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Anja Oasmaa, Eero Leppämäki, Päivi Koponen,
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Application of standard fuel oil analyses

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TECHNICAL RESEARCH CENTRE OF FINLAND
ESPOO 1997

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ABSTRACT

The main purpose of the study was to test the applicability of standard fuel oil methods developed for petroleum-based fuels to pyrolysis liquids. In addition, research on sampling, homogeneity, stability, miscibility and corrosivity was carried out. The standard methods have been tested for several different pyrolysis liquids. Recommendations on sampling, sample size and small modifications of standard methods are presented. In general, most of the methods can be used as such but the accuracy of the analysis can be improved by minor modifications. Fuel oil analyses not suitable for pyrolysis liquids have been identified. Homogeneity of the liquids is the most critical factor in accurate analysis. The presence of air bubbles may disturb in several analyses. Sample preheating and prefiltration should be avoided when possible. The former may cause changes in the composition and structure of the pyrolysis liquid. The latter may remove part of organic material with particles. The size of the sample should be determined on the basis of the homogeneity and the water content of the liquid. The basic analyses of the Technical Research Centre of Finland (VTT) include water, pH, solids, ash, Conradson carbon residue, heating value, CHN, density, viscosity, pour point, flash point, and stability. Additional analyses are carried out when needed.

PREFACE

VTT has had a central role in analysing both liquid and solid fuels for the Finnish industry over two decades. Considering these experiences, the standard fuel oil analyses developed for petroleum-based fuels were tested also for pyrolysis liquids. In this report the test results are summarised and modifications to methods are suggested. The modified methods will be used at VTT Energy for pyrolysis liquid analyses. The study was carried out at VTT Energy as part of the project "Production, properties, and utilisation of pyrolysis liquid". Project manager is Prof. Kai Sipilä. Our best thanks are due to Sulo Piepponen of VTT Chemical Technology, and Kalle Kangasmaa and the analytical group of VTT Energy. The authors also wish to thank James Diebold (Consultant, Thermalchemie Inc., Lakewood, CO), Stefan Czernik (NREL), and Thomas Milne (NREL) for their valuable support and advice during the work. Beside the above mentioned the help of the whole IEA PYRA group (1995 - 1996) Donald Huffman, Steven Gust, Jacques Léde, Jan Piskorz, Dietrich Meier, Cordner Peacocke and A.V. Bridgwater (activity leader) are greatly acknowledged. The VTT project was funded by Technology Development Centre Finland (TEKES) through the BIOENERGY Programme and by Wärtsilä Diesel Oy, Vapo Oy, Neste Oy, and Metsä-Serla Oy.

Espoo, March 1997

Authors

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1 INTRODUCTION

Biomass pyrolysis liquids differ a great deal from petroleum-based fuels in both physical properties (Table 1) and chemical composition. Pyrolysis liquids contain more water and usually more solids, are acidic, have a low heating value and are unstable when heated, especially in air. Due to these differences the standard fuel oil methods developed for mineral oils may not be suitable as such for pyrolysis liquids. The importance of the reliability of the analytical methods has been addressed already earlier [*Elliott* 1983, *McKinley et al.* 1994]. Extensive research on analysing physical properties of pyrolysis liquids has been carried out already since the 1980s at PNL, USA [*Elliott* 1983], NREL (former SERI), USA [*Chum & McKinley* 1988, *Milne et al.* 1990, *Czernik et al.* 1994], and former B.C.Research, Canada [*McKinley* 1989, *McKinley et al.* 1994]. A good review on product standards for pyrolysis liquids has been presented by *Rick & Vix* [1991]. Fuel oil specifications for pyrolysis liquids have been developed within earlier IEA work [*Elliott* 1983]. Recent publications by *Diebold et al.* [1996] and *Meier et al.* [1997] describe the state-of-the-art concerning fuel oil specifica-

Table 1. Properties of biomass pyrolysis oil liquids (wet oil basis) [Diebold et al. 1996].

Feedstock (char removal method)	Poplar (hot-gas filtered)	Maple and oak (char cyclone), heavy blend	POK 15	PORL 180; 380
Water, wt%	18.9 (0)*	23.3 (0)	0.025	0.7
Elemental				
Carbon	46.5 (57.3)	44.8 (58.5)	-	-
Hydrogen	7.2 (6.3)	7.2 (6.01)	-	-
Oxygen	46.1 (36.2)	47.8 (35.4)	-	-
Sulphur	0.02 (0.02)	<0.01 (<0.01)	0.2	1.0
Nitrogen	0.15 (0.18)	0.1 (0.1)	-	-
K+Na, ppm	9.9	328	-	-
Cl, ppm	7.9	3	-	-
Ash, wt%	0.01	0.09	0.01	0.1
Conradson carbon, wt%	14	20	0.2	-
HHV, MJ/kg	18.7 (22.3)	18.1 (23.5)	-	-
LHV, MJ/kg	17.4 (21.2)	16.6 (22.2)	40.3	-
Density, kg/m^3	1 200	1 230	890	900 - 1020
Flash point, °C	64	>106	60	65
Pour point, °C	-36	-9	-15	15
Viscosity @ 40 °C	-	-	3.0 - 7.5	-
@ 50 °C, cSt	13.5	70	-	140 - 380
Ethanol insoluble filtered solids, wt%	0.045	0.3	-	-
pH	2.8	2.8	-	-

** Numbers in parentheses are on a moisture-free basis, POK15 = light-medium fuel oil, PORL180; 380 = heavy fuel oils*

tions and physical properties of pyrolysis liquids. A number of other important studies have been reviewed by *Fagernäs* [1995] in this project and hence are not discussed in this publication. A report on biomass feedstock analyses has been prepared by *Wilen & Kurkela* [1996]. Properties and handling of pyrolysis liquids have been studied at VTT since the early 1990s [*Solantausta et al.* 1993, *Oasmaa & Sipilä* 1995]. Refractive index, thermal capacity and thermal conductivity are not included in this study, but these characteristics have been tested for pyrolysis liquids by *Peacocke et al.* [1994].

The analytical work supports utilisation of pyrolysis liquids in diesel engines and boilers as well as contributes to better understanding of the chemical characteristics of the liquids. This study focuses on testing and modifying the standard fuel oil analyses routinely used at VTT. Recommendation for an analytical protocol for analysing pyrolysis liquids is suggested. This work will be continued by monitoring the quality of pyrolysis liquids systematically in pilot and demonstration plants.

2 PRODUCTION AND HOMOGENEITY OF PYROLYSIS LIQUIDS

2.1 PRODUCTION

The flash-pyrolysis liquids used in the physical characterisation tests were produced from eucalyptus and pine by Union Fenosa (Spain), from wheat straw and pine by VTT (Finland), and from different hardwood (oak-maple, oak, birch) and wheat straw by Ensyn Ltd. (Canada).

The pyrolysis process of Union Fenosa (150 kg/h) [*Cuevas et al.* 1996] is based on the Waterloo Fast Pyrolysis Process (WFPP) [*Scott et al.* 1988, *Piskorz et al.* 1996], in which the biomass is rapidly pyrolysed in a fluidised bubbling sand bed reactor at atmospheric pressure and at temperatures typically from 450 to 500 °C. Ensyn RTP (Rapid Thermal Processing) process uses fast fluidised-bed reactor [*Graham et al.* 1994, *Freel et al.* 1996]. The heat-carrying medium is circulated and hence, the residence time of solids is well-controlled and high heating rates (10 000 °C/s) are obtained. The biomass feed and the solid heat carrier pass through a tubular transport reactor at temperatures normally ranging from 450 to 500 °C and in a residence time of less than one second. The flash-pyrolysis liquids at VTT were produced at 525 °C by using a small atmospheric bubbling fluidised sand bed reactor (1 kg/h). The NREL (National Research Energy Laboratories) pyrolysis liquid was produced in a Vortex reactor [*Diebold et al.* 1994], into which the biomass particles are entrained by carrier gas tangentially and at high velocity.

2.2 HOMOGENEITY

Pyrolysis liquids contain a high number of compounds having different chemical functionalities. The homogeneity of the liquids is connected with the complex solubility and reactivity of these various chemical compounds in the liquid. Typically, the pyrolysis liquids are single-phase liquids containing varying amounts of solids. The tar-containing solids of the pyrolysis liquid sediment gradually on the bottom of the barrel forming a thick sludge. The degree of sedimentation depends on the density difference of the liquid and the particles [*Särkilahti* 1996].

Layering and phase separation may take place already in the fresh liquid product or after a certain storage time. Some feedstocks, like peat and rape seed, may yield two to three distinct phases in the product liquid. A slight phase separation can be detected, for example, by measuring the distribution of water in the liquid or by microscopic examinations. Phase separation takes place, i.a., as soon as the total water content of the pyrolysis liquid exceeds a

Table 2. Pyrolysis liquids used in the analyses.

VTT batch	Process	Raw material	Comments
Hardwood liquids			
Ensyn 7/91	RTP-2, 100 kg/h commercial prototype	Mixed hardwood (oak, maple)	
Ensyn 2,4/92	RTP-3, 40 kg/h pilot plant	Mixed hardwood	
Ensyn 4/93	RTP-3, 40 kg/h pilot plant	Mixed hardwood	
Ensyn 1/94	RTP-3, 40 kg/h pilot plant	Mixed hardwood	Filtered liquid
Ensyn 8/94	RA, 1000 kg/h commercial chemicals plant	Mixed hardwood	Heavy condenser fraction
Ensyn 2/95	RTP-3A, 2 kg/h research unit	Birch wood	Hot-vapour filtered, solvent recovered
Ensyn 6/95	RA, 1000 kg/h commercial chemicals plant	Mixed hardwood	Heavy blend
Ensyn 10/95	RA, 1000 kg/h commercial chemicals plant	Mixed hardwood	Heavy blend
Ensyn 12/95	ENEL plant, demonstration runs	Oak	
Ensyn 11-12/96	1000 kg/h commercial chemicals plant	Mixed hardwood	
UF 5/94	150 kg/h	Eucalyptus	
UF 8/94	150 kg/h	Eucalyptus	
UF 10/94	150 kg/h	Eucalyptus	
UF 3/95	150 kg/h	Eucalyptus	
NREL #175	20 kg/h Vortex reactor	Poplar	Hot-vapour filtered
Softwood liquids			
UF B-Pine 3/95	150 kg/h	Pine	
UF B-Pine 4/96	150 kg/h	Pine	
VTT test 1, 11/95	1 kg/h	Pine	Condenser fraction
VTT AFBP 1/4, 2/96	1 kg/h	Pine	
VTT AFBP 1/6, 2/96	1 kg/h	Pine	Hot-vapour filtered
Straw liquids			
Ensyn 1/94	RTP-3A, 20 kg/h research unit	Wheat straw	Solvent recovered
Ensyn 8/94	RTP-3, 40 g/h pilot plant	Wheat straw	
VTT AFBP 1/7, 2/96	1 kg/h	Wheat straw	Hot-vapour filtered

certain limit (for some hardwood liquids above 30 wt%) that is dependent on the pyrolysis liquid and its origin. A phase separation may also take place in liquids even with lower water contents. In these cases the reason may be found in an unadvantageous balance of chemical compounds in the liquid, e.g. lack of light dissolving compounds (i.e., alcohols, acids) and a high proportional amount of lignin-derived water-insoluble fraction. This type of liquid cannot be homogenised properly and consequently unreliable analytical results are obtained. The use of this type of liquids as fuels is questionable unless the two- or multi-phase liquid can be emulsified before use.

The properties of the pyrolysis liquids analysed vary a lot depending on the feedstock, the process, pyrolysis conditions, and the liquid recovery systems used. In some cases all liquid recovery fractions were not combined (heavy blend, condenser fraction) and consequently the liquids may differ from the total liquid product. However, all these pyrolysis liquids are included this study and some declaration is provided when necessary. Table 2 summarises the processes and raw materials for the pyrolysis liquids used.

3 SAMPLING

Pyrolysis liquid samples at VTT were obtained in small (1 - 20 l) containers, in 200 l barrels or in 1 m^3 totes. All containers were made of polypropylene. The small samples were homogenised by a routine way using laboratory mixers. The pyrolysis liquid in barrels was homogenised by mixing with a propeller mixer and the homogeneity of the liquid was ensured by analysing both the upper and lower part of the barrel (Appendix 1/1). Six 1 m^3 totes containing liquids from the same batch were homogenised by pumping at room temperature from bottom to top and reversed for an hour and analysed (Appendix 1/2). The liquids were stored at +14 °C.

Mixing and sampling methods depend on the type and size of the pyrolysis liquid container. The sampling procedure at VTT is presented in Appendix 1/3. Attention should be paid to proper mixing of the liquid. Mixing of pyrolysis liquids in large totes is easy to carry out if the liquid has originally been in one phase. The homogeneity of the liquid after mixing should be verified, for example, by sampling from different depths and analysing the moisture and solid content. The sampling device should be wide-mouthed for obtaining a homogenous sample. Heating of the liquid should be avoided to prevent evaporation of volatiles and/or viscosity increase due to instability of the liquid. Handling, storage, and pumping may all affect the pyrolysis liquid properties in different ways.

