been carried out in Canada, and limited results are available. Other work has been discussed in a recent review by Czernik & Bridgwater (2004).

In 2003 Fortum has successively carried out field tests with their product Forestera^{TM} in 200 kWth LFO-boilers. The emissions were good, and there was no boiler damages (Gust 2004). More than 12 m^3 of Forestera^{TM} has been combusted (Table 5), in over 1,500 cycles where the boiler function was totally automated and operated under the control of a thermostat performed to test critical components, and determine the required fuel quality. One of the more important findings of this work was that it is critical in these applications to reduce solids to < 0.1% and to ensure that inorganics in the form of ash and sand left over from the feedstock are present in concentrations less than 0.03 weight percent. There are special expensive pumps, like monopumps, which are suitable for pyrolysis liquid use. However, cheaper resistant pumps are requested for keeping the costs satisfactory low.

Firing of pyrolysis liquids in boilers of varying capacities has identified a variety of problems and issues as detailed in Table 8. Some of these can be dealt with by modifying the liquids, however, other necessitate modifications to the equipment itself. Oilon Oy has developed (Kytö et al. 2003) with Fortum a special burner head for pyrolysis liquid combustion.

Therefore for pyrolysis liquids to be used or to be acceptable for boiler applications, the following requirements must be met at the least:

- Reduce viscosity by preheating to 80 ºC but not continuously heating the liquids to this temperature as it causes secondary polymerisation reactions
- Startup and shutdown on conventional fuel
- Allow solids to settle or pressure filter/centrifuge prior to combustion < 80 ºC to remove particles

Table 5 Boiler emissions - some examples

Liquid Source	Ensyn		Union Fenosa[1]		Ensyn			Ensyn	Dynamotive	Fortum
Feedstock	Hardwood		Eucalyptus		Hardwood			Hardwood	Pine	Spruce
Solids	0.5		0.7					~0.4	0.17	0.01
Boiler	Arimax Eetta 200 kW boiler		Arimax Eetta 200 kW boiler		Water-wall utility boiler 10 MW$_{th}$			10 MW$_{th}$ boiler, Oilon Lenox GRT-5L	10 MW$_{th}$ boiler, Oilon Lenox GRT-5L	200 kW$_{th}$ LFO boiler
Experimental period, h										
O_2 (vol%)	4	6	5	6	--	--	--	3.3-3.6	3.3-3.4	
CO (ppm)	32	28	40	20	32	32	67	1-2	10-25	
NOx (ppm)	142	137	170	150	195	198	208	159-164	108	
THC	--	--	--	--	0.8	1.0	1.4			
Particulate (mg/MJ)	--	--	--	--	105	144	161	15	92	
Bacharach No.	5	5	2.5	2.8	--	--	--	2	2.8	
Reference	Gust 1997		Gust 1997		Huffman 1997			Oasmaa 2001	Oasmaa 2001	Gust 2004

[1] With additional 3wt% ethanol and 3wt% water, modified refractory in boiler to ensure complete combustion, BFB (Bubbling Fluidized Bed)

4.2 Engine application

The first work on engines was carried out by VTT on a 55 kWe Valmet engine with limited success, due to nozzle erosion by particulates in the liquids (Sipilä et al. 1996). Wärtsilä carried out single-cylinder tests (Gros 1995) and material testing (Jay et al. 1995).

Ormrod Diesels have developed significant experience on pyrolysis liquids since 1993 using a 250 kWe modified dual fuel diesel engine (Webster 2001). Liquids from Union Fenosa, BTG, Dynamotive and Ensyn have been tested. The thermal efficiency of the engine when operating on diesel fuel was 34.3 wt% and on pyrolysis liquid with pilot diesel injection 32.4 wt%. The exhaust emissions (Table 6) indicate the characteristic rise in CO and a reduction in NO_x when operating on pyrolysis liquid (JOR3-CT97-0197 Final report). Problems and possible solutions are included in Table 8.

University of Florence carried out engine tests with pyrolysis liquid emulsions. (Chiaramonti et al. 2002). They concluded that compared to straight use of pyrolysis liquid the use of pyrolysis liquid emulsions in diesel engines requires less modifications to the engines. The most important results from the tests were that the injector as well as the fuel pump should be made of stainless steel or similar material and much more research in erosion-corrosion properties of emulsions are needed.

Table 6 Engine and burner emissions (Peacocke et al. 2003)

Liquid Source	BTG			BTG
Feedstock	Mixed hardwood			
Solids (wt%9				0.35
Pilot fuel	Diesel			None
Engine & User	250 kWe Mirrlees 6 cylinder. Ormrod Diesels, UK			25 kWe Stirling Engine, FLOX® [1] burner, ZSW Germany
Pilot fuel (wt%)	7	17	100	
O_2	15	15	15.8	6-10
CO (ppm)	3475	2057	271	<35-125
CO_2 (vol%)	4.4	4.6	3.9	
NO (ppm)	240	313	510	
NO_2 (ppm)	41	77	76	
NOx (ppm)	384	266	586	20-95
SOx (ppm)	0	33	86	
THC (mg/m^3)	--	--	--	20-40
Particulate (mg/Nm^3)	--	--	--	
Reference	JOR3-CT97-0197 2001			Bandi & Baumgart 2001

[1] Flameless oxidation

For engine applications, at least the following property specifications are required:

- Solids below 0.1 wt%
- Viscosity to be adjusted to 10-20 cSt
- Maximum variation within 10%
- Improved lubricity

4.3 Turbine application

Most of the research with turbines has been carried out in Canada and USA. There has been very little turbine development work in the EU (Czernik & Bridgwater 2004). The University of Rostock (Strenziok et al. 2001) has tested pyrolysis liquids in a small commercial gas turbine type T 216 (Klöckner-Humboldt-Deutz AG, Germany) with a rated electric power output of 75 kW. Pretreatment of the liquids was required to remove all solids. The gas turbine combustion behaviour was examined in numerous tests during 1999 and 2000. The emissions were measured for both bio-oil and diesel fuel operation. When compared to diesel fuel, characteristically, the emissions of CO and NO_x were higher for bio-oil at part load operation (0.56 g/kWh CO compared to 0.13 g/kWh for diesel fuel and 0.37 g/kWh NO_x compared to 0.18 g/kWh for diesel).

Since 1995 Orenda Aerospace Corporation (Canada) has actively worked on the application of pyrolysis liquid in gas turbine combustion in a 2.5 MW_{el} class GT2500 engine. During 2004 Orenda (Orenda Aerospace Corporation, Canada) has carried out long-duration turbine tests (Table 7) with three various pyrolysis liquids from large producers. Orenda (Button 2003 and 2004) has set up preliminary specifications (Table 2), through which they evaluate the suitability of pyrolysis liquid for the gas turbine.

5 FUEL OIL SPECIFICATIONS AND STANDARDS

An important issue in commercialisation of fast pyrolysis for the production of heat and power is the need for pyrolysis liquid specifications. ASTM and similar organisations in respective countries have established the specifications for standard fuel oils. They define property ranges for different classes of fuels marketed for different applications. Standards are required also for fast pyrolysis liquids to assist in their uptake into fuel infrastructure. At present, there are no nationally or internationally recognised standards of fuel specifications for biomass-derived fast pyrolysis liquids.

Based on feedback from potential end-users (Gust 1997, Button 2004, Oasmaa & Meier 2003) specifications were addressed to be tighter with maximum variation of ± 10 %. Stability, homogeneity, water, solids, and ignition are the most critical properties. Stability (measured as viscosity increase by time) is necessary for proper adjustment of pumps, nozzles, burners and other equipment. Slight phase-separation may results in poor combustion. High (above 30 wt%) water content yields high particulate emissions (Oasmaa et al. 2001). These emissions can be decreased to certain extent by using a support fuel and optimising the atomisation viscosity by temperature adjustment. Solids content of pyrolysis liquid is detrimental for the equipment, especially for injectors and turbine blades, also results in high particulate emissions. The limit for flash point is defined according to legislation for transportation and storage.

An approach was made to specify only the properties, which can be influenced (Table 7). These include homogeneity, water and solids contents, stability, and flash point. As fuel oil specifications cover a range of applications from boilers to turbines, the grade of fuel required also increases, for a wider range of physical and chemical properties. This means that properties important for one application may not be as important for another. The size of unit will also influence the properties of the liquids, as smaller domestic boilers require liquids with low viscosities, while larger commercial boilers may accept a liquid with a higher viscosity. Properties of pyrolysis liquids, problems, and possible solutions are listed in Table 8. Additional data has been included to address the wide spectrum of properties that may be required in different fuel applications and to assist in the design of process equipment and power generation systems.

Table 7 Issues relating to using pyrolysis liquids as a fuel in boilers, engines and turbines

Property	Specification to be met	Current value	Problem	Solution
Variation	Max 10%	> 50%	Changes in feed and in process parameters	Quality control system
Water	< 27 wt%	18-40	Inhomogeneity, phase separation (> 30 wt% water)	Feedstock drying Increase (< 50 °C) of condensation temperature
Solids	< 0.01wt%	≤ 0.5 wt%	Wear of injectors Increased liquids instability High CO emissions	Homogenous particle size distribution of the feed Hot vapour filter Three cyclones on reactor exit Liquids filtration/centrifugation
Ash	< 0.01 wt%	< 0.1 wt%		Feedstock choice Hot vapour filter Three cyclones on reactor exit Liquids filtration/centrifugation
Homogeneity	Single-phase	Variation	Uneven liquid quality	Feedstock moisture < 12 wt% Liquid water content < 27 wt%
Stability	Max 100% increase in viscosity in ageing test (24h 80°C, viscosity measurement @40°C)	50-150%	Changes in liquid properties during storage and use	Alcohol addition
Flash point	Depends on country	> 40 °C	Safety regulations for transportation	Adjusting the liquid condensation temperature
pH	FDS	2-3	Corrosion of fuel lines	All pipework, vessels, and gaskets must be acid resistant
LHV	FDS	16-19 MJ/kg	50% lower than fuel oil Does not auto-ignite at start-up	Increase pump pressure to injectors Increase diameter of fuel lines Dual fuelling required (%)
Viscosity	FDS	> 50 cSt @20°C	Too high for most fuel injectors	Preheat liquids to reduce viscosity Add co-solvent (alcohol) Use of emulsions
Lubricity	FDS	Not determined	Build up of lacquer on the injection needle and fuel pump plunger	Lubricity/flow properties improvement Additives

FDS = Cannot be influenced/specified. Value to be included in Fuel Data Sheet

Based on all feedback from end-users as well as the research carried out earlier prelimary specifications are presented in Table 8.

Table 8 Preliminary specifications for pyrolysis liquids

Property\Application	Boiler		Gas turbine	Diesel engine
Size class	$0.2\text{-}1\ MW_{th}$	$1\text{-}10\ MW_{th}$	$2.5\ MW_{e}$	
Variation	Max 10%			Max 10%
Homogeneity	single-phase		single-phase	single-phase
Stability	single-phase		single-phase	single-phase
Water, wt %	Max 27		Max 25	Max 27
Char, wt %	Max 0.05		Max 0.25	0
Flash point, °C	Min 40			0
Ash, wt %			Max 0.05	0
Si, wt %	Max 0.01			0
Particle size, µm			90% < 5	
Viscosity @80°C, cSt			Max 7	
LHV, MJ/kg			Min 15	
Lubricity				To be improved

6 STANDARDISATION

Standardization work under CEN is ongoing for biomass feedstocks (CEN/TC 343/W63). CEN has also approved (CEN www-pages) the proposal made by SIS, Sweden (Lundström & Olaru 2002) for the initiation of the standardization of alternative fuels, where pyrolysis liquid is included. The aim is the creation of a CEN/BT/WG liquid and gaseous Alternative Fuels with the task to initiate a European collective view of the general strategy for improvement of standardisation on alternative fuels. Acting as an investigation group the WG aims primarily at:

- Analyzing and listing the need of European and global standards regarding specifications, classification systems, test methods, etc for fuels given priority to,
- Making an inventory of which specifications, classification systems, test methods, etc already exist in CEN, ISO, national standardization bodies and other international and national organisations (one of these organisations is IEA), and last but not least in industry,
- Analyzing from this inventory the possibility to use wholly or partially existing specifications, test methods, etc. and
- Analyzing and listing the need of future research development regarding test methods and proposing how to solve this need

The working group will provide CEN with a proposal on how to proceed with the standardization of alternative fuels. The final report of the BT/WG 149 Alternative Fuels will be given to CEN/BT by end-2004.

7 CONCLUSIONS

There is encouraging operational experience on fast pyrolysis liquids in boilers, and turbines, which create confidence to implementation of heat or CHP plants. Production of even quality liquids has been demonstrated by Dynamotive in Canada and Fortum in Finland. First long term testing of liquids in boilers and turbines have been successively carried out. However, technical difficulties concerning the use of the liquids still remain due to lack of long-term research and there are insufficient commercial pyrolysis plants producing liquids for long duration testing. Related to fuel oil quality of pyrolysis liquids, some properties can be changed by improving the quality of the fuel, and some not where the solution is to change the hardware (Table 8).

Biomass fast pyrolysis technologies have seen a slow growth over the past 4 years, primarily due to low oil costs and low base electricity prices throughout most of Europe. The demand for a renewable liquid fuel for heat and power generation has therefore been reduced and other competing technologies have come to the fore, namely for transport fuels, which have a higher market value. There are a range of incentives in the EU for renewable energy technologies, although the level and form of support vary significantly and in some cases do not make any distinction in the level of technological development in renewable energy technologies, with all being classed as commercially available.

Some harmonisation in support measures is required. Due to the limited deployment and development of the technology, there is not enough empirical data to allow full norms and standards for biomass derived fast pyrolysis liquids to be determined. 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 be in the replacement of domestic heating fuel. There is the opportunity for liquids to enter the power generation market for domestic applications, but only in selected countries.

Further long-term test work is required to establish performance and operability data for engines and turbines on pyrolysis liquids. Pyrolysis liquids can compete on 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, opportunities exist for pyrolysis liquids, however, further work is required to establish its long term performance.

8 SUMMARY

The commercialization of biomass-derived pyrolysis liquids for use in heat and power applications depends on the ease of use and acceptability of the fuel by the end user and equipment providers and on the cost. One of the aims of the study was to derive standards for biomass derived pyrolysis liquids, based on a consensus between equipment providers (boilers, engines and turbines) and the liquids producers. Five basic properties (homogeneity, water content, solids content, stability, flash point) for the liquids are used as the primary criteria for pyrolysis liquid evaluation. Specific values are proposed to ensure that pyrolysis liquids meet a minimum grade acceptable for use as a fuel oil in boilers and engines. Data on emissions from boilers, engines and turbines are presented. First long-duration data is available to allow further more detailed specifications on secondary properties to be made, or define standards for liquids in turbines. The aim is to ensure that a realistic set of specifications are determined to allow the introduction into existing fuel infrastructures and markets.

Part 2 Development of Test Methods

1 INTRODUCTION

Extensive work has been done in characterization of physical properties of fast pyrolysis liquids (Milne et al. 1990, Elliott, 1983, McKinley et al. 1994, Rick &Vix, 1991, Fagernäs, 1995, Oasmaa et al. 2001, Oasmaa et al, 2003). Because of significant differences between pyrolysis liquids and mineral oils, modifications to standard methods have been made and new methods developed.

One of the most critical property of pyrolysis liquids is their instability. During storage the properties of pyrolysis liquids change (Czernik 1994, Diebold % Czernik, 1997). Major reactions take place within the first 3-4 months of storage. Due to condensation/polymerisation reactions the molecular weight of the liquid increases, which is seen as an increase in viscosity (Meier 1999, Oasmaa & Kuoppala, 2003). In order to predict the increase in viscosity during the storage, an accelerated aging test was developed. In the test pyrolysis liquid a certain temperature is kept at for a certain time and the change in viscosity compared to the original viscosity is measured. Other proposed indicators for measuring stability include change in Mw or in carbonyl groups.

Determination of chemical composition of pyrolysis liquids is very complicated because pyrolysis liquids are not distillable and only 25-35 wt.% of the liquid can be quantified by the conventional GC/MSD method (Meier 2003). The liquid consists of 20-30 wt.% water, which can be determined by the Karl-Fischer titration. The amount of lignin-derived material in the pyrolysis liquid can be measured by water extraction Piskorz et al., 1988, Oasmaa et al., 1997, Scholze & Meier, 2001.

2 TEST METHODS FOR PHYSICAL CHARACTERISATION

In order to use pyrolysis liquids as heating fuels, fuel specifications are needed. Based on feedback from end-users and other research (Peacocke et al. 2003) following properties have been suggested to specify: water, solids, Si, homogeneity, stability, and flash point. These properties can be influenced during pyrolysis liquid production. Properties, which cannot directly be influenced but are important for liquid end-use, like viscosity, heating value and density, are included in fuel data sheet. For determining the specifications, uniform test methods as base for standards, are needed.

2.1 Water

Water is thought to be chemically dissolved in pyrolysis liquids. The change in water indicates i.e. a change in feedstock moisture, process parameters, or an oxygen leak. It can easiest be adjusted by affecting the feedstock moisture. Water content affects for example to heating value, density, and viscosity of the liquid (Fig. 1).

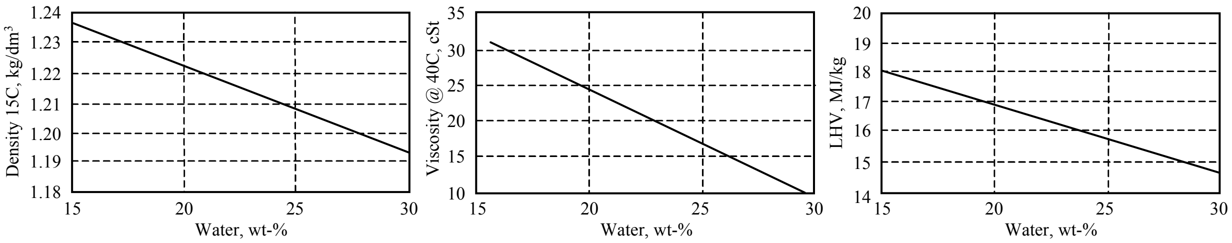


Fig. 1 Approximate correlation of water content to density, viscosity, and heating value of pyrolysis liquids (Peacocke et al. 2003).

Water content of pyrolysis liquids is recommended to be measured by Karl-Fischer titration according to the standard ASTM E 203. In the method a weighed sample (about 0.2 g) is injected into the sample solvent (chloroform:methanol, 1:3) and the water is titrated using a titration reagent (e.g. 2-methoxy ethanol). The system is calibrated with pure water (25 µm distilled water), water standards (e.g. 5mg water/ml MERCK 1.09259 250), and using the water addition method. In the water addition method known amounts of water is added to pyrolysis liquid and the measured water values are compared to calculated ones. Accuracy of the titre is re-checked on daily basis. Titration is done in triplicates.

2.2 Solids and its components

Solids of pyrolysis liquids originate from feedstock ash, pyrolysis char, and sand from reactor bed or from dirt of feedstock (Fig. 2). The particle size of the solids is typically below 10 µm. Ash includes metals originating from feedstock and sand from feedstock and/or from reactor bed. Solids content can be influenced e.g. using homogenous feedstock size, efficient cyclones, or hot-vapour-filtration.

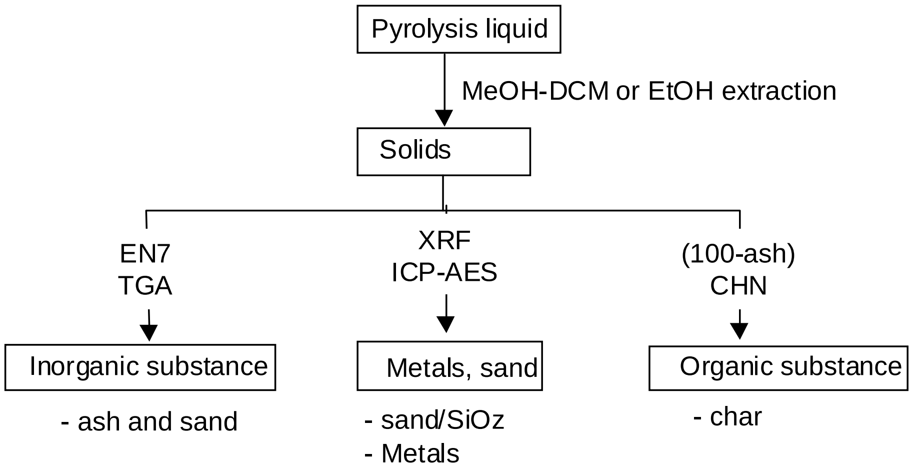


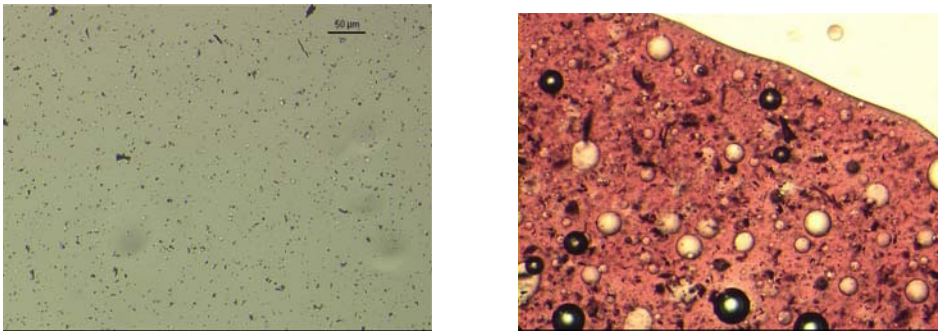
Fig. 2 Characterisation of solids of pyrolysis liquids.