4 WATER, ASH AND ELEMENTAL

4.1 WATER CONTENT

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

Pyrolysis liquids contain, for example, aldehydes, ketones and carboxylic acids that may form water by reaction with methanol in the solvent. Hence, two standard methods for Karl Fischer titration were tested. In ASTM D 1744 the titration solvent is a mixture of chloroform and methanol (3:1) and in ASTM E 203 a mixture of pyridine and ethyleneglycol monomethylether (1:4). The latter method is suitable for determining moisture in samples containing aldehydes and ketones. In both methods the material to be analysed is dissolved in a titration solvent and titrated by a standard Karl Fischer reagent (Merck 9248, methanol-free, main components: 2-methoxy-ethanol, pyridine) to an electrometric end point. It should be borne in mind that both the ASTM D 1744 and ASTM E 203 methods have been specified for measuring very low water contents (5 to 1 000 ppm).

The water content was measured for hardwood and straw pyrolysis liquids by both standard methods (Appendix 2/1). The equipment used was a Metrohm 633 titrator. The results were reproducible and the percentage standard deviation was 0.1 - 0.6 % (stdevp% = stdevp x 100 / average). The accuracy of the Karl-Fischer titration [ASTM D 1744] was determined by a water addition method (Appendix 2/2). An increasing amount of water was added to the pyrolysis liquid, the water content of the mixture determined, and the results compared with the calculated ones. The accuracy of the titration was ± 0.1 wt%.

Because the ASTM E 203 method uses pyridine which is a very irritant solvent another solvent was tested. HYDRANAL Composite 5 K [*Riedel-de Haen* 1988] is a special titration reagent intended for the determination of water in aldehydes and ketones. It contains imidazole, sulphur dioxide and iodine dissolved in diethyleneglycol monomethylether. HYDRANAL - Working Medium K is the corresponding solvent system which contains 2-chloroethanol and chloroform. HYDRANAL K-solvents were used in the ASTM D 1744 method for replacing the chloroform-methanol mixture.

The water content was measured for different pyrolysis liquids (hardwood mix, eucalyptus, pine, straw) according to ASTM D 1744 using chloroform-

methanol (3:1), and HYDRANAL-K solutions (methanol-free) as titration solvents. For hardwood liquid also methanol with and without a buffer (imidazole) solution was used for comparison. The buffer was used for neutralising the acidic sample. However, it did not have any influence because of the small sample size used. The difference in water content determined using these solvents was rather small (<0.5%). For hardwood liquid the lowest water content was obtained by using the chloroform-methanol mixture (Appendix 2/3).

The possible reaction, e.g., formation of water can be observed as a fading titration end-point. This means that the titration rate decreases significantly before reaching the titration end-point. This happened in some determinations and hence the stabilisation time for end-point determination was tested (Appendices 2/3 and 2/4). For hardwood liquid the stabilisation time (30 s) typically applied with HYDRANAL K solutions yielded a large variation in results (stdevp% 2.3). By using a longer stabilisation time (30 s + 30 s) lower stdevp% (0.2) was obtained. This may be caused by poor dissolution of the sample in HYDRANAL K reagent. If the sample is dissolved properly in the solvent the stabilisation time of 30 s is sufficient. However, in case of poor dissolution the particles disturb the function of electrodes, the titration rate decreases before the end-point and disturbs the end-point detection. The dissolution of pyrolysis liquids from hardwood (oak-maple) and softwood (pine) was best in the chloroform-methanol mixture. For some batches of hardwood liquid (oak-maple) the dissolution in methanol, HYDRANAL K solvent or pyridine-ethyleneglycol monomethylether was inadequate and the precision of the measurement slightly worse. Pyrolysis liquid from wheat straw dissolved better in the HYDRANAL K than in the chloroform-methanol-solvent.

It was concluded that both Karl-Fischer titration methods [ASTM E 203 and ASTM D 1744] can be used. The inadequate dissolution of the sample may cause an error to the water content. In these cases another solvent, longer stabilisation time, or smaller sample size may be considered. No practically significant difference was found between different solvents. As in most cases the dissolution of pyrolysis liquids was easiest in chloroform-methanol this solvent was chosen for routine use. As the use of chlorinated solvents is not recommended methanol may be considered as a solvent when the dissolution of the sample is not a problem. If the sample has dissolved properly the fading titration end-point may be due to a reaction of ketones and aldehydes and the water content should also be measured using HYDRANAL K reagents. One additional source of error in the Karl-Fischer titration is the small sample size both for the sample and for the water equivalent. Attention should be paid to proper sample homogenisation. At VTT the sample size of 0.25 g is typically used for pyrolysis liquids containing about 20 wt% water.

The final water content is calculated on the basis of the water equivalent determined and the consumption of the titration reagent. For example, a variation of 5.70 - 5.73 in water equivalent yields a variation in water content from 28.50 wt% to 28.65 wt% (0.25 g sample, 12.50 ml consumption of the titration reagent).

4.2 SOLIDS CONTENT

There are varying amounts of solids in pyrolysis liquids due to feedstock, process, and product recovery. Cyclones are designed to remove most of the char from the pyrolysis vapours before condensation. Hot gas filtration systems without cyclones or placed after cyclones have been developed for removing char fines from the hot pyrolysis vapours. These systems may be very effective in removing solids down to 0.001 wt%, but any long-term run has not yet been assessed. Liquid filtration systems have also been tried for side streams having a low viscosity due to a high water content, but are rather complicated and produce a by-product sludge.

Since the diesel fuel injection components are made with a great precision to extremely close fits and tolerances, they are very sensitive to any abrasive material in the fuel. Depending on their size, solid particles can contribute to wear in the fuel system and to plugging of the fuel filter and fuel nozzle. In addition, abrasive ash components can cause wear within the engine by increasing the overall deposit level and adversely affecting the nature of the deposits [*Dyroff* 1993].

The solids measured as insoluble material in some specific solvent contain, in addition to the actual solids, heavy organic material not dissolved in the solvent. Three solvents were tested: ethanol, methanol and acetone. The solids contents were measured first as ethanol and acetone insoluble material retained on a filter (Appendices 3/1). The amount of ethanol or acetone insoluble material was dependent both on the amount of particles in the liquid and on the feedstock used for the pyrolysis liquid generation. For pyrolysis liquids from hardwood mix (oak-maple) and eucalyptus ethanol was a more powerful solvent than acetone. The filtration of the acetone solution was also more difficult (long filtration time, sticky cake) than that of the ethanol solution. For the straw pyrolysis liquid, a clear difference (10 wt%) in solids contents determined using these two solvents was observed. Acetone either did not dissolve the straw pyrolysis liquid properly or caused precipitation.

The filter pore size (0.1 - 10 μm) did not affect the amount of solids retained except for the case of straw liquid. The selection of the filter pore size is to some extent dependent on the particle size distribution of the liquid. In case

of the straw the liquid particles were mostly of 1 μm in size and it was necessary to use a filter with a smaller mesh than for the other liquids.

The differences in solubility in ethanol and methanol were very small (Appendix 3/2). Methanol was a slightly more effective solvent than ethanol for pyrolysis liquids from pine, eucalyptus, and straw (Appendix 3/2). For an oak-maple liquid no difference in methanol and ethanol insolubles was obtained.

A number of effective solvents and several methods may be used for measuring the solids content of pyrolysis liquids. The essential task of comparison of the pyrolysis liquids is to systematically use the same method, solvent and filter size. At VTT, ethanol was chosen because its solubility power is high for several different pyrolysis liquids, and it is safer to use in routine measurements than methanol. A filter pore size of 0.1 μm is used because all particles in the liquid are removed. If the filtration time is long (high solids content) a 3 μm filter is used and the filtrate filtered through a 0.1 μm filter. A sample size of 1 - 3 g and a sample-to-solvent ratio of 1:100 yielded the most accurate results by the apparatus used (Appendix 3/3). The polycarbonate film filters used are also suitable for microscopic analyses of particles.

4.3 PARTICLE SIZE DISTRIBUTION

Particle size distribution is an important parameter in diesel engine use. The tolerances in the injection needles are small in order to provide an efficient atomisation of the fuel. For small engines particles of larger than 10 μm are not accepted. For larger engines in which pyrolysis liquids have been tested particle size should not exceed 20 - 25 μm.

There are several methods for determining particle size distribution for pyrolysis liquids. At VTT two optical methods have been used: a particle counter and an image analyser. In the former method the sample is diluted in ethanol (1:500) and led through an automatic particle counter which detects particles larger than 5 μm. A dark colour of the pyrolysis liquid may disturb the detection. Overlapping of several particles can be detected as one large particle. The flow rate may have some effect on the particle size distribution (Appendix 4/1).

In the image analysis the sample was placed between two glass plates and photos were taken by a video camera connected to a polarisation microscope. Three randomly chosen photos were taken using three different enlargements (25X, 40X, 63X). Photos were transferred to an image analyser and the two-dimensional shape and amounts of particles were analysed. The largest particles were thin, but broad. The smallest particles were of spherical shape. The

particle size distribution can be determined by this method on the basis of both amount and weight. Assumption of the three-dimensional shape and density of particles was employed.

The results of the both methods mentioned above can be combined if needed. Using the image analyser the amounts of particles smaller than 5 μm are obtained. On the other hand, the automatic particle counter detects particles larger than 5 μm and the total amount of particles is obtained (Appendix 4/1).

The weight-based particle size distribution can be determined roughly by filtering. The filtration efficiency (and retention of the particles on the filter) is achieved not only due to a small pore size but also because of the presence of the filter cake. That is why this method provides only a very rough estimate. This estimate is better for a low amount of solids. Hence, the sample size should be small compared to the diameter of the filter. A sample of pyrolysis liquid was dissolved in the solvent, for example, ethanol and filtered through the largest filter. An efficient washing of the filter cake was carried out. The filtrate was then filtered through a finer filter and continued depending on the objective (Appendix 4/2). Care has to be taken in proper sampling, sample size determination, and washings.

4.4 CONRADSON CARBON RESIDUE

The carbon residue is a measure of carbonaceous material left in a fuel after all the volatile components are vaporised in the absence of air. There is no real correlation between Conradson carbon results for diesel fuels and deposit formation on injector nozzles. The significance of the Conradson carbon test results also depends on the type of the engine in which the fuel is being used. Fuels with up to 12 wt% Conradson carbon residues (CCR) have been used successfully in slow-speed engines [*Dyroff* 1993]. Pyrolysis liquid was tested in a boiler designed for heavy fuel oil [*Hallgren* 1996]. An increased dust load was reported, which may be attributed to a high CCR of pyrolysis liquid.

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

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

the liquid sample. The accuracy of the method according to the standard is ± 2 wt% when CCR is above 20 wt%. The CCR has typically been 18 - 23 wt% (22 - 23 wt% on dry pyrolysis liquid) for pyrolysis liquids from hardwood (oak-maple, eucalyptus) and softwood (pine) and 17 - 18 wt% (22 - 23 wt% on dry basis) for pyrolysis liquids from wheat straw. A low CCR value of 14 wt% (17 wt% on dry basis) was determined for NREL hot-vapour filtrated pyrolysis liquid (poplar). The CCR has also been on low side for hot-vapour filtered pyrolysis liquids from pine (21 wt% on dry basis) and straw (22 wt% on dry basis). This may be an indication of change in the chemical composition of the liquid, e.g., sticking and possibly also thermal cracking of heavy compounds on the filter cake during hot-vapour filtration, as the amount of solids alone does not explain it.

Normally Conradson Carbon is only specified for light diesel fuels. The pyrolysis liquids are of different chemical nature compared to mineral oil based heavy diesel fuels. There is not yet adequate information of diesel performance data for pyrolysis liquids, and therefore also this test was selected for evaluation.

4.5 ASH CONTENT

Ash content is measured according to DIN EN 7. In the standard method the sample is ignited and burnt in a crucible (Pt, quartz or porcelain). Carbon-containing residue is ashed at 775 °C, cooled, and weighed. Due to the high amount of water that causes foaming or splashing during heating of the sample a controlled evaporation of water is needed. A sample of 20 ml pyrolysis liquid may be let to heat in a porcelain crucible on a heating plate or in an oven (at 105 °C over night) for evaporation of water and other volatile components. Addition of ash-free filter paper for absorbing the water or addition of isopropanol also prevents splashing.

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

Ash contents have typically been low (0.1 - 0.2 wt%) for wood pyrolysis liquids and higher (0.2 - 0.3 wt%) for straw liquids. The main metals in ash (Appendix 5/1) for a wood liquid were Ca (540 ppm), K (440 ppm), Si (330 ppm), Mg (71 ppm), Fe (71 ppm), S, Al, P (30 ppm), Na, and Zn (15 ppm). For hot-vapour filtered pyrolysis liquids, low ash contents

(0.01 wt% for NREL#175 hardwood liquid) have been obtained due to efficient removal of char fines with the alkali (Na, K, Ca, Mg) metals (10 ppm for NREL#175). Similar results have also been obtained with VTT hot-vapour filtered liquids from pine (<7 ppm alkalis) and straw (<5 ppm).