Solids content of pyrolysis liquids is recommended to be measured as insoluble material in MeOH (methanol)-DCM (dichloromethane)-solution (1:1). In the method the sample size (1, 5, 10 g) is determined in order to obtain 10 - 20 mg of dry solid residue. A representative sample of pyrolysis liquid is dissolved in excess (10 folds) of solvent. The solution is filtered through a 1 µm pore size filter (i.e. Schleicher & Schüll, GF50, ф 47 mm, glass fibre papers). The filter paper is first soaked on to the filter by the solvent used. The sample bottle, filter and residue are washed with solvent until the filtrate is clear. The filter paper with the residue is air-dried for 15 min and in an oven at 105 °C for 30 minutes, cooled in a desiccator and weighed. The solids content is calculated based on the original pyrolysis liquid sample. Maximum 10 wt.% difference between duplicates can be accepted. Ethanol can also be used for white wood liquids if similar solid content is obtained. This solvent does not dissolve properly all extractives in bark-containing liquids.

Si and metals can be analysed from ash either by XRF (X-Ray Fluoresence spectrometry) or by ICP (Inductively Coupled Plasma Emission spectrometry).

2.3 Homogeneity

High water content has a negative effect on homogeneity of pyrolysis liquids. During production the homogeneity of the liquid is controlled by visual observations. Microscopic determination gives information (Fig. 3) on possible phase-separation or presence of solid material, e.g. extractive crystals or inorganics, in the liquid.



A B

Fig. 3 Good (A with very small char particles) and poor (B with water droplets) quality pyrolysis liquids.

A 7-day standing test is recommended for homogeneity verification. In the method a homogenous sample is let to stand for a week in room temperature and the water content from different depths are determined by KF titration. Criterias for poor-quality liquid product are: water content above 30 wt-% and/or duplicates differ more than 1 wt%.

2.4 Stability

Main chemical changes during storage happen within the first 3-4 months. Main changes include the increase in water-insoluble material, which increases the average molecular weight and is observed as an increase in viscosity. Stability of pyrolysis liquids can be monitored by following any of these parameters. They all correlate with each others (Oasmaa et al. 2003). The use of accelerated ageing test (24 h @80°C, viscosity @40°C) is recommended as a rapid test for measuring the stability. The increase in viscosity in these conditions correlate with the change in a year at room temperature storage. The accelerated aging test correlates well with the chemical changes in the liquid (Oasmaa % Kuoppala, 2003).

In the method pyrolysis liquid is mixed properly and let to stand, until the air bubbles are removed. 90 ml of the sample is poured in 100 ml tight glass bottles (or 45 ml in 50 ml bottles). The bottles are firmly closed and pre-weighed before placing to 80 °C in a heating oven. The bottles are re-tightened a few times during the heating-up period. After 24 hours the closed sample bottles are cooled under tempered water, weighed, and analyses are performed. The samples are mixed and measured for viscosity and water. The viscosity of the liquid at 40°C is measured as kinematic viscosity by the standard method ASTM D 445. The water content is analysed by Karl Fischer titration according to ASTM E 203. For obtaining representative results the test should each time be carried out exactly by the same way.

2.5 *Flash point*

The test method ASTM D 93 covers the procedure for the determination of flash point of petroleum products by manual Pensky-Martens closed cup apparatus. The method is applicable to all petroleum products with flash point above 40 °C and below 360 °C except fuel oils. Flash point is the lowest temperature at which application of an ignition source causes the vapours of the sample to ignite under specified conditions of test. This method has been used with pyrolysis liquids. However, the flash point cannot be measured for pyrolysis liquids at 70–100°C, where the evaporation of water suppresses the ignition (Oasmaa et al., 1997). The flash point of pyrolysis liquid does not correlate with its ignition properties as with petroleum fuels.

2.6 Viscosity and pour point

Viscosity of pyrolysis liquids can be affected indirectly by changing the water content or by solvent addition. Viscosity of pyrolysis liquid is recommended to be determined as kinematic viscosity according to the standard ASTM D 445. Considering the behaviour of pyrolysis liquids no prefiltration is done and Canon-Fenske capillaries are recommended because of the better flow direction of the sample (Oasmaa et al., 1997). Based on round robin the viscosity is suggested to be determined both at 20 and 40 °C.

Dynamic viscosity by rotating viscotesters can also be used for measuring the viscosity of pyrolysis liquid. However, it is not as accurate as kinematic viscosity. The evaporation of the sample can cause too high viscosity values, especially above 60°C, and hence a cover should be used on the sample cup.

Test method for pour point is described in the standard ASTM D 97. After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3 °C for flow characteristics. The lowest temperature at which movement of specimen is observed is recorded as pour point. When measuring the pour point of pyrolysis liquid preheating of sample should be excluded due to thermal instability of the liquid

2.7 Heating value

The heating value is measured as higher heating value (HHV) by DIN 51900. The high water content of pyrolysis liquids may lead to poor ignition, and therefore a fine cotton thread is used as a wick. The heat content of the thread is subtracted from the result. The lower heating value (LHV) is calculated from HHV and the hydrogen content (ASTM 529192) by equation (1). No subtraction of free water has to be done because the water in the pyrolysis liquid cannot be removed by centrifugation as for heavy petroleum fuel oils.

$$\text{LHV [J/g]} = \text{HHV [J/g]} - 218.13 \times \text{H\% [wt.\%]} \qquad (1)$$

The heating value of pyrolysis liquids is a function of water content of the liquid (Fig. 4). It can also be seen that the extractive-rich top phase of forestry residue owns a high energy content and its dissolution in the bottom phase would be beneficial.

2.8 *Density*

The density of pyrolysis liquid can be determined with digital density-meter according to standard ASTM D 4052. The method covers the materials which can be handled as liquids between 15 °C and 35 °C. Vapor pressure of the samples should be lower than 80 kPa and viscosity below 15 000 mm^2/s. The method is based on the effect of change in the mass of the sample tube in oscillating frequency. The density of pyrolysis liquids correlate well with the water content of the liquid (Oasmaa & Peacocke, 2001). The density of the extractive-rich top phase of forestry residue liquid is lower than that of the bottom phase.

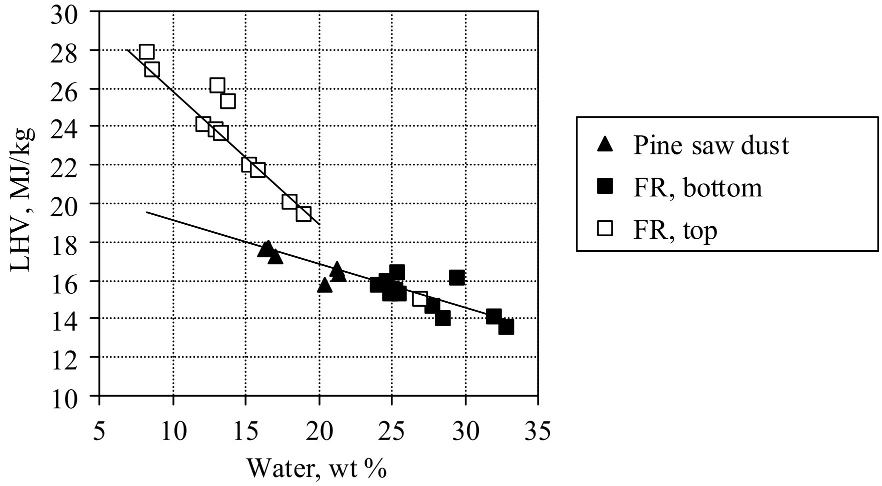


Fig. 4 Correlation of water content to the heating value of pyrolysis liquids from pine and forestry residue (FR) (Oasmaa et al. 2003).

3 METHODS FOR CHEMICAL CHARACTERISATION

3.1 *Volatile compounds by solid-phase micro-extraction*

A rapid and inexpensive technique for the isolation of volatile compounds is the Solid Phase Micro Extraction (SPME). It has two important functions: extracting analyses and desorbing them into analytical instruments. A fused silica fiber, coated with an adsorbing material, is exposed into the head space of the sample. After the sampling time is over, the fiber is drawn back into the needle and the needle is introduced into the hot injector of a gas chromatograph. The fused silica fiber is pushed out of the needle so that adsorbed compounds can be desorbed from the fiber through the heat of the injector. A typical chromatogram is shown in Fig. 5. Run conditions are described in GC/FID paragraph. The compounds analyzed from a hardwood pyrolysis liquid are listed in Table 9.

Table 9 Identified compounds in SPME analysis

No.	Compound
1	acetic acid methyl ester
2	acetic acid
3	Acetol
4	Furfural
5	unknown silicon compound from SPME needle
6	2-hydroxy-3 methyl-2-cyclopentene
7	Phenol
8	Guaiacol
9	guaiacol TMS derivative
10	4-methyl-guaiacol
11	4-ethyl-guaiacol
12	unknown silicon product from SPME needle
13	cis-isoeugenol
14	Syringol
15	Eugenol
16	trans-isoeugenol
17	4-methyl-syringol

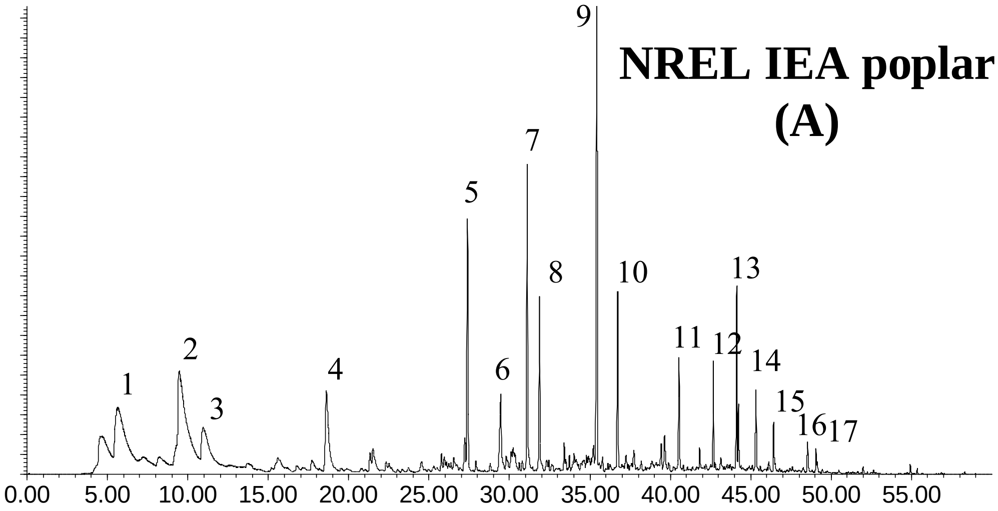


Fig. 5 Head space analysis of volatiles of a liquid from fast pyrolysis of poplar wood.

3.2 Volatile carboxylic acids and alcohols

Acidity of pyrolysis liquids can be determined by measuring the pH. The fouling of electrodes causes error to the result. Hence pH is recommended to be used mainly for determination of pH level (Oasmaa & Meier, 2003).

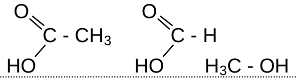
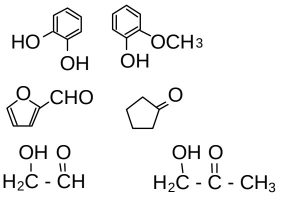
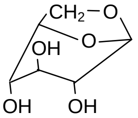
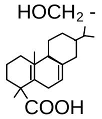
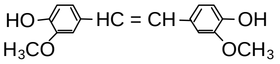
Quantitative analysis of volatile carboxylic acids and alcohols can be carried out by gas chromatography using the above mentioned method for whole pyrolysis liquids.

Alen et al. 1985, developed a method for quantitative determination of C_1-C_6 hydroxy acids from alkaline cooking liquors. This method was modified at VTT for determination of C_1-C_6 carboxylic acids in acidic aqueous phase of pyrolysis liquids. The quantitative analysis of alcohols in the water fraction can be carried out by GC/FID. For alcohol determination an HP-Innowax crosslinked polyethylene glycol capillary column (60 m * 0.25 mm i.d., film thickness 0.25 µm) is used. The difference of the various methods can be seen in Table 10.

3.3 Extractives

Extractives (Table 10) of pyrolysis liquids are recommended to be determined as n-hexane-soluble material. There is no solvent, which could dissolve specifically the extractives. With pyrolysis liquids a part of lignin monomers (guaiacols) dissolve in n-hexane.

Table 10 Average chemical composition of softwood (pine saw dust, forestry residue) pyrolysis liquids based on solvent extraction (Oasmaa & Kuoppala 2003). Solids are included in DCM-insolubles.

FRACTIONS	wt %	COMPOUND TYPES	C	H	N	O
	(wet basis)		wt % (dry basis)			
WATER-SOLUBLES	75-85					
Acids, alcohols	5-10		36.0	6.0	0	58.0
Ether-solubles	5-15		60.0	6.0	0.1	33.9
Ether-insolubles	30-40		46.0	6.3	0.3	47.4
Water	20-30		0	11.1	0	88.9
WATER-INSOLUBLES	15-25		66.2	6.6	0.3	26.9
n-Hexane-solubles	2-6	$CH_3-(CH_2)_n-CO_2H$ n = 10-30 $HOCH_2-(CH_2)_n-CO_2H$ n = 10-28 	77.4	10.4	0	12.2
DCM-solubles	5-10		68.1	6.7	0.4	24.7
DCM-insolubles	2-10	Degraded lignin	64.1	5.9	1.5	28.4

In the method homogenous pyrolysis liquid (2 g) which water content is known is weighed into an Erlenmeyer bottle. n-Hexane is added and the bottle is closed and shaken for an hour in a mixer. The sample is let to stand for settling of the phases and the top hexane layer is decanted into a weighed evaporation flask. The extraction (20 ml of n-hexane) is repeated and the sample is shaken over night. Hexane extract is decanted off and added into the evaporation flask. Hexane is evaporated in mild conditions (≥ 40 °C, 40 - 200 mbar) and the residue is dried in a vacuum desiccator under constant pressure. The result is calculated of the dry matter. Quantitative analysis of extractives is demanding and is suggested to be done in a laboratory specialized for these analyses.

3.4 Water-insolubles

Water-insoluble material is determined by extracting pyrolysis liquid with water. Two methods are compared in Table 11.

Table 11 Water-insolubles of a spruce pyrolysis liquid by three variations of water-insoluble method.

	RTI	VTT
Bio-oil/water	1:2	1:50
Biooil. g	1-2	2
Duplicates	12	5
Average	**24.6**	**22.0**
Stdev	4.2	1.0

In the simple and fast RTI method (Piskorz et al. 1988) a weighed 1-2 g sample of homogenous pyrolysis liquid is mixed with 2-4 g weight amount of warm (40 °C) distilled water. The precipitate/separated phase is filtered out (after cooling) using a micro-syringe filter (25 mm, 0.45 µm, Chromatographic Specialties or similar). The clear filtrate is titrated by the KF method to find the new water concentration. The water-insolubles (WIS) is calculated using equation (2).

$$X_{ins} = (X_{aqx} - X_{pyrolysis\ liquid} - ((M_w/M_{pyrolysis\ liquid}) * (1-X_{aqx})))/X_{aqx} \qquad (2)$$

$$\text{WIS (wt.\%)} = 100 * X_{ins}$$

where

$X_{pyrolysis\ liquid}$ = Mass fraction of pyrolysis liquid
X_{aqs} = Mass fraction of aqueous extract
X_{ins} = Mass fraction of precipitated water-insoluble fraction
M_w = Mass of distilled water added, g
$M_{pyrolysis\ liquid}$ = Mass of pyrolysis liquid, g

The accuracy of KF titration is the most determining factor in this method for obtaining repeatable results. Hence, attention should be paid on proper calibration of KF water titration. Several duplicates are recommended.

Little lower results were obtained using VTT method. This method is used as a pretreatment method for chemical characterisation. In the method 2 g of pyrolysis liquid is extracted with water using water:pyrolysis liquid ratio of 1:50. The water-insoluble fraction is removed by filtration and the dried residue is weighed.

The results using the IWC method are even lower. In the method very efficient mixing (7000 rpm) is used for the pyrolysis liquid-water (1:10) mixture, which causes emulsification of extractives and small lignin fragments into the aqueous phase. Very clean lignin powder is obtained. This fraction is similar to the DCM-insoluble HMM (high-molecular-mass) lignin fraction.

RTI´s method is recommended for fast (even though several duplicates are made) determination of water insolubles (WIS). The VTT method is suggested to be used if the sample of WIS is needed. IWC method produces purest lignin sample by removing the extractives from the WIS.

3.5 *Quantitative characterisation of individual components*

In the literature often wet chemical methods such as solvent extraction or acid/base reactions are used to separate bio-oil fractions prior to gas chromatographic separation of the volatile bio oil constituents. However, high resolution gas chromatography (HRGC) can be used to separate most of the monomeric components in bio-oils without any sample treatment, just by using the proper concentration and separation conditions. Reliable and reproducible results can be obtained using the following method:

prepare a sample concentration of ca. 5 % based on the organic fraction of the bio-oil by adding acetone with a known amount of internal standard. If necessary, filter the solution through a 0.45µ filter. GC conditions are as follows:
Injection: split injection, split ration 30:1; temperature 250 °C, constant flow 1 mL, 114 kPa helium pressure
Oven: 45 °C for 4 min const., heating rate 3 °C/min to 280 °C, hold 20 min.
Detector: FID, 280 °C, Column: 60m x 0.25mm, 0.25µm film thickness, phase composition: 14%-cyanopropyl-phenyl-86%-dimethylpolysiloxane (1701).
The GC-eluted part of pyrolysis liquid is typically 25-40 wt.% of wet liquid. About 70-90 % of the eluted fraction can be identified.

A typical GC chromatogram is presented in Fig. 6.

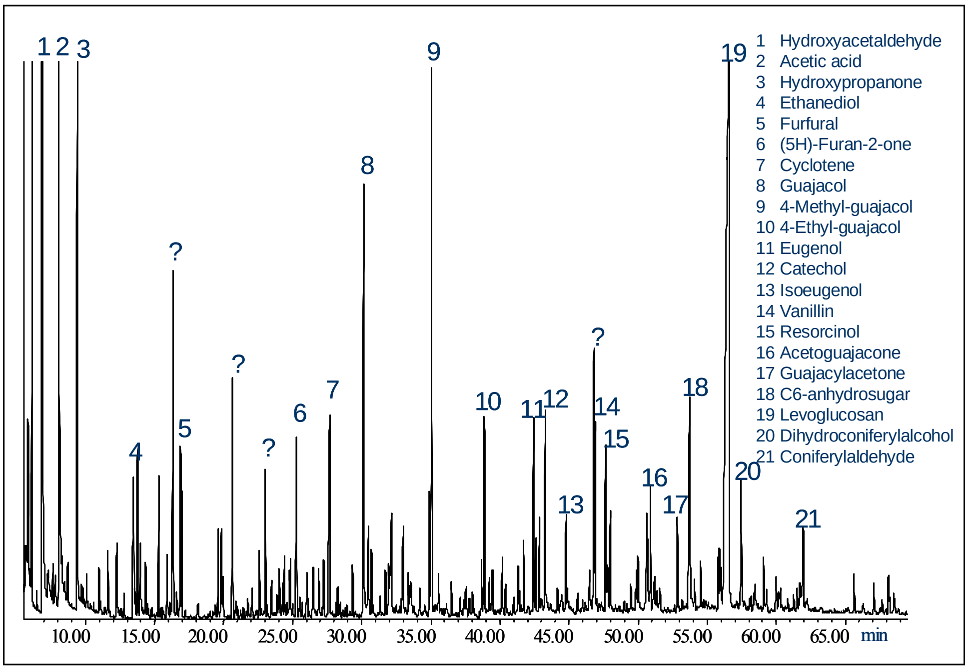


Fig. 6 Typical bio-oil gas chromatogram from fast pyrolysis of spruce wood

3.6 *HPLC*

High Performance Liquid Chromatography (HPLC) is one of the best ways to determine polar and higher molecular mass compounds. The resin columns have unique ability to retain and separate neutral molecules such as sugars and alcohols. So far the best HPLC column has been Aminex HPX-87. The recommended conditions for HPLC are as follows:

Column: high performance cation exchange resin in hydrogen form, Aminex HPX-87, 300*7.8 mm, (Biorad Laboratories) with equivalent guard column (similar resin columns: Rezex, Shodex, PE Brownlee, Polypore-H)

Mobile phase:	0.007 N H_3PO_4
Flowrate:	0.6 ml/min
Mode:	isocratic
Temperature:	30 °C
Internal standard:	n-propanol
Detector:	Waters R 401 Differential Refractometer, 35 °C

Some retention times of key components and relative (relative to n-propanol) response factors (Waters R 401 Refractometer) are given in Table 12.

Table 12 Retention times of key components and relative (to n-propanol) response factors (Waters R 401 Refractometer).

Compound	Retention time (min)	Relative response factor
Cellobiosan	8.16	0.63
Glyoxal	9.95	0.50
Methylglyoxal	11.61	0.66
Hydroxyacetaldehyde	11.91	0.65
Levoglucosan	12.35	0.63
Formaldehyde	13.59	0.91
Formic Acid	14.0	1.46
Diacetyl	15.44	1.33
Acetic Acid	15.49	1.23
Propylene Glycol	16.80	Nd
Acetol	17.90	1.73
Methanol	19.10	4.32
Ethanol	21.40	1.42
Propanol	26.85	1
Glucose	8.85	0.58
Mannose	9.42	0.62
Xylose	9.50	0.62
Galactose	9.52	0.60
Arabinose	10.47	0.62

3.7 Carbonyl group determination by oximation

Aldehydes and ketones participate in ageing reactions during storage. Hence, it has been suggested to use carbonyl group content as a stability indicator. The carbonyl group determination (Meier, 1999) is based on the quantitative reaction of hydroxylamine hydrochloride with a variety of aldehydes and ketones in the presence of pyridin. The function of pyridine in the reaction system is to force oxime formation to completion. The acid liberated in the form of pyridine hydrochloride is determined by titration and is a direct measure of the amount of carbonyl groups originally present in the sample. Due to the specific oximation reaction other oil compounds do not interfere and a routine analysis is possible. Typically, the carbonyl content for a fresh pyrolysis liquid is in the range of 4 - 6 mol carbonyl/kg liquid.