TGA (thermogravimetric analyser) analysis was also carried out for ash determination. The TGA analysis was not reproducible for pyrolysis liquids possibly due to the small maximum sample size (0.5 g).

4.6 ELEMENTAL ANALYSIS

4.6.1 Ultimate analysis

Elemental analysis for carbon, hydrogen, and nitrogen was carried out by LECO CHN-600 according to ASTM D 5291-92. In the method, carbon, hydrogen, and nitrogen are simultaneously determined as gaseous products (carbon dioxide, water vapour, and nitrogen).

The accuracy of the method was tested for two wood pyrolysis liquids (Appendix 6). Stdevp% for carbon (0.4) and hydrogen (0.6 - 1.3) were low, but high (36 - 49) for nitrogen. This is due to low concentrations of nitrogen (0.1 wt% or below) in wood liquids. The detection limit of the method for nitrogen is 0.1 wt%. Pyrolysis liquids from straw contain higher (0.2 - 0.4 wt%) concentrations of nitrogen and hence stdevp% is lower (7). Because of the small sample size the reproducibility of the elemental analysis is dependent on the homogeneity of the pyrolysis liquids.

The CHN content of pyrolysis liquids from hardwood and softwood analysed at VTT varied as follows: carbon 31.5 - 49.2 wt% (48.0 - 60.4 wt % on dry basis), hydrogen 6.9 - 8.6 wt% (5.9 - 7.2 wt% on dry basis), and nitrogen 0 - 0.1 wt%. The highest carbon and lowest hydrogen values were obtained for heavy blends (C 58.4 - 60.4 wt%, H 5.9 - 6.0 wt% on dry basis). For straw liquids the following values were obtained: carbon 36.9 - 44.3 wt% (51.4 - 55.3 wt% on dry basis), hydrogen 7.5 - 8.3 wt% (6.1 - 7.1 wt% on dry basis), and nitrogen 0.3 - 0.4 wt% (0.4 - 0.6 wt% on dry basis).

The sulphur content of wood (hardwood, softwood) pyrolysis liquids is typically very low (60 - 500 ppm). The straw liquid has also a low sulphur content (400 - 500 ppm). The detection limit for sulphur analysis by LECO SC 32 according to ASTM D 4208 is 0.1 wt%. Lower concentrations can be analysed, for example, by ICP (Inductively Coupled Plasma). The detection limit for analysing pyrolysis liquids with ICP by using wet oxidation as the pretreatment method is about 5 ppm. Low sulphur contents have been analysed at VTT by capillary electrophoresis technique after combusting the sample in an oxygen bomb according to ASTM D 4239. Simultaneously, the

total chlorine is detected. The chlorine content for pyrolysis liquids from different feedstocks has been 3 ppm for hardwood (oak-maple) liquid, 75 ppm for softwood (pine) liquid, and 330 ppm for straw (wheat) liquid.

Oxygen (dry basis) is estimated by difference by following equation:

$$O\ wt\% = 100 - (C\ wt\% + H\ wt\% + N\ wt\% + S\ wt\% + ash\ wt\%) \quad (1)$$

Pyrolysis liquids with high amounts of sodium and potassium the ash should be replaced in equation (1) by the total amount of metals.

For the oxygen content the following values of various pyrolysis liquids (as difference) were obtained: 43.8 - 59.8 wt% (33.6 - 44.9 wt% on dry basis) for hardwood and softwood liquids, and 53.4 - 53.9 wt% (38.1 - 42.5 wt% on dry basis) for straw liquids. The lowest values (33.6 - 39.6 wt% on dry basis) were obtained for heavy blends of wood pyrolysis liquids.

4.6.2 Metals

For one sample of hardwood pyrolysis liquid, the metals (Appendix 5/1) were analysed using ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) for the original pyrolysis liquid, the filtrate, and the filter cake. The pyrolysis liquid had been stored for a few months before the analysis. The liquid contained 540 ppm Ca, 440 ppm K, 21 ppm Na, and 71 ppm Mg. Silicon (330 ppm) most possibly originate from the heat-carrying sand. Other metals included Al (43 ppm), Fe (71 ppm), Zn (15 ppm), Cu (2.8 ppm), Cr (2 ppm), Ni (1.6 ppm), Pb (0.5 ppm), V (0.06 ppm), and Co (0.04 ppm).

In filtration silicon and heavy metals (Cr, Pb, V, Co, Al) concentrated mainly in the ash and other solids in the filter cake. Alkali metals (K, Na, Ca) with Zn and S were mainly in the filtrate. It must be pointed out that the alkali metals had time to leach out from the ash during storage of the liquid. The mass closure was satisfied for all other metals than sodium (65 %) and iron (73 %). Sodium may have been partly evaporated during dry combustion.

The ICP-AES method was developed further for analysing metals from pyrolysis liquids (Appendix 5/2). Wet oxidation was chosen for the pretreatment method. Due to the limited amount of tests, sample pretreatment, and small sample sizes, the detection limits for the metals analysed by ICP were set fairly high.

For analysing Na, K, Ca, and Mg, an AAS (Atomic Absorption Spectrometer) determination was carried out for pyrolysis liquids from hardwood (oak-maple, eucalyptus), and straw (Appendix 5/3). Wet oxidation was used as the sample pretreatment method. The sample size ranged from 1 to 3 g. The

precision of the analysis was poor (stdevp% 8 - 59) for low concentrations (below 100 ppm) of alkalis. The straw liquid contained a high amount of alkali metals (401 ppm Na, 9 250 ppm K, 996 ppm Ca, and 239 ppm Mg) due to the high content of alkalis in the feedstock. Both hardwood samples contained alkali metals of much lower quantities. None of the pyrolysis liquids were filtered.

Different sample pretreatment methods were tested (Appendix 5/4): a) dry combustion (sample size 10 g, Appendix 5/4), b) wet oxidation (sample size 3 - 5 g, Appendix 5/3), and c) straight dissolution in isopropanol (IPA, sample size 0.5 - 1 g, Appendix 5/4). The straight dissolution in IPA was inaccurate due to incomplete dissolution of the sample. Dry combustion was time-consuming because the water has to be evaporated carefully before ashing, or else the liquid may swell out from the Pt crucibles. If a hard core forms on the surface of the sample before the end of drying the water may suddenly "explode" and the sample is lost. Wet oxidation was the easiest and fastest method. Similar concentrations of alkali metals (Na, K, Ca, Mg) were obtained with both dry combustion (ashing temperature 520 °C for 2 hours) and wet oxidation. Stdevp% was reasonable low (0 - 14) when using sample sizes of 3 - 5 g even for alkali concentrations of 10 ppm.

Metals may be analysed by ICP-AES or AAS. If all metals are to be analysed, ICP-AES (Appendix 5/2) is suggested as an easier (several metals from one run) and hence cheaper method. However, AAS is more sensitive in some cases. If only heavy metals (Cu, Fe) are to be determined dry combustion (ashing temperature 520 °C) may be used as a sample pretreatment method. As the ash content of pyrolysis liquids is low, the sample size should be as large as possible (minimum 10 g). Due to splashing of the sample a controlled evaporation of water is needed. Wet oxidation (Appendix 5/3) is suggested as a fast and easy pretreatment method especially for analysing alkali metals and easily volatilised toxic metals like Cr, As, Pb, Hg, and Cd. Because large samples are difficult to handle with acids a sample size of 3 - 5 g is suggested as adequate. The same acid or acid mixture and concentrations should be used both in the sample and in the standard solutions.

It should be pointed out that for accurate analysing of traces of alkali metals the whole procedure from the recovery of the pyrolysis liquid to the sample pretreatment should be re-checked in details. If traces of alkalis are to be analysed the use of a method requiring no sample pretreatment may be advantageous. For example, at NREL (USA) a neutron activation (NA) analysis or atomic emission spectrometer (AES) is used. Contaminations from the glass containers and from the dust in air may have influence on the results [*Diebold et al.* 1996]. The use of Teflon (polytetrafluoroethylene, PTFE) bombs for sample pretreatment should be considered.

5 FUEL OIL PROPERTIES

5.1 DENSITY

The density is measured according to ASTM D 4052 at 15 °C by a digital density meter. A small volume (approximately 0.7 ml) of liquid sample is introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube is used in conjunction with calibration data to determine the density of the sample. Anton Paar DMA 55 density meter was used. The density of pyrolysis liquids is typically 1.2 - 1.3 kg/dm^3. The precision of density measurements is good (variation below ± 0.1 %).

A viscous pyrolysis liquid with large particles may disturb the measurement and cause erroneous results. In addition, the air bubbles may disturb the determination near ambient temperatures and, therefore, vigorious shaking of the sample just before the analysis should be avoided. Instead, the sample can be rotated carefully. At elevated temperature (50 °C) the air bubbles are easily avoided by preheating the sample in a closed vessel. Densities of wood pyrolysis liquids as received are shown as a function of water content in Figure 1. As presented by *Diebold et al.* [1997] it can be seen that pyrolysis liquids of relatively higher densities typically have lower water contents.

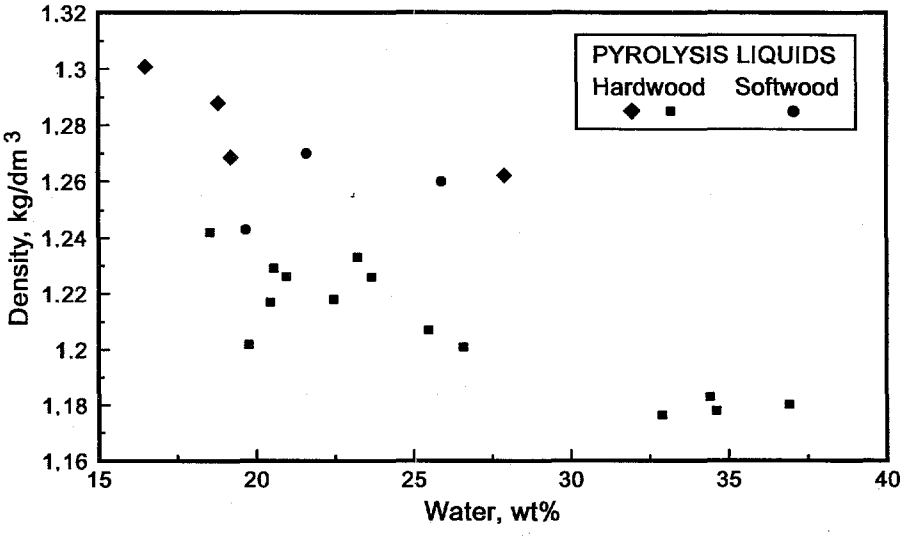


Figure 1. Densities of different fast pyrolysis liquids from wood as a function of water content (♦ eucalyptus).

5.2 VISCOSITY

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

The viscosity of standard fuels is typically measured as a kinematic viscosity according to ASTM D 445. In the standard method the time is measured in seconds for a fixed volume of liquid to flow under gravity through the capillary of a calibrated at a closely controlled temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer. For pyrolysis liquids, typically the viscosity is determined as dynamic viscosity using rotational viscometers. The correlation between the kinematic and dynamic viscosity can be presented by the following equation:

$$[\text{cSt}] = \eta\ [\text{mPa} \cdot \text{s}] / \rho\ [\text{kg/dm}^3], \qquad (2)$$

where ν = kinematic viscosity at temperature T, η = dynamic viscosity at temperature T, and ρ = density of the liquid at temperature T.

Leroy et al. [1988] have carried out an extensive study on rheological characterisation of several different pyrolysis liquids. They concluded that all pyrolysis liquids analysed exhibited an essentially Newtonian behaviour in the range of shear rate examined (10^{-1} to 10^3 s^{-1}). For Newtonian liquids the viscosity stays constant when increasing the shear rate.

Two samples of pyrolysis liquids possessing different viscosities were tested at Haake Application Laboratory (Karlsruhe, Germany) using a RT 20 allround-rheometer with mechanical bearing. A temperature unit TEF/Z48 for liquid circulators was used, in which the pressure cell D35/200 was introduced. A sensor system PZ 36 and a rotor with a 2 mm gap were used. Due to the magnetic coupling in the pressure cell there was some additional friction contributing to the total torque. Haake concluded that the samples were Newtonian liquids. The flow curves were measured (Appendix 7/1) and the viscosity was calculated from regression models, but a major measuring error (±10 %) was obtained for the low-viscous liquid.

Kinematic viscosity can be determined by using Cannon-Fenske or Ubbelohde capillaries (Appendix 7/2). The basic difference between these methods is the flow direction of the sample. For non-transparent liquids Cannon-Fenske was easier to use at room temperature because of upflow system and wider capillaries. In the Ubbelohde method the sample flows downwards and the capillary is much thinner. This lead to an uneven flow of viscous pyrolysis liquid in the capillary. In addition, the determination near ambient temperature may be disturbed by air bubbles and therefore vigorious shaking of the

sample just before the analysis should be avoided. The sample can be instead rotated carefully. At elevated temperature the air bubbles were easily removed during preheating of the liquid. The dynamic viscosity is measured at VTT using a Haake VT 550 controlled-rate (CR) rotaviscotester equipped with a cover for preventing the evaporation of volatiles. The maximum temperature for this rotaviscotester is 100 °C. Two sample cups are used: MV-DIN (46 ml) and NV (8 ml). The equilibration times of 15 minutes for 20 °C and 50 °C, and 10 minutes for 80 °C were used.

The comparison of the methods was carried out for one hardwood pyrolysis liquid. At 20 °C there was a small variation between viscosity results obtained either by Cannon-Fenske (672 cSt, stdevp 0.6 %) or Ubbelohde (650 cSt, stdevp, 0.2 %) method. At 50 °C (52 cSt, stdevp 0.3 %) and 80 °C (11-12 cSt, stdevp below 0.5 %) no significant difference in viscosity of pyrolysis liquid measured by these methods was observed.

When compared the kinematic viscosities with the viscosity results obtained by a rotaviscotester Haake VT 550 (Appendix 7/2) using a NV cup the precision was good. The viscosities converted (divided by the density) to same units were 676 cSt @ 20 °C (stdevp 0.1 %), 58 cSt @ 50 °C (stdevp 0.7 %), and 14 cSt @ 80 °C (stdevp 4.8 %). At 80 °C the evaporation of volatiles was observed visually already during sample equilibration. The viscosity of the sample increased by almost 1 % in a minute during measuring at 80 °C. Also the stdevp at 80 °C was higher than by using the capillary system where the evaporation of volatiles is not as significant (Appendix 7/3). By using the MV-DIN cup (46 ml, equilibration time 15 minutes, shear-rate 40 - 200 1/s) a smaller viscosity value (627 cSt) was obtained at 20 °C. At 50 °C results similar to those with the NV cup were obtained.

The small difference (650 - 672 cSt) in viscosities measured by the two capillary methods according to ASTM D 445 may be explained by difficulties in reading the volume in the Ubbelohde method (downward flow). Variation in viscosity at 20 °C was also obtained by using two different cups (NV and MW-DIN) in the rotaviscotester. On the basis of the viscosity ranges, both cups are suitable for the pyrolysis liquid analysed. This difference may be explained by a small deviation in temperature in the larger MW-DIN cup. Pyrolysis liquids are known to be more sensitive at temperatures close to room temperature than at 50 °C or higher, and the control of the temperature is achieved better for the NV cup due to its design. The viscosity values at 20 °C measured by Cannon-Fenske (672 cSt) and by the rotaviscotester using the NV cup (676 cSt) were similar.

At 50 °C the viscosity measured by the two capillary methods was equal (52 cSt) and a little higher (58 cSt) with the rotaviscotester (with both cups). No significant evaporation from the sample was observed.

At 80 °C a slightly higher viscosity was measured by the rotaviscotester compared to the glass capillary measurements [ASTM D 445]. This was due to the evaporation of volatiles during the measurement. The evaporation in glass capillaries is much more limited due to the small open surface.

Viscosities as a function of water content of the pyrolysis liquid are shown in Figure 2. The determinations were carried out at 50 °C because of comparison to heavy fuel oil. Several liquids are shown for different processes and varying conditions. It can be concluded from the scattering of the data that the water is only one determining factor in the viscosity.

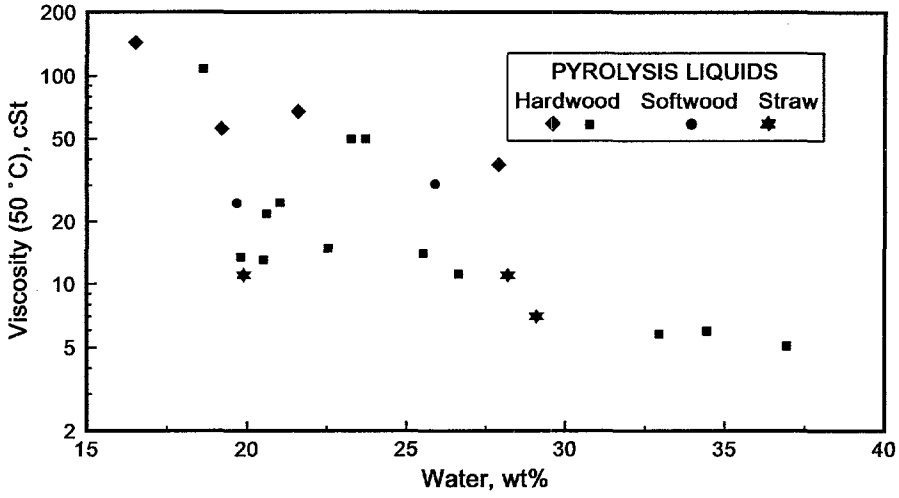


Figure 2. Kinematic viscosity as a function of water content (♦ eucalyptus).

5.3 POUR POINT

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

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

batches. For the pyrolysis liquids analysed the low viscosity was an indication of a low pour point.

5.4 CLOUD POINT

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

The cloud point is determined as the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under conditions described in the method ASTM D 2500. Despite practically no paraffin compounds in pyrolysis liquids the cloud point was measured for the pyrolysis liquid according to this method to check if other components can cause a similar phenomenon. The sample was cooled at a constant rate down to -21 °C at which the sample was no more fluid. No "clouding" was observed which may be due to the dark colour of pyrolysis liquid.

It was concluded that this test is not suitable for dark pyrolysis liquids. However, it would be of great interest to learn when precipitates are formed in the pyrolysis liquids, as they are cooled even if the precipitates do not consist of paraffin waxes, but of some other material, which might plug the filters. One alternative method could be the Cold Filter Plug test [DIN EN 116]. In the pre-test with the NREL#175 hot-filtered pyrolysis liquid the filtration succeeded only at above 50 °C. It came out that the test should be modified to be suitable also for high-viscous pyrolysis liquids.

5.5 HEATING VALUE

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

The heating value was measured as calorimetric value (higher heating value, e.g. HHV) by DIN 51900. A Parr adiabatic bomb with a Parr Calorimeter Controller 1720 was used. The heat of combustion is determined by measuring the temperature increase in the Calomel water and then calculated from energy balance for the system. The high water content of the pyrolysis liquids

led to poor ignition and a fine cotton thread was often used as a wick. The heat content of the thread was subtracted from the result. The lower heating value (LHV) was calculated from HHV and hydrogen content [ASTM 5291-92]by the equation (2). No subtraction of free water was done [*Rick & Vix* 1991] because the water in pyrolysis liquid cannot be removed by centrifugation (chapter 7.1) as for heavy petroleum fuel oils.

$$\text{LHV [J/g]} = \text{HHV [J/g]} - 218.13 \times \text{H-\% [wt\%]} \qquad (3)$$

The heating values (HHV) for different batches of pyrolysis liquids analysed by VTT vary a lot. A clear correlation with the water content of pyrolysis liquids is seen in Figure 3. It should be borne in mind that samples analysed are produced in different processes by varying pyrolysis temperatures and applying different kinds of recovery system.

The heating values calculated for dry matter (water-free liquids) are very similar. LHV based on dry matter is 19 - 22 MJ/kg for hardwood (oak-maple, eucalyptus) and softwood (pine) liquids, and 18 - 21 MJ/kg for straw (wheat) liquids. The highest values for LHV (22 - 23 MJ/kg) were obtained for liquids rich in lignin-derived water- insoluble fraction. At 25 wt% water the typical LHV is 15 - 16 MJ/kg. The heating value of the pyrolysis liquid is roughly half (of dry matter) from that of petroleum fuels (Table 1).

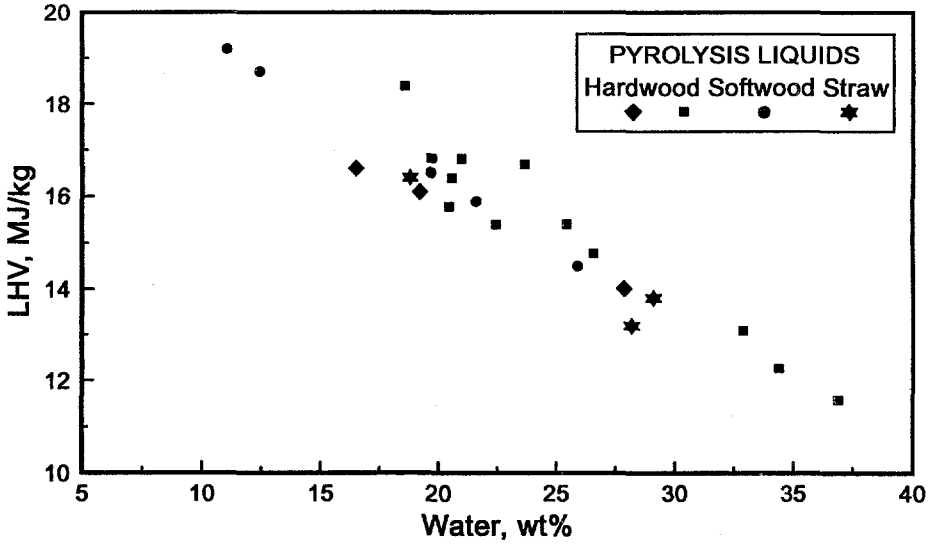


Figure 3. Heating value as a function of water content (♦ eucalyptus).

5.6 FLASH POINT

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

In practice, the flash point is important from the viewpoint of fuel handling. Too low a flash point will cause fuel to be a fire hazard, subject to flashing, and possible continued ignition and explosion. In spite of its importance from a safety standpoint, the flash point of a fuel is of no significance to its performance in an engine. Autoignition temperature is not generally influenced by variations in flash point nor are other properties, such as fuel injection and combustion performance [*Dyroff* 1993].

Flash point has typically been 50 - 66 °C for hardwood (oak-maple), softwood (pine), and straw liquids. This is due to a high amount of low-boiling volatile compounds in pyrolysis liquids. A low flash point also indicates a high vapour pressure (not analysed in this study). For liquids low in volatile the flash point is much higher (above 100 °C). The flash point could be measured for pyrolysis liquids at temperatures at which the evaporation of water did not disturb the analysis. Above 70 - 75 °C the release of water vapour may have disturbed the flash of burning vapours and the determination of the exact value was difficult. Before sampling, air bubbles should be eliminated from the liquid to assure that the exact sample size is achieved.

5.7 AUTOIGNITION

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

The cetane number is used for light oils and diesel fuels and is measured at VTT according to ASTM D 613. In the method, the tested fuel is ignited by compression, the ignition delay is measured and the results are then compared with those of known fuels. Autoignition of a pyrolysis liquid was tested at VTT in a 500 cm^3 single cylinder Petter AVB diesel engine instrumented for cylinder pressure analysis [*Solantausta et al.* 1993]. The pyrolysis liquid ignited only after adding ignition-improver. However, the properties of pyrolysis liquids vary a lot depending on feedstock, process, and product recovery. Hence, autoignition with a higher-quality pyrolysis liquid may

succeed as stated in a recent publication by *Suppes et al.* [1996]. Suppes' work was carried out with a combustion bomb to simulate the diesel engine environment, not with a diesel engine.

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

6 ACIDITY AND MATERIAL CORROSION

The pH of pyrolysis liquids is low (2 - 3) due to high amounts (8 - 10 wt%) of volatile acids, mainly acetic and formic acids. These acids with water are claimed to be the main reasons for the corrosiveness of pyrolysis liquids especially at elevated temperatures [*Aubin & Roy* 1980]. When processing pyrolysis liquids an even black coating is formed on the steel surface of the process equipment. This "coating", analysed by ESCA (Electron Spectroscopy for Chemical Analysis), contained metals from pyrolysis liquid, mainly silica, potassium, and calcium. In the standard corrosion test (ASTM D 665 A) no rust was formed but a clear weight loss in carbon steel (AISI 01) was observed. *Aubin & Roy* [1980] reported no corrosion for carbon steel at ambient temperature in low acid (3.6%) and water (4.4%) concentrations but they observed clear corrosion at elevated temperature (45 °C) in high acid (17.5%) and high water (55.7%) contents. In the copper corrosion test (ASTM D 130) no corrosion or weight loss on copper stem (99.9 % electrolytic copper) was observed for different pyrolysis liquids (hardwood, softwood, straw) at 40 °C.

In the material corrosion study (Appendix 8) the resistance of different metals and coatings was tested. The weighed test rods were submerged into hardwood pyrolysis liquid in glass bottles at different temperatures (from room temperature to 80 °C) for a certain time (mostly 6 weeks). After the test the rods were removed and cleaned properly by ethanol. The rods were weighed and visual observations were made.