3.8 Composition by solvent fractionation

In the solvent fractionation pyrolysis liquid is divided into water-soluble (WS) and water-insoluble (WIS) fractions. The water-soluble fraction is analyzed for volatile carboxylic acids, alcohols, ether-soluble (ES) fraction (aldehydes and ketones), water, and ether-insolubles (EIS, ‘sugars’). The water-insoluble fraction consisted mainly of lignin-derived materials of varying molecular mass distributions, extractives, and solids.

The water-soluble fraction is further extracted with diethylether. Diethylether-solubles and diethylether-insolubles are evaporated (≤ 40 °C) and residues are dried and weighed. Ether-solubles is calculated by subtracting the amounts of carboxylic acuds, alcohols, water, and ether insolubles from WS fraction.

Water-insolubles are divided by dichloromethane (DCM) extraction further into two fractions having different molecular size distribution. Dichloromethane-insoluble material is powder-like high-molecular-mass (MM 1050 Da, dp 2.3) lignin-derived material. There are no GC-eluted compounds. Solids are included in this fraction. Dichloromethane-soluble fraction consists of low-molecular-mass lignin material (Mw 400 Da) and extractives. GC-eluting compounds of this fraction are poorly water-soluble lignin monomers (guaiacol and catechol derivatives) and lignin dimers (stilbenes).

In the solvent extraction scheme a part of the ether-solubles were lost when the extract was evaporated. The compounds are mainly small aldehydes (acetaldehyde, 2-furaldehyde, 5-methylfurfurale, glycolaldehyde), and ketones (1-hydroxy-2-propanone, 1-hydroxy-2-butanone, 2-cyclopenten-1-one, 1-acetyloxypropan-2-one, 5H-furan-2-one). These compounds are mainly ether-soluble and hence are included in that fraction in the composition diagramme. The volatile compounds were analysed as a function of time by GC/MSD for the water-soluble fraction at IWC (Germany) according to the method described above. The ether-solubles (WS-EIS-acids-alcohols) measured by the solvent fractionation scheme correlated well with the amount of ether-solubles quantified directly from the original pyrolysis liquid by GC/MSD during the 12 months of storage. About 60 compounds were analyzed in the ether-soluble fraction.

3.9 Molecular mass determination

The average molecular mass (Mw) can be used as a stability indicator and is determined by GPC using successive RI and UV detectors. Tetrahydrofuran (THF) is used as a solvent. Columns used include HP PLgel 10.000, 500 and 50 Å in series (VTT). The sample is dissolved in THF to a fixed concentration of 10 wt.%.

3.10 Elemental analysis

Elemental analysis of carbon, hydrogen, and nitrogen is recommended to be carried out according to ASTM D 5291. In the method, carbon, hydrogen, and nitrogen are simultaneously determined as gaseous products (carbon dioxide, water vapour, and nitrogen). For wood pyrolysis liquids the accuracy of carbon and hydrogen is good, but poor for nitrogen. This is due to low concentrations of nitrogen (≤0.1 wt.%) in wood liquids and to the low nitrogen detection limit (0.1 wt.%) of the method. Pyrolysis liquids from straw and forest residue contain higher (0.2–0.4 wt.%) concentrations of nitrogen and hence stdev is lower. Because of the small sample size, the reproducibility of the elemental analysis is dependent on the homogeneity of pyrolysis liquids. At least triplicates are recommended, if the sample is inhomogeneous.

Chlorine and sulphur can be determined by CEF after ashing and dissolution of the sample according to ASTM D 4208. Metals are analyzed by ICP or XRF. Oxygen is obtained as a difference.

4 SUMMARY

For introducing new fuel into markets norms and standards are needed. Uniform test methods form the base for standardisation. In this paper a recommendation for test methods for determination the fuel oil quality of pyrolysis liquids is made. Main methods include water content by Karl-Fischer titration, solids content as methanol-dichloromethane extraction, homogeneity as water distribution, stability by accelerated ageing test at 80 °C for 24 hours, and water-insolubles by water extraction. As a criteria for good quality fuel (stays homogenous minimum six months of storage) the ratio of water:water-solubles:water-insolubles of (25:50:25) ± 5 % is suggested.

Suggested test methods for physical characterization are summarised in Table 13. For chemical characterization various methods can be used depending on the purpose. Most critical is the verification of the method used. For controlling the fuel oil quality determination of water, and WIS are suggested as most significant factors (Fig. 7). As a rule of thumb the ratio of water, water-solubles and water-insolubles should be 25:50:25. Large variation (approximately ± 5%) from this rule may result in problems with phase stability.

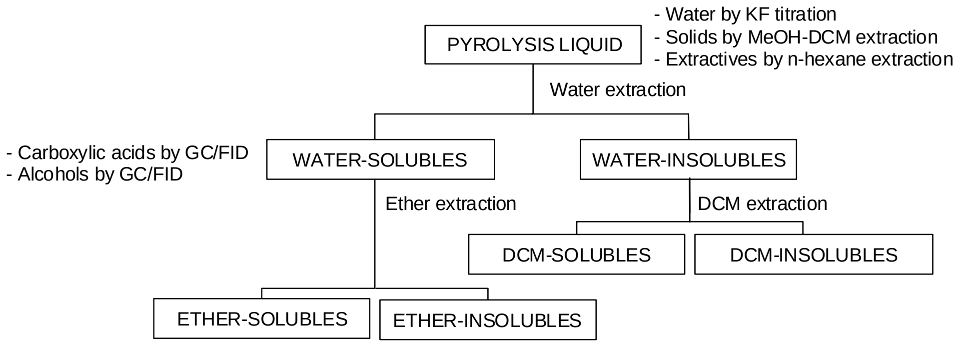


Fig. 7 Fractionation scheme for chemical characterization (Oasmaa & Kuoppala 2003).

Table 13 Analytical methods for wood-based pyrolysis liquids (Oasmaa 2003, Oasmaa & Peacocke 2000)

Analysis	Unit	Applied standard	New method/ modification	Equipment	Instructions
Water	wt.%	ASTM E 203			1
Solids	wt.%		MeOH-DCM-insolubles		2
Si	wt.%			XRF, ICP, AAS	3
Metals	wt.%			XRF, ICP, AAS	3
Homogeneity	wt.%		7-day standing test		4
Stability test	wt.%		80 °C, 24 hours		5
Flash point	°C	ASTM D 93			6
Ash	wt.%	EN 7			7
CHN	wt.%	ASTM D 5291			8
Sulfur and chlorine	wt.%			Capillary electrophoresis	9
Viscosity (20, 40 °C)	cSt	ASTM D 445		Cannon-Fenske Glass capillaries	10
Viscosity (20, 40 °C)	mPas			Rotational viscometry	11
Density (15 °C)	kg/dm 3	ASTM D 4052			12
Pour point	°C	ASTM D 97			13
Heating value	MJ/kg				
HHV	MJ/kg	DIN 51900			14
LHV	MJ/kg				

1 Karl-Fischer titration. Methanol-trichloromethane (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.%). Stabilization time 30 s.

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 bark-free wood liquids, MeOH-DCM for forestry residue liquids.

3 Wet combustion as a pre treatment method. In samples with a large amount of silicates, Si can precipitate as SiO_2 during the sample pre treatment. This may yield an error in Si. For accurate determination of Si, the sample should be ashed by dry combustion and a fusion cake prepared from the ash.

4 90 ml (45 ml) pyrolysis liquid in 100 ml (50 ml) tight glass bottles, heating in a heating oven. Measurement of increase in viscosity and water. Viscosity determination at 40 °C according to ASTM D 445.

5 Elimination of air bubbles before sampling.

6 Controlled evaporation of water to avoid foaming.

7 Proper homogenization. For forestry residue liquids careful rolling of the sample bottle. As large a sample size as possible. Triplicates.

8 Sample pre treatment by combustion according to ASTM D 4208.

9 Cannon-Fenske viscometer tubes at room temperature and for non-transparent liquids, Ubbelohde tubes may be used for transparent liquids. No prefiltration of the sample if visually homogeneous. Elimination of air bubbles before sampling. Equilibration time 15 minutes.

10 Precise temperature measurement. Cover on the sample holder above 40 °C.

11 Careful mixing of foam-prone forestry residue liquids in order to avoid air bubbles.

12 No preheating of the sample.

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

Part 3 Round Robin Test with Pyrolysis Liquids

1 INTRODUCTION

Biomass pyrolysis liquids differ significantly from petroleum-based fuels in both physical properties and chemical composition. These liquids are typically high in water and solids, acidic, have a heating value of about half of that of mineral oils, and are unstable when heated, especially in air. Pyrolysis liquids contain about 50 wt.% oxygen (ca. 40 wt.% of dry matter), while mineral oils contain oxygen in ppm levels. Due to these differences, the standard fuel oil methods developed for mineral oils are not always suitable as such for pyrolysis liquids.

Research on analysing physical properties of pyrolysis liquids has been carried out since the 1980s (Elliott 1983, Chum & McKinley 1988, McKinley 1989, Milne et al. 1990, Czernik 1994, McKinley et al. 1994, Peacocke et al. 1994). The first round robin on pyrolysis liquids was organised in 1988 as part of the IEA (International Energy Agency) Voluntary Standards Activity led by BC Research (McKinley et al. 1994). The main conclusions were: the precision for carbon was excellent, while hydrogen, oxygen by difference and water were more variable, and oxygen by direct determination was poor. It was recommended to use a wider variety of samples in the future studies.

Two separate round robins were initiated in 1997: one within EU PyNe (Pyrolysis Network) and the other within IEA PYRA (Pyrolysis Activity). The objective of the EU PyNe round robin was to compare existing analytical methods without any restrictions. Two pine pyrolysis liquids were analysed by eight laboratories for viscosity, water, heating value, elemental analysis, pH, solids, and density. The accuracy for hydrogen, water by Karl-Fischer, and density were good. The xylene-distillation method was stated to yield erroneous results. High variations were obtained for nitrogen, viscosity, pH, and solids. Ethanol was concluded to be more suitable for solids determination than acetone (Meier 1998).

The main objective of the IEA PYRA round robin was to determine the inter-laboratory precision and methods applied for elemental composition, water, pyrolytic lignin and main compounds. Two poplar liquids were analysed by the IEA PYRA participants. It was concluded that the precision of carbon and hydrogen was very good, sample handling plays a very important role in the C, H analysis, water by Karl-Fischer titration was acceptable, but should be checked carefully, and the method for the determination of pyrolytic lignin should be improved (Bridgwater et al. 1999).