Many plastics like PTFE (polytetrafluoroethylene), PP (polypropylene), and HDPE (high density polyethylene) are very resistant to pyrolysis liquids.They are excellent materials for containers in storing, transportation and sampling of pyrolysis liquids. Their use could possibly be extended to replacing copper or, in special cases also AISI 316. A common carbon steel AISI 01 corroded clearly in a standard corrosion test at 60 °C. The acid-resistant steel AISI 316 (17 % Cr, 11 % Ni, 2.2 % Mo, 0.05 % C) is resistant at least at temperatures below 50 °C. One reason why the AISI 316 is better than AISI 304 is a small amount of Mo that serves to make the steel more resistant to general corrosion in non-oxidising acids, stress corrosion and especially localised corrosion (pitting and crevice corrosion) caused by agressive components like halogens.

Nickel and nickel-based materials are not resistant to pyrolysis liquids even at room temperature. On the other hand, cobolt-based HAYNES 188 (39.4 % Co, 22 % Cr, 22.9 % Ni, 14.5 % W, 1.2 % Fe) shows no corrosion up to 80 °C. Pure copper is resistant at least up to 50 °C. Copper is a noble metal and hence has generally a good corrosion resistance to non-oxidising acids. However, if connected with other metals, there is a possibility of electro-

chemical corrosion. Copper and its alloys (brass, bronze, cupronickel) are widely used in piping applications (tubes, valves, etc.) mostly because of the excellent availability of different components. However, it should be borne in mind that copper and brasses are subject to erosion and corrosion, when high fluid velocities are used or abrasive particles are present especially at higher temperatures. It should also be pointed out that brasses with 15 % Zn or more cannot be used with pyrolysis liquids due to dezincification.

7 MISCIBILITY

7.1 MISCIBILITY WITH WATER AND CONCENTRATION OF WATER-INSOLUBLE MATERIAL

Pyrolysis liquids contain an abundance of water (15 - 35 wt%) due to the moist feed and the water formed during pyrolysis. The water is dissolved in the pyrolysis liquid (wood, straw) and cannot be separated, for example, by centrifugation [*Scott et al.* 1988, *Elliott* 1994]. A sample of pyrolysis liquid was centrifuged using G-values of 180 000 without any separation of water.

Fast pyrolysis liquids have a high oxygen content due to carboxylic acids, aldehydes, ketones, carbohydrates, alcohols, esters, phenols, and lignin-derived material. These compounds cause the polarity of pyrolysis liquids and hence the high solubility in other polar solvents.

The pyrolysis liquids analysed differ in their ability to dissolve water. For example, water was very easily added to eucalyptus liquids but pyrolysis liquids from a mixture of oak and maple did not dissolve water properly. When water was added to the latter an emulsion was formed. The water content of the emulsion could be measured in a representative way by the Karl-Fischer titration. Eventually, while not mixing, flakes and finally a clear precipitation was detected in prepared samples. A clear phase separation was observed in both cases at the water content of about 30 wt%. A few batches of pyrolysis liquids contained more than 30 wt% of water as received and had two-phase systems.

By adding increasing amounts of water to pyrolysis liquids a phase separation can be forced to occur (Appendix 2/2). When adding excess water the aqueous phase is finally separated. For one hardwood pyrolysis liquid (VTT batch 10/95) the water-insoluble fraction was determined using different oil-water ratios (Table 3). The physical appearance of the water-insoluble fraction changed from a black sticky material (pyrolysis liquid:water ratio> 1:3) to lignin-type yellow-brownish powder (1:10). The water-insoluble material

Table 3. The water insoluble fraction as a function of pyrolysis liquid-water ratio.

Hardwood liquid: water	Water insoluble, wt% (dry basis)	Determinations
1:1	55.2	1
1:2	54.2 ± 1.1	3
1:3	50.0 ± 0.1	4
1:10	50.1 ± 2.2	4
1:20	50.7±0.1	1

Hardwood liquid: Ensyn liquid, oak-maple, VTT batch 10/95 (water 23.3 wt%)

started to melt at above 60 °C. It did not contain any GC-eluted compounds. It should be pointed out that this batch of pyrolysis liquid was a heavy blend and the amount of water-insolubles was unusually high.

The most efficient method for separating water-insolubles was to add pyrolysis liquid slowly into a large amount of water. This enables a good solubilisation of the liquid and a powder-like fraction is formed. If the solubilisation is carried out other way around, the water may dissolve only the outer part of the pyrolysis liquid sample and the dissolution is not complete. An excess of water (pyrolysis liquid:water ratio of 1:10...20) and good mixing should be provided for obtaining a homogenous dry powder. Heating of the washed product should be avoided as the powder melts at above 60 °C. The filtering of the aqueous-phase removes the particles that disturb the analysis. The method description is presented in Appendix 9/1. For some pyrolysis liquids from pine, the water-insoluble fraction remained sticky. As a consequence, a higher variation in duplicates was observed.

The amount of water-insolublesvaries for different pyrolysis liquids: 34 - 35 wt% (dry basis) for hardwood (oak, birch, eucalyptus), 32 - 35 wt% (dry basis) for softwood (pine), and 17 - 28.5 wt% (dry basis) for straw (wheat) liquids. The hardwood liquid in Table 3 is a heavy blend and hence is not included in the comparison. The material, water and carbon balances are shown in Appendix 9/2.

7.2 MISCIBILITY WITH OTHER SOLVENTS

The solubility of pyrolysis liquids in other solvents than water is significantly affected by the degree of polarity. Good solvents for pyrolysis liquids (wood, straw) include alcohols like ethanol and methanol. These solvents dissolve practically the whole pyrolysis liquid excluding the solids (char). The pyrolysis liquids (wood, straw) also dissolve in higher alcohols like isopropanol and polyglycols. Acetone is also a good solvent but not as effective as low alcohols. A clear difference was seen between wood and straw liquids as mentioned in chapter 4.2.

A very limited solubility is observed in biomass-derived liquids (rape seed oil) or ethers (rape seed methyl ether, tall oil methyl and ethyl ethers). Wood pyrolysis liquids do not dissolve in hydrocarbons like hexane, diesel fuels and polyalfaolefines.

8 LUBRICITY

Viscosity does not describe the lubricating properties of the oils. Lubrication properties are crucial, for example, for selection of supply pumps [*Rick & Vix* 1991]. For determining the lubricity of the fuel oil Cameron-Plint TE77 High Frequency Friction equipment is normally used at VTT Energy. In the test a solid steel ball is moved using a constant weight against a steel plate on which the sample is poured. The pyrolysis liquid formed quickly a glue-like surface on the plate. The ball stuck in the liquid and the test was meaningless. This open system cannot be used for pyrolysis liquids due to the volatility of the sample sprayed as a thin layer on a large surface area.

The lubricity of pyrolysis liquid was also tested using a four-ball wear test according to IP 239/69T [ASTM D 2783]. In the test one steel ball (diameter 12.7 mm) is rotated against three fixed steel balls in the liquid sample. The test time is one hour. The load (40 kp, i.e. 390 N) and speed (1 430 rpm) are constant. The average wear of the balls is used as a measure of lubricity. The smallest wear indicates the best lubricity. The system is closed but not air-tight. Hence it can be used only at room temperature. Considering the preliminary tests it seems that the pyrolysis liquids possess some lubricating properties. The observed wear was 0.5 - 0.7 mm, compared to 1.7 mm for diesel fuel in the same conditions. It must be pointed out that the viscosity of the sample affects the results and no exact conclusions can be drawn due to the large difference in viscosity between pyrolysis liquids and diesel fuels. Some additives were added for improving the lubricity. However, no practically significant improvement was obtained by addition of 1 - 5 wt% rape seed oil, white oil, castor oil, or polyethyleneglycol. One reason for this may be that for accurate comparison the viscosity of the liquid mixtures should be of the same size. The surface of the steel balls darkened due to deposit of silicon, potassium and calcium from the pyrolysis liquid. For more detailed conclusions additional tests should be carried out using liquid samples and reference oils possessing the same viscosity, using larger loads and longer-term tests. The results are presented in Appendix 10.

9 STABILITY

Pyrolysis liquids are not stable like conventional petroleum fuels due to their high amount of reactive oxygen-containing compounds and low-boiling volatiles. Due to the instability of the pyrolysis liquids special care has to be taken in handling, transporting, storing, and using the liquids.

When exposed to air in an open vessel fast pyrolysis liquids change gradually to a glue-like thick material. The main reason for this is the evaporation of low-boiling dissolving compounds (alcohols, acids) including water. During a long-term storage the liquids tend to polymerise, which can be observed as an increase in average molecular-weight distribution in water and in viscosity (Figure 4).

The stability of some hardwood liquids (eucalyptus, oak-maple) was studied (Appendices 11/1 - 2). At ambient temperatures (20 - 35 °C) the viscosity roughly doubled in a year. At higher temperatures the change in viscosity was faster (Figure 5). The viscosity change is different for various pyrolysis liquids. For example, at 80 °C the viscosity of the pyrolysis liquid doubled in three days for the eucalyptus liquid and in less than a day for the hardwood liquid (Appendix 11/2). Water formation takes place with time in storing at elevated temperatures (Appendices 11/1). The scattering of the water results

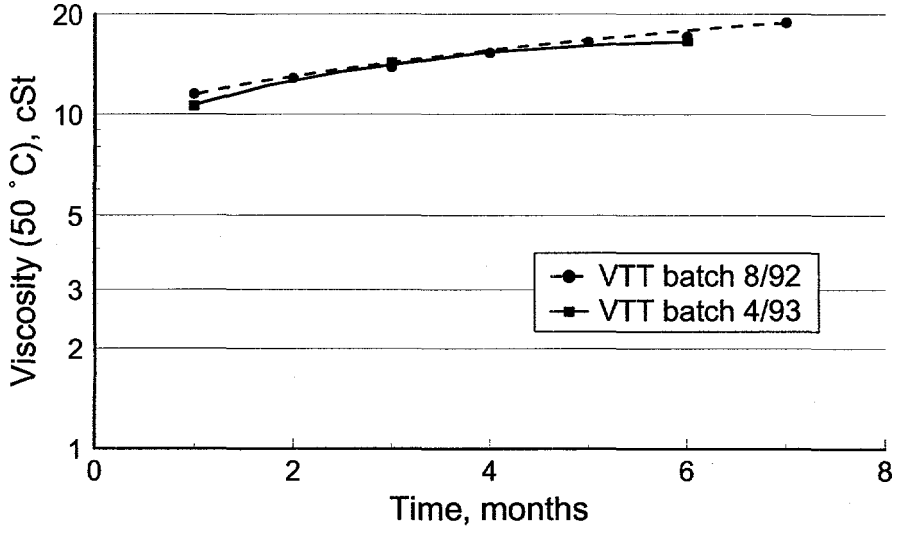


Figure 4. Stability of hardwood pyrolysis liquids during storage at ambient temperature. Water contents (original): 25.6 wt% for VTT batch 8/92, 25.5 wt% for VTT batch 4/93.

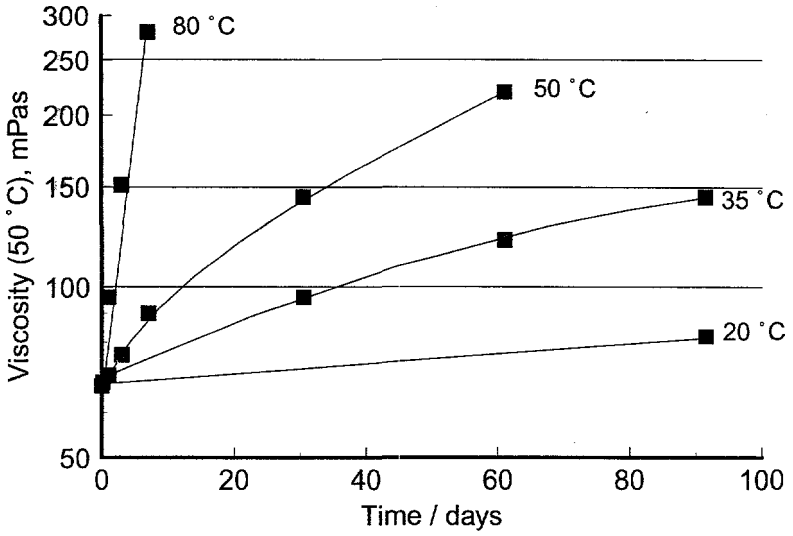


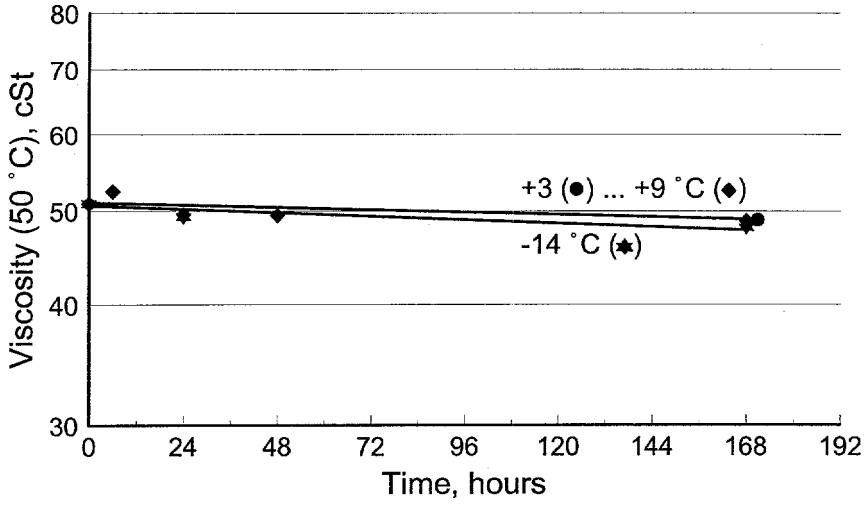
Figure 5. Viscosity change of a hardwood (eucalyptus) pyrolysis liquid (VTT batch 5/94) at 20 - 80 °C.

in Appendix 11/2 may be explained by heterogeneous distribution of water and hence errors in water determination. The pyrolysis liquid from oak and maple stored at room temperature separated into light and heavy fractions within about a year after production. This may be connected to the high proportional amount of high-molecular-weight water-insoluble lignin-derived material (chapter 7.1) and in contrast to the low proportional amount of dissolving compounds (acids, alcohols, etc.).

When storing below room temperature (- 14 °C to + 9 °C) the viscosity of the pyrolysis liquid decreased first slightly but systematically (Figure 6a). Similar results have been obtained by *Rick & Vix* [1991]. When storing at 20 °C for several months (Figure 6b) there was a clear increase in the viscosity of the pyrolysis liquid tested. At -14 °C storage the viscosity of the liquid started to increase after the first week, but very slowly. In a period of 13 months the increase in viscosity was less than 5% (from 51 cSt to 53 cSt). Simultaneously, the water content of the liquid increased from 22.7 wt% to 23.2 wt%.

Addition of a light solvent, e.g., methanol or ethanol improves the stability of the pyrolysis liquid as earlier presented [*Maggi & Elliott* 1997]. By addition of 5 wt% ethanol to the pyrolysis liquid the viscosity increase was only half compared to the original liquid in four-month storing (Figure 7 a). At higher temperatures (Figure 7 b) the ethanol addition had also a favourable effect on viscosity.

a)



b)

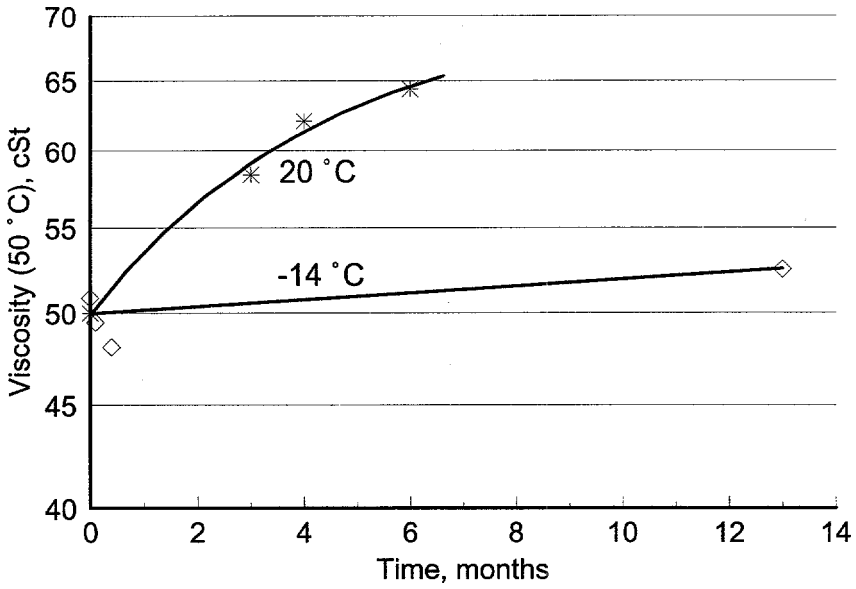
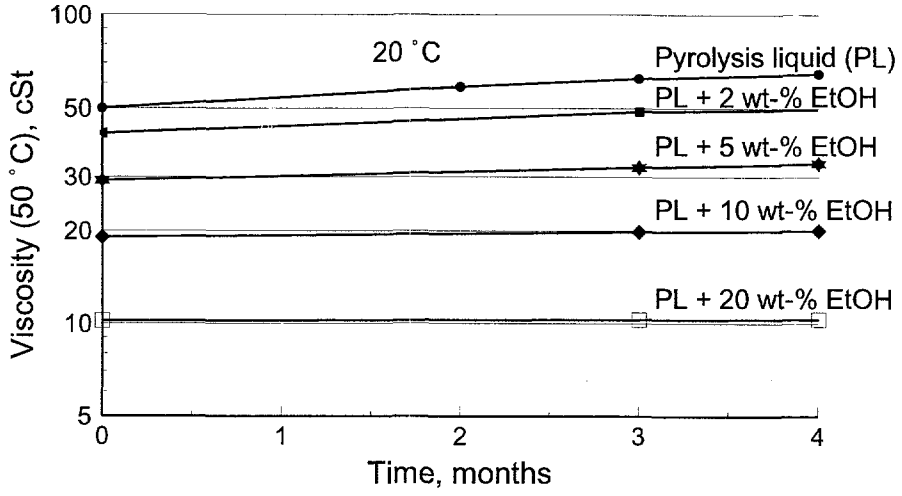


Figure 6. The effect of storage conditions on the viscosity of hardwood (oak-maple) pyrolysis liquid (VTT batch 10/95, original water content 23.3 wt%) at -14 - +20 °C in a short time (a) and in a longer-term storage (b).

a)



b)

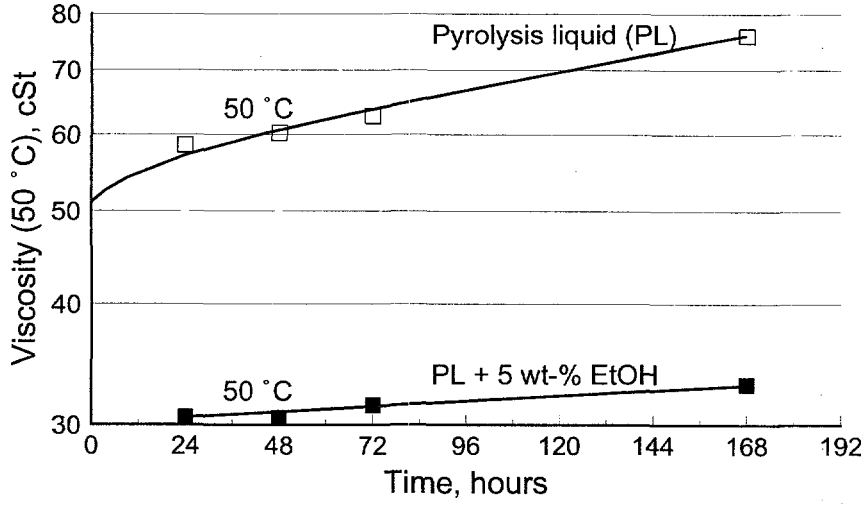


Figure 7. The effect of solvent (ethanol) additions on the viscosity of hard-wood (oak-maple) pyrolysis liquid (VTT batch 10/95) at 20 °C (a) and at 50 °C (b).

A simple test was needed for a quick comparison of the stability of different pyrolysis liquids. A proposed method is described in Appendix 11/3. The method was tested by preparing eight samples in the same manner. Four samples (52cSt, 20.8 wt% water) were purged with nitrogen before sealing. All samples were aged at 80 °C for 25 hours. After the tests the water and the viscosity at 50 °C were determined. There was no significant difference in the viscosity between samples stored under nitrogen (128 cSt, stdevp 3.0%) and under a small amount of air (129.5cSt, stdevp 2.0%). The water content was same 21.6 wt%, stdevp 0.3 - 0.5%) for both series. The maximum weight loss in ageing was 0.06 wt% of the original liquid. Based on the tests the ageing condition of 24 hours at 80 °C was chosen. A change in viscosity (and water) is observed and samples with weight losses over 0.1 wt% are abandoned.

10 RECOMMENDATIONS

The criteria for fuel oil quality may vary depending on the use of the liquid. For diesel engine applications, density, viscosity, particles, and lower heating value are the most important factors. For boiler use flash point, viscosity, and stability are the most important ones. To determine the fuel oil quality of pyrolysis liquid the analyses listed in Table 4 are suggested for routine use at VTT. Comments on modifications to the standards are presented. A quick

Table 4. Basic fuel oil properties for pyrolysis liquids.

Analysis	Method	Provided size of the sample [1]
Water, wt%	ASTM D 1744 [2]	1 g
pH	pH meter [3]	50 ml
Solids, wt%	Ethanol insolubles [4]	3 g
Ash, wt%	EN 7 [5]	40 ml
Conradson carbon, wt%	ASTM D 189 [6]	2 - 4 g
Heating value, MJ/kg calorimetric (HHV) effective (LHV)	DIN 51900 [6]	1 ml
Carbon, hydrogen, nitrogen, wt%	ASTM D 5291-92	1 ml
Density (15 °C), kg/dm^3	ASTM D 4052	4 ml
Viscosity (50 °C), cSt	ASTM D 445 [7]	80 ml
Pour point, °C	ASTM D 97 [8]	80 ml
Flash point, °C	ASTM D 93 [9]	150 ml
Stability	80 °C 24 hours [10]	200 ml

[1] *Minimum amount of pyrolysis liquid needed for two determinations.*

[2] *Karl-Fischer titration. Chloroform-methanol (1:3) solvent. HYDRANAL-K reagents (Composite 5K and Working Medium K) in case of a fading titration endpoint. 50 ml solvent for two determinations. Sample size about 0.25 g (water content >20 wt%). Stabilisation time 30 s.*

[3] *Frequent calibration of the pH meter.*

[4] *Millipore filtration system, 0.1 µm filter, sample size 1 - 3 g, sample:solvent = 1:100 (Appendix 3/3).*

[5] *Controlled evaporation of water to avoid foaming.*

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

[7] *Cannon-Fenske viscometer tubes at room temperature and for non-transparent liquids, Ubbelohde tubes may be used for transparent liquids. No prefiltration of the sample if visually homogenous. Elimination of air bubbles before sampling. Equilibration time 30 minutes.*

[8] *No preheating of the sample.*

[9] *Elimination of air bubbles before sampling.*

[10] *90 ml pyrolysis liquid in 100 ml tight glass bottles, heating in a heating oven (Appendix 11/3). Measuring of increase in viscosity and water. Viscosity determination at 50 °C according to ASTM D 445.*

stability test is included. Additional fuel oil analyses are presented in Table 5. All the standard fuel oil analyses at VTT Energy are listed in Appendix 12.

Table 5. Additional fuel oil analyses carried out at VTT.

Analysis	Method	Provided size of the sample[1]
Viscosity (20 °C or 80 °C), cSt	ASTM D 445 [11]	80 ml
Sulfur and chlorine, wt%	Capillary electrophoresis [12]	2 - 10 ml
Alkali metals, wt%	AAS [13]	50 ml
Metals, wt%	ICP, AAS [13]	50 ml

[11] *Cannon-Fenske viscometer tubes at room temperature and for non-transparent liquids, Ubbelohde tubes may be used for transparent liquids. No prefiltration of the sample if visually homogenous. Elimination of air bubbles before analysis. Equilibration time 30 minutes at 20 °C, 20 minutes at 80 °C.*

[12] *Sample pretreatment by combustion according to ASTM D 4208*

[13] *Wet combustion as a pretreatment method.*

Based on this analytical study an analytical package has been built for testing the injection system of a diesel engine by a so-called bench-test (Appendix 13).

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HOMOGENEITY OF PYROLYSIS LIQUIDS

Sample: Ensyn pyrolysis liquid, Hardwood mix, VTT batch 6/95 (received in June 1995).

Method: The barrel was turned up-side down for overnight. The pyrolysis liquid was mixed thoroughly by a propeller mixer (1 - 2 hours at room temperature). Care was taken to mix also the very bottom layer of the barrel (a thick slurry). Two samples were taken by a wide mouthen piston pump from surface (10 - 20 vol% below the surface) and bottom (10 - 20 vol% above the bottom) part of the liquid.