Since then a lot of progress has been made both in the field of pyrolysis liquid production (Bridgwater 2003) and liquid analysis (Oasmaa et al. 1997, Meier & Scholze 1997, Sipilä et al 1998, Oasmaa & Meier 1999, Meier 1999, Brigdwater et al. 1999, Oasmaa & Peacocke 2001, Oasmaa 2003).

Twelve laboratories participated in the round robin discussed in this paper. The aim was to compare the analyses, not the pyrolysis liquids. Four different types of pyrolysis liquids were provided from various producers. Based on the feedback from previous round robins it was decided to add instructions for handling and analysis. The numbers of laboratories are randomly choosen.

2 MATERIAL AND METHODS

Pyrolysis liquids used for the round robin test are shown in Table 14. The criteria of liquid quality was reasonable homogeneity. The sample size for each laboratory was set to one liter.

Table 14 Pyrolysis liquids for RR

Producer No.	Feedstock	Additional information
1	85% pine, 15% spruce feedstock moisture 7 %	production date: 07.10.1999 pyrolysis temp. 460 °C fluid bed
2	softwood mixture (spruce and fir) feedstock moisture 10-12 % particle size 0.8-1.1 mm	production date: 11.01.2000 pyrolysis temp. 500 °C rotating cone
3	softwood bark (1/3 fir and 2/3 spruce with traces of hardwood bark feedstock moisture 12 %	production date : 29.09.1999 pyrolysis temp. 510 °C vacuum pyrolysis
4	hardwood mix	transported bed

The homogeneity of pyrolysis liquids was verified by analysing the water gradient in the shipping containers. A maximum of 10 wt.% variation was accepted. The liquids were then mixed thoroughly by intensive shaking and divided into 1 liter sample bottles for shipping to the laboratories.

2.1 Instructions

Instructions for laboratories were established as follows:

- After receiving the sample please indicate date of arrival.
- Assure that the sample is being stored at refrigerator conditions.
- Stability tests with analyses should be carried out within a week after receiving the sample and all other analyses within a month. Please indicate date of analyses.
- Before sampling let the sample reach room temperature, then shake it to ensure homogeneous sampling.
- After usage please store the sample again in a refrigerator.
- Please report dates of arrival and analyses, sample size used, all duplicates, methods used, possible difficulties, and suggestions.

The proposed analytical methods for the round robin test are shown in Table 15.

Table 15. Analytical methods for round robin test

Property	Method	Reporting unit
Water content	Karl Fischer Titration	wt.% water based on wet oil
Viscosity	Capillary or rotary viscosimeter, 2 temp. @ 20 and 40°C	cSt @ 20°C and 40 °C
Solids	Insolubles in ethanol, filter pore size 3µm or lower	wt.% based on wet oil
pH	Use pH-meter	pH unit
Stability[1]	Store samples for 1) 6 h @ 80 °C, 2) 24 h @ 80 °C, and 3) 7 days @50 °C, viscosity @ 20 and 40 °C and water by K-F titration	cSt wt.% water based on wet oil
Elemental analysis	Elemental analyzer (complete oxidation)	wt.%C, wt.%H, wt.%N, wt.%O, based on wet oil
Pyrolytic lignin	add 60 ml oil to 1 L of ice-cooled water under stirring, filter and dry precipitate below 60 °C	wt.% based on wet oil
GC	column type DB 1701 dimensions: 60m x 0.25 mm film thickness: 0.25 µm injector: 250 °C, split 1:30 FID detector: 280 °C oven programme: 45 °C, 4 min const., 3 °C/min. to 280 °C, hold 20 min. sample conc.: 6 wt.%, solvent acetone	

[1] Pyrolysis liquid sample is mixed properly and let to stand until the the air bubbles are removed. 90 ml of the sample is poured in 100 ml tight glass bottles (or 45 ml in 50 ml bottles). The bottles are firmly closed and pre-weighed before placing in a heating oven for a certain time. The bottles are re-tightened a few times during the heating-up period. After a certain time the closed sample bottles are cooled rapidly under cold water, weighed, and analyses are performed. The possible difference in the weights before and after the test is an indication of leakage and the test should be repeated if the net weight loss is above 0.1 wt.% of original weight. The samples are mixed and measured for viscosity and water. The viscosity of the liquid at 20 and 40 °C is measured as kinematic viscosity according to ASTM D 445. The water content is analysed by Karl Fischer titration according to ASTM D 1744 (Oasmaa et al. 1997).

$$\text{Viscosity index} = \frac{(\nu_2 - \nu_1)}{\nu_1}$$

$$\text{Water index} = \frac{(\omega_2 - \omega_1)}{\omega_1}$$

ν_1 = viscosity of the original sample, cSt

ν_2 = viscosity of the aged sample, cSt

ω_1 = water content of the original sample, wt.%

ω_2 = water content of the aged sample, wt.%

3 RESULTS AND DISCUSSION

3.1 Homogeneity of the samples

The homogeneity of liquids No. 2-4 verified by water distribution (Table 16) was good. Pyrolysis liquid No. 2 was inhomogenous due to its high water content. The liquid producer pointed out some problems during production, which were later on at least partly solved. However, this liquid was included to the round robin testing as a difficult liquid.

Table 16. Water determination of the RR liquids at different levels in the shipping containers

Sample		Water, wt.% before mixing	Water, wt.% after mixing containers
No. 1 I	top	20.9	21.1
	middle	21.1	
	bottom	20.7	
No. 1 II	top	19.1	
	middle	20.2	
	bottom	21.6	
No. 2	top	32.1	28.3
	middle	32.4	
	bottom	20.3	
No. 3 I	top	13.5	15.7
	middle	13.9	
	bottom	13.7	
No. 3 II	top	15.2	
	middle	14.9	
	bottom	15.9	
No. 4	top	20.8	20.4
	middle	20.5	
	bottom	19.0	

3.2 Water

Variation in water content was acceptable (Table 17).

Table 17. Water content determined by Karl-Fischer titration

Liquid\Laboratory	1	2	3	4	5	7	8	9	10	11	12	Average	Stdev
No. 1	20,2	20,4	21,1	20,8	21,1	21,0	21,2	23,0	20,9	21,8	20,3	21,1	0,8
No. 2	29,6	29,9	30,5	29,4	31,1	30,8	31,0	35,0	30,9	30,2	30,8	30,8	1,5
No. 3	15,9	15,5	15,7	15,6	15,3	14,5	16,5	16,0	15,5	16,4	15,7	15,7	0,5
No. 4	19,4	20,0	20,4	20,2	20,5	20,4	21,1	21,0	19,9	20,8	20,1	20,3	0,5

Some laboratories got systematically high (No. 9) or low (No. 1) results. This may be due to calibration errors (water equivalent, wrong standards) or fading titration end-point. If the results of laboratories No. 2 and No. 9 are excluded the stdev decreases from 0.5-1.5 to 0.4-0.6. Method checking by use of standard solutions and application of the water addition method [**Error! Bookmark not defined.**, **Error! Bookmark not defined.**] for system calibration are recommended. Also triplicates are recommended to be carried out.

3.3 pH

pH values varied approximately by ± 0.3 units (Table 18).

Table 18. pH of RR pyrolysis liquids

Liquid\Laboratory	1	2	3	4	6	8	9	10	12	Average	Stdev
No. 1	2,3	2,3	2,3	2,3	1,9	2,3	2,2	2,4	2,4	2,3	0,16
No. 2	2,5	2,7	2,5	2,5	2,3	2,5	2,5	2,6	2,6	2,5	0,11
No. 3	2,8	3,0	2,8	2,8	2,4	2,9	2,7	2,9	2,7	2,8	0,16
No. 4	2,5	2,7	2,6	2,4	2,5	2,6	2,5		2,4	2,5	0,10

Two laboratories obtained for each liquid either the highest (No. 2) or the lowest (No. 6) values of all others. This may be due to inadequate calibration (e.g. wrong pH range, altered standards), or fouling of electrodes. If these values are excluded the stdev decreases from 0.10-0.16 to below 0.10. The pH measurement is a rapid method for determining the acidity level of pyrolysis liquids. However, it is not recommended to be used as indicator for accurate follow-up for changes in acidity.

3.4 Solids

Solids content measured as ethanol insolubles for pyrolysis liquids No. 1, 2, and 4 were quite similar if the systematically high results of one laboratory are excluded [Table 19].

Table 19. Solids content of pyrolysis liquids measured as ethanol insolubles

Liquid\Laboratory	1	2	3	4	7	9	10	Average	Stdev
No. 1	0,11	0,07	0,07	0,05	0,27	0,07	0,05	0,10	0,08
No. 2	0,04	0,04	0,04	0,03	0,26	0,04	0,07	0,07	0,08
No. 3	1,19	0,29	0,86	1,52	1,14	0,85	1,27	1,02	0,40
No. 4	0,43	0,43	0,39	0,39	0,47	0,39	0,47	0,42	0,04

Possible reasons for these too high results of laboratory No. 7 include inadequate washing and/or drying of the solid residue. If the results of laboratory No. 7 and all results of No. 3 liquid are excluded the stdev decreases from 0.04-0.4 to 0.01-0.03. Ethanol is not powerful enough for liquids from bark (No. 3 liquid) or forest residues, because extractives with non-polar character do not dissolve well in polar solvents such as alcohols. Solids content for No. 3 liquid determined with a mixture (1:1 vol.%) of MeOH (methanol) and DCM (dichloromethane) was 0.02 wt.% (measured at VTT.

Eventhough the sub-micron particles of char may not be included into solids, solids content analysis using ethanol for white wood liquids can be accepted being accurate enough for its present purpose. However, proper washing and drying of the sample is essential. Microscopic analysis of the liquids showed a high amount of particles of about 1µm. Hence, the pore size of filter paper is recommended to be maximum 1 µm. A mixture of a polar and a neutral solvent, like methanol (or ethanol) and dichloromethane, is recommended. Because of health and safety reasons ethanol can be used as a solvent when possible.

3.5 *Carbon, hydrogen, nitrogen*

The results of carbon and hydrogen analyses (Table 20, Table 21) were good.