Results after homogenisation:

Analysis, wet basis	Upper layer	Lower layer
Water, wt%	23.6	23.8
Acetone insolubles, wt%		
0.6 μm filter	0.7	0.7
25 μm filter	0.04	0.03
45 μm filter	<0.01	<0.01
Ash, wt%	0.1	0.1
Carbon, wt%	44.8	44.9
Hydrogen, wt%	7.2	7.1
Nitrogen, wt%	0.1	0.1
HHV, MJ/kg	18.3	18.3
LHV, MJ/kg	16.7	16.7

HOMOGENEITY OF PYROLYSIS LIQUIDS

Sample: Ensyn pyrolysis liquid, Hardwood, VTT batch 10/95

Method: A large batch of pyrolysis liquid was mixed and divided into totes of 1 m^3 at the production plant. Six totes were randomly chosen, homogenised by pumping and analysed. The liquid was pumped using a vane pump at room temperature from bottom to top and other way around for about one hour per tote. The temperature of the pyrolysis liquid may have increased to some extent by pumping (below 30 °C). The viscosity of the liquid was 370 mPa s @ 25 °C. Samples were taken from the homogenous mixture by pouring from the hose at the outlet of the pump.

Results:

Analyses, wet basis Tote no.	A	B	C	D	E	F
Water, wt%	23.2	23.2	23.3	23.3	23.3	23.3
Acetone insolubles, wt%	0.7	0.6	0.7	0.6	0.7	0.6
Particles below 45 µm, % of the total amount	100	-	100	-	100	-
Particles below 25 µm, % of the total amount	100	-	100	-	100	-
Ash, wt%	0.08	0.09	0.08	0.09	0.09	0.09
Carbon, wt%	44.6	44.7	44.7	44.7	44.7	44.7
Hydrogen, wt%	6.9	7.0	6.9	6.9	6.9	6.9
Nitrogen, wt%	0.1	0.1	0.1	0.1	0.1	0.1
HHV, MJ/kg	18.1	18.0	18.1	18.1	18.1	18.1
LHV, MJ/kg	16.5	16.7	16.6	16.6	16.6	16.6

HOMOGENISATION AND SAMPLING AT VTT

Sample bottles: PP (polypropylene), HDPE (high-density polyethylene), PTFE (polytetrafluoroethylene) or other resistant polymeric materials. Glass bottles cannot be used if trace levels of alkalis are to be analysed.

Homogenisation:

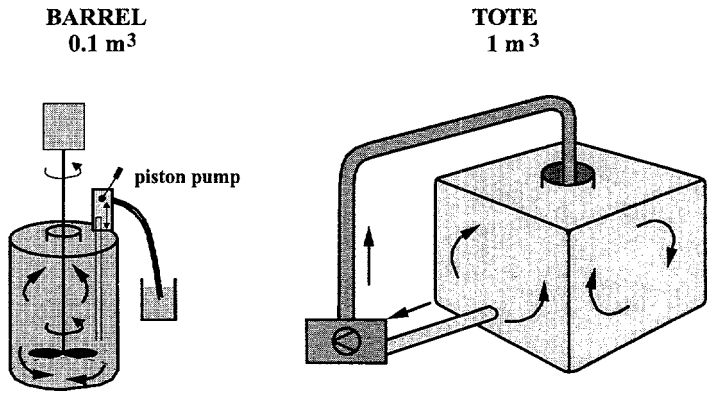
A small (containers <10 l) sample vessel is homogenised in a laboratory mixer (about one hour at room temperature).

Larger (10 - 100 l) containers are mixed by a propeller mixer. The barrel (100 - 200 l) is turned upside down for overnight. The pyrolysis liquid is mixed thoroughly by a propeller mixer (abt one hour at room temperature). Care is taken to mix also the very bottom layer of the barrel (a thick slurry).

In case of totes (1 m^3) a pump is connected by hoses to the bottom and upper opening of the tote. One sample valve is connected to the bottom opening. VTT has used a vane pump for homogenisation. For very viscous liquids a high-shear gear pump is claimed to be suitable. The liquid sample is at room temperature. If the viscosity of the liquid is still too high for pumping a warm water (30 - 40 °C) circulation on the opening of the tote may be used. The pyrolysis liquid is pumped from bottom to up and other way around for about one hour. The homogeneity of the liquid is ensured by analysing the water and solids content from upper and lower part of the liquid. If the difference in water and solids between upper and lower part of the liquid is more than 5 %, homogenisation of the sample is continued.

Sampling:

Samples can be taken by a wide mouthen piston pump or using a large syringe from upper (10 - 20 vol% below the surface) and lower (10 - 20 vol% above the bottom) part of the liquid.



Sampling procedure.

DETERMINATION OF WATER CONTENT

Comparison of the standard methods ASTM E 203 and ASTM D 1744

Water determination for pyrolysis liquids by ASTM E 203, titration solvent pyridine: ethyleneglycol monomethylether (1:4).

	Pyrolysis liquids		
	Hardwood 1	Hardwood 2	Straw
Water, wt%	18.64	27.28	27.6
	18.61	26.88	27.62
	18.65	27.23	27.61
	18.69	27.04	27.98
	-	27.22	27.65
	-	27.22	-
Average, wt%	18.65	27.11	27.70
Stdevp, abs.	0.03	0.16	0.16
Stdevp, %	0.15	0.59	0.58

Hardwood 1 = Ensyn pyrolysis liquid, Oak-maple, VTT batch 8/94. Hardwood 2 = Union Fenosa bio-oil, Eucalyptus, VTT batch 10/94. Straw = Ensyn pyrolysis liquid, Wheat straw, VTT batch 9/94.

Water determination for pyrolysis liquids by ASTM D 1744, titration solvent chloroform-methanol (3:1).

	Pyrolysis liquids		
	Hardwood 1	Hardwood 2	Straw
Water, wt%	18.73	27.37	27.6
	18.66	27.25	27.6
	18.75	27.29	27.6
	18.56	27.21	27.56
	18.75	-	-
Average, wt%	18.68	27.28	27.59
Stdevp, abs.	0.07	0.06	0.02
Stdevp, %	0.40	0.22	0.06

Water addition test

Water is added to pyrolysis liquid. Glass beads are added in order to enable an effective mixing. Samples are shaken in a mixer for about 30 minutes and let stand overnight in air-tight bottles at room temperature. Before water determination the samples are mixed again both in a mixer and by hand.

Water addition method.

No.	Hardwood 3 g	Water g		Water wt%		Difference wt%
		Added	Total	Calculated	Analysed	
0	0	0	-	-	16.55	0.04
1	44.0831	1.9444	9.2402	20.08	20.16	+ 0.08
2	40.4548	3.1465	9.8418	22.57	22.60	+ 0.03
3	40.3653	4.8412	11.5217	25.49	25.40	- 0.09
4	41.7695	6.9478	13.8607	28.45	28.52	+ 0.07
5	41.4419	8.8210	15.6796	31.20	two phases	-
6	abt. 40	11	-	abt. 35	two phases	-
7	abt. 40	13	-	abt. 38	two phases	-

Hardwood 3 = Union Fenosa bio-oil, Eucalyptus, VTT batch 8/94

Water addition method.

No	Hardwood 4 g	Water g		Water wt%		Difference wt%
		Added	Total	Calculated	Analysed	
0	0	0	-	-	23.57	-
1	93.39	2.10	24.11	25.25	25.13	- 0.12
2	96.37	4.16	26.87	26.73	27.75	+1.02
3	93.99	6.30	28.45	28.37	28.37	0.00
4	92.34	7.98	29.74	29.65	two phases	-

Hardwood 4 = Ensyn pyrolysis liquid, Hardwood mix, VTT batch 6/95

Use of different solvents in ASTM D 1744

Water determination for a hardwood pyrolysis liquid (Ensyn pyrolysis liquid, hardwood mix, 10/95) by ASTM D 1744. Titration solvents: a. chloroform:methanol (3:1), b. methanol, c. methanol with a buffer (imidazole), d. HYDRANAL-solutions (Composite 5 K, Working medium K).

Titration solvent	a	b	c	d	d[1]
Water, wt%	23.2	23.6	23.5	22.1	23.2
	23.2	23.5	24.4	22.8	23.3
	23.2	23.6	23.2	23.1	23.3
	23.3	23.5	-	22.6	-
	23.2	23.5	-	22.2	-
	23.2	-	-	21.7	-
	-	-	-	23.5	-
	-	-	-	22.9	-
	-	-	-	22.5	-
Average, wt%	23.2	23.5	23.7	22.6	23.3
Stdevp, abs.	0.04	0.05	0.51	0.52	0.05
Stdevp, %	0.16	0.21	2.15	2.29	0.20

[1] *Stabilisation time 30 + 30 s. In all other determinations 30 s.*

Effect of the stabilisation time

Water determination for pyrolysis liquids, using 30 s stabilisation time, from hardwood (Ensyn pyrolysis liquid, oak, VTT batch 12/95), softwood (VTT pyrolysis liquid, test 1 11/95, pine) and straw (VTT pyrolysis liquid, AFPB 1/7, straw, 2/96) by ASTM D 1744, titration solvents: a. chloroform:methanol (3:1), b. HYDRANAL-solutions (Composite 5 K, Working medium K).

	Pyrolysis liquids					
	Hardwood		Softwood		Straw	
Titration solvent	a	b	a	b	a	b
Water, wt%	25.87	26.18	20.44	20.85	19.13	19.49
	25.58	25.93	20.39	20.74	19.02	19.71
	-	26.06	-	-	-	-
Average, wt%	25.7	26.1	20.4	20.8	19.1	19.6

Change in water content by using additional 30 s stabilisation time.

	Pyrolysis liquids					
	Hardwood		Softwood		Straw	
Titration solvent	a	b	a	b	a	b
Water, wt%	+ 0.1	0	0	0	+ 0.03	0
	+ 0.3	0	0	0	+ 0.21	+ 0.21
	-	0	-	-	-	-
Average, wt%	25.9	26.1	20.4	20.8	19.2	19.7

SOLIDS CONTENT

Equipment: Millipore filtration system (Appendix 3/3).

Filters: Ethanol and methanol insolubility: polycarbonate film filters (Isopore track-etched membrane) of 0.1, 3, 10 µm; acetone insolubility: Whatmann filter papers (white ribbon[a], about 6 µm and blue ribbon[b], about 2 µm).

Solids in pyrolysis liquids as ethanol insolubles.

	Pyrolysis liquids								
	Hardwood 1			Hardwood 2			Straw		
Filter pore size, µm	10	3	0.1	10	3	0.1	10	3	0.1
Solids, wt%	0.43	0.49	0.45	0.90	0.93	0.89	0.82	0.62	0.80
	0.51	0.54	0.53	0.89	1.03	0.97	0.81	0.79	1.37
Average, wt%	0.47	0.52	0.49	0.90	0.98	0.93	0.75	0.71	1.09

Hardwood 1 = Ensyn pyrolysis liquid, oak-maple, VTT batch 8/94 (water 18.6 wt%). Hardwood 2 = Union Fenosa bio-oil, Eucalyptus, VTT batch 10/94 (water 27.9 wt%). Straw = Ensyn pyrolysis liquid, wheat straw VTT batch 8/94 (water 28.2 wt%).

Solids in pyrolysis liquids as acetone insolubles.

	Pyrolysis liquids			
	Hardwood 1		Hardwood 2	
Filter pore size, µm	about 6 [a]	about 2 [b]	about 6	about 2
Solids, wt%	0.48	0.66	1.05	1.20
	0.45	0.65	0.91	1.09
Average, wt%	0.47	0.66	0.98	1.15

Solids in pyrolysis liquids measured as ethanol and acetone insolubles.

	Solids, wt%	
Solvent	ethanol	acetone
Filter pore size, µm	3	about 2[b]
Hardwood liquid 3	0.28	0.70
	0.30	0.65
Average, wt%	0.3	0.7
Straw liquid	0.80	11.3
	0.77	9.9
Average, wt%	0.8	10.6

Hardwood 3 = Ensyn pyrolysis liquid, VTT batch 10/95 (water 23.3 wt%).

Solids measured as ethanol and methanol insolubles.