Table 20. Carbon analysis of RR liquids

Liquid\Laboratory	2	3	4	6	8	9	11	Average	Stdev
No. 1	44,6	43,9	44,3	44,9	46,3	43,9	44,9	44,7	0,82
No. 2	37,5	37,0	37,5	37,4	37,1	36,5	36,3	37,0	0,48
No. 3	50,6	50,2	52,6	52,6	50,0	50,1	54,0	51,4	1,60
No. 4	47,2	46,8	47,2	47,9	47,5	45,9	46,8	47,0	0,63

Table 21. Hydrogen analysis of RR liquids

Liquid\Laboratory	2	3	4	6	8	9	11	Average	Stdev
No. 1	7,2	7,6	7,0	7,1	6,6	7,5	7,4	7,2	0,34
No. 2	7,5	8,0	7,2	7,5	7,7	8,0	7,8	7,7	0,30
No. 3	6,9	7,1	6,6	6,8	7,0	7,1	7,3	7,0	0,22
No. 4	6,9	7,2	6,3	6,8	7,2	7,3	7,2	7,0	0,35

Table 22. Nitrogen analysis of RR liquids

Liquid\Laboratory	2	3	4	6	8	9	11	Average	Stdev
No. 1	0,10	0,20		0,05	0,00	0,1	0,50	0,16	0,18
No. 2	0,10	0,33		0,05	0,10	0,1	0,50	0,20	0,18
No. 3	0,20	0,54		0,26	0,40	0,3	0,50	0,37	0,14
No. 4	0,10	0,33		0,05	0,10	0,2	0,50	0,21	0,17

Variation in nitrogen (Table 22) is mainly due to low detection limits for nitrogen, but possible also due to wrong N-standards. The sample size for CHN analysis is suggested to be as large as possible and at least triplicates should be carried out. The systematically high values of one laboratory (No. 11) may be due to method calibration. The N content of the used standard is recommended to be checked before each measurement.

3.6 *Viscosity*

The viscosity results at 20 °C and 40 °C were good (Table 23). No systematic errors were observed. Maximum and minimum values were obtained randomly. The largest error was obtained with high viscous No. 2 liquid at 20 °C. High solids content, large particle size of solids, high viscosity, and inhomogeneity of pyrolysis liquid may cause problems when using capillary tubes. In these cases the viscosity is recommended to be measured as dynamic viscosity in a closed-cup rotaviscotester. Laboratory No. 8 measured the viscosity as dynamic viscosity.

Table 23. Viscosity of RR liquids. Laboratory No. 8 values at 20°C have been converted to cSt by dividing the density and included to the comparison.

Viscosity@20°C, cSt

Liquid\Laboratory	1	2	3	6	7	8 (mPas)	9	10 (@25°C)	Average	Stdev
No. 1		105	106	96	89	130	48	89	92	23
No. 2		26	26	25	24	28	29	27	25	2
No. 3		1296	1282	1075		1406	1330	839	1020	509
No. 4		1614	1842	1443	1379	2245	1930	1103	1667	225

Viscosity@40°C, cSt

Liquid\Laboratory	1	2	3	6	7	8 (mPas)	9	10	11	Average	Stdev
No. 1	28	27	27	31	27		31	29	32	29	2
No. 2	9	10	10	11	10	12	11	13	11	10	1
No. 3	196	196	194	210	200	225	216	189	229	198	10
No. 4	229	204	225	234	202	265	248	203	243	220	17

If the values are converted to cSt, values similar to others are obtained. White wood pyrolysis liquids possess Newtonian behaviour (Leroy et al.1988) hence viscosity can be measured either as kinematic or as dynamic viscosity. Bark/forest residue liquids also possess Newtonian behaviour after the extractive-rich top phase has been removed. The small standard deviation at 40 °C is possibly due to the high temperature sensitivity of pyrolysis liquids. The effect of one degree C error causes a higher error in viscosity at 20 °C than at 40 °C.

3.7 Stability index

The results of liquid No. 2 were excluded, because of the unhomogeneity of the liquid. High water content leads to phase-separation. Thus, the viscosity measurement as kinematic viscosity gives erroneous values. The stability results for other liquids are not acceptable (Table 24, Table 25, Table 26). There are several reasons for that. The instructions for the round robin test were not specific enough. In addition, because the stability is measured as a change in viscosity an error in viscosity measurement causes a larger error in the stability index. The test conditions should be reproducible. The calibration of the heating oven should be checked. Weighing of samples before and after the test indicate possible leaks from the sample and too high results are obtained. The authors wish to express, that in some cases (No. 9), the instructions had not been delivered to technicians, which led to mistakes in handling resulting in erroneous results.

There are no significant differences in stdev of various stability test. However, the 24 hours test at 80 °C is recommended due to the fact that the ageing obtained (1 year @ room temperature) under these conditions is not anymore sensitive to small errors in test conditions, because major ageing reactions happen during the first 3-4 months of storage. It is recommended to measure the viscosity at 40 °C because the stdev is lower at higher temperature (see Table 23).

Table 24. Viscosity index. Test conditions: 6 hours at 80 °C

6h 80°C
Viscosity@20°C

Liquid\Laboratory	1	2	3	7	8	9	10	Average	Stdev
No. 1		0,78	0,18	0,27	0,19	2,68	0,06	0,69	1,0
No. 3		0,08	0,07		0,03	0,25	-0,07	0,07	0,1
No. 4		0,24	0,18		0,14	0,60	0,01	0,24	0,2
Viscosity@40°C									
No. 1	0,60	0,65	0,13	0,23	0,10	0,32	0,07	0,30	0,2
No. 3	0,96	0,05	0,06	0,12	-0,02	-0,01	-0,03	0,16	0,4
No. 4	0,52	0,10	0,07	0,17		0,30	0,06	0,20	0,2

Table 25. Viscosity index. Test conditions: 24 hours at 80 °C

24h 80°C
Viscosity@20°C

Liquid\Laboratory	1	2	3	7	8	9	10	Average	Stdev
No. 1		0,78	0,74	1,63	0,70	5,68	0,65	1,70	2,0
No. 3			0,58		0,66	1,39	0,33	0,74	0,5
No. 4		2,22	1,72		1,57	2,41	0,72	1,73	0,7
Viscosity@40°C									
No. 1	0,49	0,65	0,60	0,69	0,33	0,98	0,48	0,60	0,2
No. 3	0,38	0,42	0,39	1,01	0,32	0,81	0,06	0,48	0,3
No. 4	0,48	0,80	0,74	0,86	0,70	1,38	0,49	0,78	0,3

Table 26. Viscosity index. Test conditions: 7 days at 50 °C

7 days 50°C
Viscosity@20°C

Liquid\Laboratory	1	2	3	7	8	9	10	Average	Stdev
No. 1			0,58	1,12	0,17	3,08	0,59	1,11	1,2
No. 3			0,35		0,09	1,38	0,62	0,61	0,6
No. 4			0,65		0,07	0,86	0,63	0,55	0,3
Viscosity@40°C									
No. 1	0,49		0,40	0,45	0,03	0,40	0,41	0,36	0,2
No. 3	0,36		0,25		0,04	0,85	0,49	0,40	0,3
No. 4	0,45		0,37	0,57	0,05	0,57	0,50	0,42	0,2

Chemical characterization was performed by four laboratories.

3.8 Water-insolubles

The large variation (Table 27) in water-insolubles ("pyrolytic lignin") content can be explained by the method choosen. In the method (Table 15) vigorous mixing (6,000 rpm) should be provided in order to avoid formation of a sticky precipitate derived from extractive material.

Table 27. Pyrolytic lignin fraction of RR liquids

Liquid\Laboratory	2	3	5	8	9	10	12	Average	Stdev
No. 1	23	13	28	21	25	32	32	25	6,7
No. 2	9		18			6	2	9	6,7
No. 3	37	30	46	40	49	59	45	44	9,5
No. 4	39	32	55	63	60	84	47	54	17,1

The application of the method yields pure lignin powder, when most of the poorly water-soluble extractives and small lignin fragments are emulsified with the aqueous phase. However, only few laboratories had the possibility to use this type of mixing. When "normal" mixing/shaking is provided the water-insoluble fraction contains beside the lignin material also extractives (Oasmaa & Kuoppala 2003). Proper washing is therefore utmost important. Possibly the high results of laboratory No. 10 are caused by insufficient washing. Hence, water-insolubles should be better defined and a simple determination method provided [i].

3.9 Organic Acids

Three laboratories used GC and one HPLC for the determination of organic acids. Two laboratories (9 and 12) using GC, derivatized the samples to their benzylic esters prior to analysis. Derivatization increases the volatility of compounds and hence the amount of eluting compounds from the GC column increases. The use of this pretreatment method gave the most comprehensive list of organic acids (see labs. 9 and 12 in Table 28). As expected, formic and acetic acid form the bulk part of the acids with a portion of 70-80 %. However, there is a systematic error in the method applied by laboratory No. 12 giving far too high acid concentrations.

It is concluded from the results that derivatization of the organic acids to benzylic esters (Alén et al, 1985) is recommended prior to GC analysis because this technique increases the volatilization of the acids during injection into the gas chromatograph. When derivatized formic acid (CHCOOH) is detected as a sharper peak and can be properly quantified. However, with respect to acetic acid it can be concluded that derivatization is not required and lab. 9 (with derivatization) got similar results as lab. 3 (without derivatization).

The acid number (see Table 29) is a measure of the acidity of the liquid and might correlate with corrosion problems. From these results it is concluded that with pyrolysis liquids the acid number does not correlate with the content of organic acids because also phenolic compounds are neutralized with KOH.

Table 28. Determination of acids (wt.% based on wet liquid)

	No. 1				No. 3				No. 4				No. 2			
Laboratory No.	**9**	**12**	**3**	**5**	**9**	**12**	**3**	**5**	**9**	**12**	**3**	**5**	**9**	**12**	**3**	**5**
Formic acid	0.29	9.35		5.3	0.48	8.26		3.3	0.52	11.32		2.3	0.9	13.55		4.8
Acetic acid	2.7	7.84	3.31	5.0	2.05	5.26	2.17	2.5	4.6	11.2	5.27	3.9	4.01	8.98	3.23	5
Acrylic acid	0.05	0			0.08				0.05	0.02			0.06	0.22		
Propionic acid	0.17	0.63			0.19	0.35			0.31	0.26			0.21	0.64		
Iso-butyric acid	0.02	0.35			0.03	0.32			0.02	0.1			0.02	0.11		
Methacrylic acid	0.01				0.01				0.01				0.01			
N-Butyric acid	0.07	1.89			0.1	2.75			0.2	1.66			0.08	2.07		
Lactic acid	0.18				0.08				0.09				0.21			
Glycolic acid	0.34	0.62			0.82	1.32			0.36	0.25			0.44	0.69		
Crotonic acid	0.04	0			0.06				0.04	0.05			0.08	0.06		
Valeric acid	0.01	0.66			0.02	0.27			0.01	0.67			0.01	0.09		
Tiglic acid	0.01	0.06			traces	0.26			traces				0.01	0.01		
4-Methylpentanoic acid	0.01				0.02								0.01			
3-Hydroxypropanoic acid	traces				0.04				0.02				0.02			
2-Oxobutanoic acid	0.17				0.15				0.13				0.18			
Levulic acid	0.11				0.23				0.11				0.12			
Benzoic acid	0.02				0.05								n.d.			
Hexanoic acid		0.14				0.16				0.16				0.05		
TOTAL	**4.2**	**21.5**	**3.3**	**10.3**	**4.4**	**19.0**	**2.2**	**5.8**	**6.5**	**25.7**	**5.3**	**6.2**	**6.4**	**26.5**	**3.2**	**9.8**

Table 29. Determination of the acid number (mg KOH/g oil)

No. 2	60.3
No. 1	67.9
No. 3	72.1
No. 4	80.3

3.10 Aldehydes, ketones and alcohols

These compounds were analyzed both by GC and HPLC (see Table 30). Laboratory 9 transformed the aldehydes and ketones into hydrazones by derivatization with dinitrophenylhydrazine (DNPH) prior to analysis with GC and HPLC. By this method also low volatile aldehydes such as formaldehyde and acetaldehyde could be detected. Laboratory 12 used a packed column to detect formaldehyde and acetaldehyde. Some basic error has happened with the method used by laboratory No.12 resulting in too large concentrations.

Table 30. Determination of aldehydes, ketones, and alcohols (wt.% based on wet liquid)

	No. 1				No. 3				No. 4				No. 2			
Laboratory No.	9	12	3	5	9	12	3	5	9	12	3	5	9	12	3	5
Formaldehyde	0.84	8.92		3.3	0.51	2.6		1	0.25	5.23		1.4	1.15	9.37		4.1
Acetaldehyde	0.14	1.88			0.004	1.1			0.01	1.34			0.17	1.67		
Hydroxyacetaldehyde		3.32	6.42	7.7		1.09	3.18	3.2		1.81	3.34	2.9		6.89	8.2	11.1
Glyoxal		0.24		2.4		0.33		1.5		0.67		1		0.91		2.1
Acetol		2.07	7.82	7.1		0.84	3.17	1.8		1.48	3.65	1.8		3.28	7.1	7.3
1-Hydroxy-2-butanone			0.31				0.17				0.17				0.27	
2-Hydroxy-2-cyclopentene 1-one			0.46				0.1				0.06				0.3	
2-Hydroxy-3-methyl-2-cyclopentene-3-one			0.5				0.52				0.32				0.43	
Propionaldehyde	0.05				0.01				0.01				0.03			
Acetone	0.08	0.21			0.01	0.27			0.02	0.27			0.05	0.18		
Furfural	0.49	0.2	0.81		0.39	0.15	0.47		0.36	0.16	0.65		0.31	0.2	0.54	
(5H)-Furan-2-one			0.6				0.53				0.32				0.54	
5-Hydroxymethylfurfural			0.52				0.83				0.23				0.49	
Methanol		1.03				0.07				0.39				0.91		
Ethanol		0.09				0.01				0.06				0		
2-Propanol		0.37				0.06				0				0.25		
Butanol		2.85				0.8				1.29				3.15		
MEK		0.37			0.007	0.46			0.01	0.1			0.02	0.37		
TOTAL	**1.6**	**21.6**	**17.4**	**20.5**	**0.9**	**7.8**	**9.0**	**7.5**	**0.7**	**12.8**	**8.7**	**7.1**	**1.7**	**27.2**	**17.9**	**24.6**

3.11 Sugars

Determination of sugars was performed by three laboratories only (see Table 31). Laboratories 12 and 5 used HPLC and laboratory 3 GC for the determination of levoglucosan which is the most important anhydrosugar in pyrolysis liquids. There is some consistency between laboratory 12 and 3 although they used different methods.

Table 31. Determination of sugars (wt.% based on wet liquid)

	No. 1			No. 3			No. 4			NO. 2		
Laboratory No.	12	3	5	12	3	5	12	3	5	12	3	5
Levoglucosan	3.98	4.83	7.5	4.59	4.74	8.4	3.06	4.14	2.9	4.41	3.31	5.5
Glucose							0			0		
Xylose	0.14						0					
Cellobiosan			2.3			0.7						1.8
TOTAL	4.1	4.8	9.8	4.6	4.7	9.1	3.1	4.1	2.9	4.4	3.3	7.3

3.12 *Phenols*

Phenols were analyzed by three laboratories using GC with the internal standard calibration method (see Table 32).

Table 32. Determination of phenols (wt.% based on wet liquid)

	No. 1			No. 3			No. 4			NO. 2		
Laboratory No.	9	12	3	9	12	3	9	12	3	9	12	3
Phenol	0.1	0.07	0.07	0.44	0.16	0.31	0.26	0.1	0.14	0.15	0.04	0.06
Guaiacol	0.54	0.16		0.37	0.17	0.37	0.18	0.05	0.16	0.51	0.11	0.38
o,m,p-Cresols	0.23	0.17	0.11	0.75	0.4	0.49	0.32	0.13	0.16	0.2	0.06	0.04
4-Methylguaiacol	0.83		0.8	0.36		0.61	0.13		0.18	0.59		0.48
4-Ethylguaiacol	0.24		0.24	0.14		0.15	0.05		0.08	0.11		0.12
Vinylguaiacol			0.13			0.07						0.1
Eugenol	0.29	0.06	0.22	0.12	0.02	0.06	0.07	0	0.06	0.21	0.03	0.15
4-Propylguaiacol	0.2		0.07	0.05			0.07			0.11		0.03
1,2-Benzenediol	0.13			0.91			0.1					
iso-Eugenol	0.79	0.54	0.69	0.46	0.5	0.36	0.07	0.05		0.34		0.36
Syringols		0.13		0		0.58	0.26	0	1.81		0.09	
Vanillin	0.23	0.31	0.34	0.17	0.19	0.17	0.07	0.32	0.17	0.16	0.25	0.33
Coniferylaldehyde	0.36		0.36	0.09		0.07	0.06		0.11	0.27		0.42
TOTAL	3.9	1.4	3.0	3.9	1.4	3.2	1.6	0.7	2.9	2.7	0.6	2.5

Laboratory No. 9 and 12 extracted phenols with ethyl acetate prior to analysis, whereas laboratory No. 3 injected the pyrolysis liquid directly. There is fairly good consistency between lab. No. 9 and 3 results although they used different methods. The lower valus of lab. No. 12 compared to the results of No. 9 may be due to inadequate ethyl acetate extraction.

3.13 *Polyaromatic hydrocarbons (PAH)*

The knowledge of the PAH content is absolutely necessary in order to use the pyrolysis liquids in the market. PAH´s were determined only by laboratory No. 9 using both HPLC and GC (see Table 33). Samples were fractionated on silica with different solvents. The diethyl ether fraction was used for analysis. The data show the big range of PAH content which can be attributed to the pyrolysis process conditions such as temperature and residence time. The amount of PAH was high for pyrolysis liquid No. 4, and it is pointed out to pay more attention to the analysis of toxic compounds in the liquids. The producer of liquid No. 4 commented that the high PAH may be due to contamination with another fuel (heavy oil).

Table 33. Determination of polyaromatic hydrocarbons (PAH) in ppm

	No. 1	No. 3	No. 4	No. 2
Acenaphtylene	0.3	1.3	34	0.1
Acenaphtene	0.2	1.3	8.7	0.1
Fluorene	2.2	7.8	30	0.5
Phenanthrene	2	8.4	52	0.5
Anthracene	0.8	2.7	16	0.1
Fluoranthene	0.6	2.8	39	0.4
Pyrene	0.8	0.3	40	0.4
Benzo(a)anthracene & chrysene	0.7	2.5	37	0.4
Benzo(b)- and benzo(k)fluoranthene	0.2	0.2	23	0.2
Benzo(a)pyrene	0.3	0.6	20	0.1
Indeno(1.2.3cd)pyrene	0.2	0.1	16	0.1
Benzo(ghi)perylene	0.1	0.1	11	0.1
Dibenzo(ah)anthracene	0.1	0.1	7.4	<0.1
Total	8	28.2	334.1	3

4 CONCLUSIONS AND RECOMMENDATIONS

In general, the repeatability of the physical analyses was good. Karl-Fischer titration should be used for analysing water in pyrolysis liquids, pH measurement is prone to errors and it is recommended to be used only for determining the pH level.

Kinematic viscosity is applicable to white wood pyrolysis liquids because of its accuracy and the Newtonian behaviour of these liquids. For extractive-rich liquids the Newtonian behaviour should be checked by using a closed-cup rotary viscotester. The error in viscosity also causes an error in the stability index. Stability index needs more specific instructions. Another simple test method for stability may be needed. In the case of inhomogeneous liquids kinematic viscosity and stability index give erroneous results.

The elemental analysis for carbon and hydrogen is accurate. The variation in nitrogen is due to the fact that the nitrogen content of white wood pyrolysis liquids is close to the detection limit of the equipment for nitrogen. In addition, the standards used may not have contained proper concentrations of nitrogen. The solids content using ethanol as a solvent is accurate for white wood liquids. However, for extractive-rich liquids a mixture of a polar (methanol, ethanol) and a neutral (dichloromethane) solvent should be used.

Generally, the results of chemical characterization were not very consistent. It is highly recommended to prepare standard solutions with known amounts of compounds for quantitative analyses. It seems that each laboratory uses its own technique and a lot of work and adaptation will be necessary to harmonize the methods.

There was large variation in pyrolytic lignin results. The most likely reason for problems is the behaviour of poorly water-soluble material and extractives, which without vigorous mixing, separate out from the aqueous phase together with the pyrolytic lignin. These sticky compounds prevent efficient separation and drying of the residue.

The complete range of organic acids should be analyzed after derivatization of the acids into their benzylic esters. However, for the determination of the main acidic compound, acetic acid, derivatization is not necessary.

Based on the round robin results the following recommendation are made:

- It is recommended to verify homogeneity by water distribution and/or by microscopic determination.
- Karl-Fischer titration is recommended for analysing water in pyrolysis liquids. For method calibration it is suggested to use water standards and water addition method.
- pH is recommended to be used only for checking the pH level. It is suggested to be reported with one decimal place.
- Kinematic viscosity is accurate for viscosity measurement of white wood pyrolysis liquids. The Newtonian behaviour using a closed-cup rotaviscotester should be checked for extractive-rich liquids.
- Stability test should be carried out each time exactly in the same way, and, in case of weight loss (> 0.1 wt.%) during the test, the results should be excluded. The test is recommended for internal comparison of pyrolysis liquids from one specific process. The best comparison can be made when the differences in the water contents of the samples are small. Viscosity can be measured both at 20 °C and 40 °C, but 40 °C is recommended due to lower measuring error.
- For elemental analysis in cases of inhomogeneity or high solids content, the sample size should be as large as possible and at least triplicates should be carried out.
- Ethanol (or methanol) can be used for solids determination of white wood pyrolysis liquids. For new feedstocks, like bark and forest residue, the solubility of the liquid should be checked, for example, by using solvents of different polarity, for example methanol and mixtures of methanol and dichloromethane.
- A fast and simple method for determination of pyrolytic lignin should be developed.
- For chemical characterization it might be necessary to calibrate the gas and liquid chromatographic systems by preparing standard solutions with known amounts of compounds.

For future round robins following is recommended:

- Include pyrolysis liquids produced from industrially important biomass feedstocks.
- Include analyses for water, solids, homogeneity, stability, water-insolubles, average molecular weight, and GC/MSD.
- Provide detailed and clear instructions on handling, pretreatment, and analysis with needed reference samples.

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