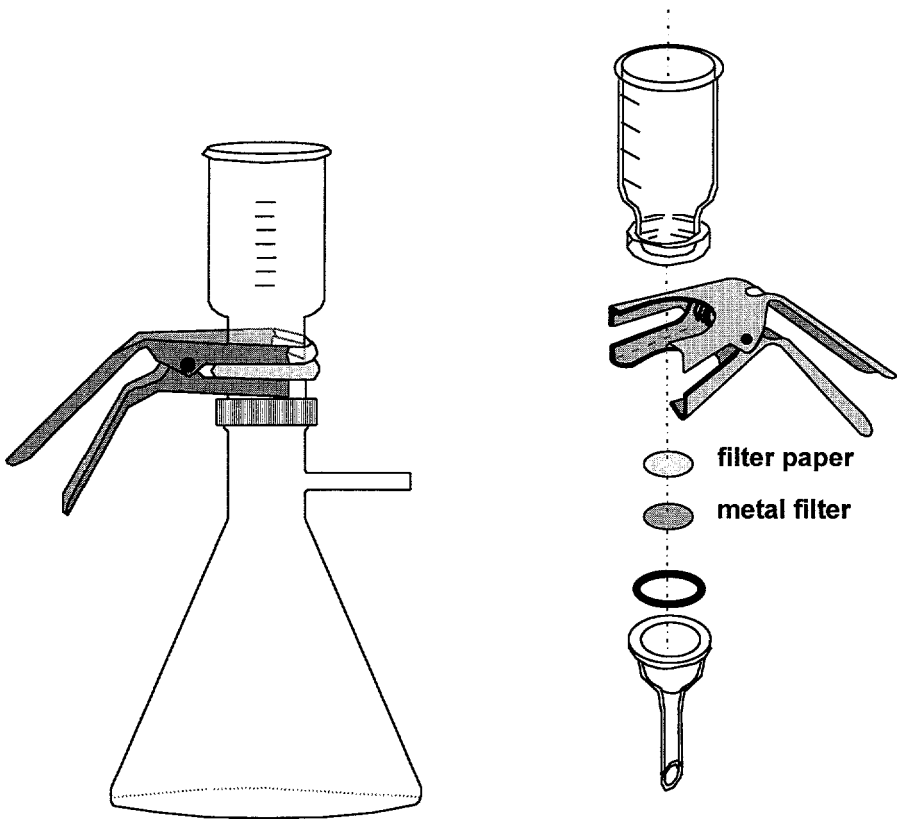
	Pyrolysis liquids			
	Hardwood 1	Hardwood 2	Softwood	Straw
Filter pore size, microns	0.8	0.8	0.8	0.8
Ethanol insolubles, wt%	0.165	1.166	1.299	0.864
	0.137	1.134	1.357	0.852
	0.186	-	-	-
	0.156	-	-	-
	0.155	-	-	-
	0.148	-	-	-
Average	0.158	1.150	1.328	0.858
Stdevp,abs.	0.015	0.016	0.029	0.006
Stdevp,%	9.5	1.4	2.2	0.7
Methanol insolubles, wt%	0.200	0.993	1.125	0.541
	0.192	1.005	1.148	0.576
	0.162	-	-	-
	0.139	-	-	-
	0.152	-	-	-
	0.173	-	-	-
	0.158	-	-	-
	0.168	-	-	-
Average	0.168	0.999	1.137	0.559
Stdevp,abs.	0.019	0.006	0.012	0.018
Stdevp,%	11.3	0.6	1.0	3.1

Pyrolysis liquids: Hardwood 1 = Ensyn pyrolysis liquid, Oak-maple, VTT batch 10/95 (water 23.3 wt%), Hardwood 2 = Union Fenosa pyrolysis liquid, Eucalyptus, VTT batch 3/95 (water 18.8 wt%), Softwood = Union Fenosa pyrolysis liquid, pine, VTT batch 3/95 (water 21.6 wt%), Straw = Ensyn pyrolysis liquid, wheat straw, VTT batch 8/94 (28.2 wt%).

SOLIDS AS ETHANOL INSOLUBLES

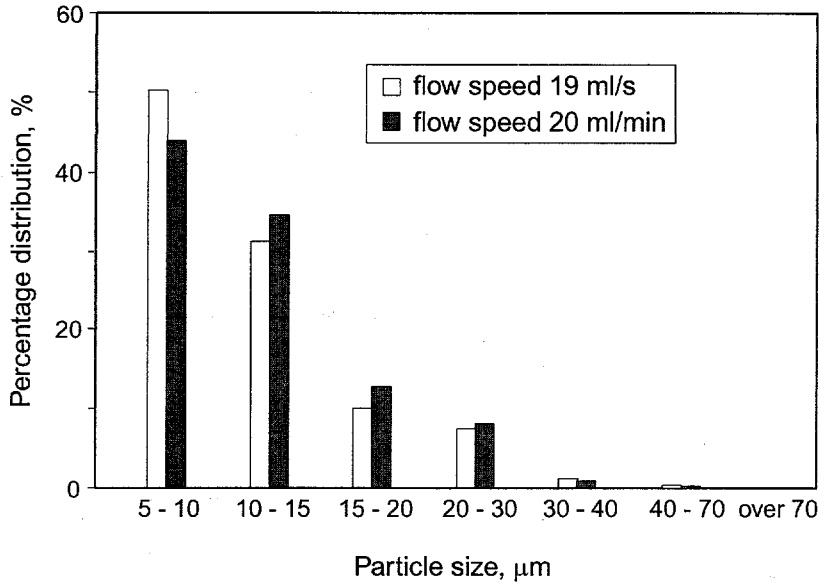
Method:

A representative sample (1 - 3 g) of pyrolysis liquid is dissolved in 100 - 300 ml of ethanol. The solution is filtrated through a Millipore filtration system. The original Millipore filter was too dense and was replaced by a larger porosity metal sinter. The sample filter is a 0.1 μm pore size, 37 mm (o.d.) polycarbonate film (TSTP 047 00) by Millipore. The solids are washed with ethanol until the filtrate is clear. The filter is removed and dried first in an oven at 105 °C for 30 minutes, then in a desiccator and weighed. The solids content is calculated based on the original pyrolysis liquid sample. If the filtration time is very long in case of high solids content, a larger filter (3 μm) may be used. The filtrate is then filtered through a 0.1 μm filter. The both solids contents are combined.

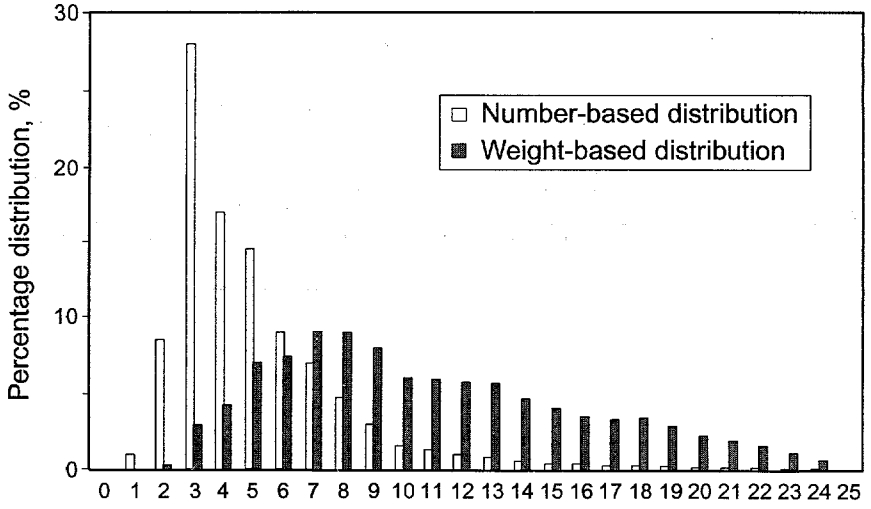


Millipore filtration system.

PARTICLE SIZE DISTRIBUTION



Effect of flow rate on particle size distribution. Ensyn pyrolysis liquid, hardwood, VTT batch 6/95 (water 23.7 wt%.)



Number- and weight-based particle distributions in pyrolysis liquid (Ensyn pyrolysis liquid, hardwood, VTT batch 6/95.

Weight-based particle size distribution by filtration

Ethanol insoluble. Sample size 2-4 g. Sample: solvent 1:100...150.

		Solids content, wt%			
		Filter, µm			Total
Pyrolysis liquid		10	10+3	10+3+0.1	
Hardwood 1	Solid content, wt%	0.45	0.03	0.02	0.50
		0.45	0.05	0.05	0.55
Hardwood 2	Solid content, wt%	0.98	0.02	0.03	1.03
		0.95	0.03	0.04	1.02
Straw	Solid content, wt%	0.74	0.02	0.06	0.82
		0.78	0.01	0.04	0.83

Hardwood 1 = Ensyn pyrolysis liquid, Oak-maple, VTT batch 8/94 (water 18.6 wt%), Hardwood 2 = Union Fenosa pyrolysis liquid, Eucalyptus, VTT batch 10/94 (water 27.9 wt%), Straw = Ensyn pyrolysis liquid, wheat straw, VTT batch 8/94

Acetone insoluble. Sample size 20 g. Sample: solvent 1:100.

		Solids content, wt%			
		Filter, µm			Total
Pyrolysis liquid		45	45+25	45+25+0.6	
Hardwood 3	Solid content, wt%	0.001	0.004	0.938	0.943
		0.000	0.000	0.963	0.963

Hardwood 3 = Ensyn pyrolysis liquid, oak-maple, VTT batch 11/96 (water 20.6 wt%)

Ethanol insoluble. Sample size 20 g. Sample: solvent 1:100.

		Solids content, wt%				
		Filter, µm			Total	Filter, µm
Pyrolysis liquid		10	10+3	10+3+0.1		0.1
Hardwood 3	Solid content, wt%	0.95	0.01	0.01	0.97	0.91
		-	-	-	-	0.89

DISTRIBUTION OF METALS IN FILTRATION

Sample: Ensyn pyrolysis liquid, hardwood, VTT batch 4/93

Sample pretreatment: Dry combustion (550 °C)

Method: ICP (Inductively Coupled Plasma)

Metal distribution

Metal	Pyrolysis liquid			Mass closure
	Original	Filtrate	Cake	%
Mass closure, %	100	92[a]	6	98
	ppm	Metals in filtrate, % of total	Metals in cake, % of total	
Calcium	540	53	40	93
Sodium	21	57	8	65
Aluminium	43	36	64	100
Iron	71	40	33	73
Magnesium	71	47	45	92
Potassium	440	84	20	104
Silicon	330	2	85	87
Phosphorous	30	34	56	90
Lead	0.5	37	65	102
Cadmium	<0.2	<92	<15	-
Arsenic	<0.5	<92	<36	-
Cobalt	0.04	46	60	106
Copper	2.8	46	47	93
Nickel	1.6	46	45	91
Zinc	15	86	16	102
Vanadium	0.06	31	60	91
Chromium	2	14	90	104
Sulphur	56	84	27	111

[a] *2 wt% loss in filtration*

METALS BY ICP-AES

Sample pretreatment: wet oxidation

Pyrolysis liquid (1 - 2 g) is boiled in concentrated nitric acid (10 - 20 ml) or if needed in a mixture of nitric and perchloric acid (2:1) until the solution is clear. The solution is then diluted with water to total volume of 50 ml. The heating time is typically about an hour. The minimum sample size needed is 10 g.

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

Metals by ICP:

Ca, Na, Al, Fe, Ti, Mg, K, Si, P, S (modified program)
Pb, Cd, As, Fe, S, Cu, Co, Ni, Zn, Hg, V, Cr (modified program)

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

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

ALKALI METALS BY AAS

Sample pretreatment: Wet oxidation

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

Standard solutions:

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

Accuracy of alkali analysis by AAS (8 duplicates). Sample size 1 - 3 g.

	Pyrolysis liquids								
	Hardwood 1			Hardwood 2			Straw		
Metal	Average ppm	Stdevp abs.	Stdevp %	Average ppm	Stdevp abs.	Stdevp %	Average ppm	Stdevp abs.	Stdevp %
Na	34	8.3	24.3	83	6.8	8.1	401	27.1	6.8
K	85	8.1	9.5	31	4.1	13.3	9 250	244.9	2.6
Ca	37	21.7	58.5	29	14.8	51.2	996	158.1	15.9
Mg	8	3.3	41.6	12	2.7	22.2	239	6.0	2.5

Hardwood 1 = Ensyn pyrolysis liquid, VTT batch 8/94 (water 18.6 wt%). Hardwood 2 = Union Fenosa bio-oil, Eucalyptus, VTT batch 10/94 (water 27.9 wt%). Straw = Ensyn pyrolysis liquid, VTT batch 8/94.

COMPARISON OF SAMPLE PRETREATMENT METHODS IN AAS-ANALYSIS

Sample pretreatment 1: Dry combustion (DC)

Pyrolysis liquid (about 10 g) is burned with isopropanol (IPA) in Pt crucibles by an open flame (Bunsen) until the organic material is burnt. The samples are ashed at 520 °C for two hours. The ash is dissolved in a mixture of concentrated HCl (1 ml) and distilled water (2 - 3 ml), heated with the Bunsen burner and cooled. The solution is diluted by water to a total volume of 25 ml.

Sample pretreatment 2: Dissolution in alcohol

Pyrolysis liquid (0.5 and 1.0 g) is dissolved in 40 ml isopropanol (IPA).

Sample pretreatment 3: Wet oxidation (WO)

See Appendix 5/3. Sample size 3 - 5 g.

Accuracy of alkali analysis by AAS

	Pyrolysis liquid, hardwood					
Sample pretreatment	Dry combustion			Wet oxidation		
Sample size, g	10			3 - 5		
Determinations	2			8		
Metal	Average ppm	Stdevp abs.	Stdevp %	Average ppm	Stdevp abs.	Stdevp %
Na	8	0.0	0.0	8	1.1	13.7
K	315	5.0	1.6	320	9.3	2.9
Ca	180	0.0	0.0	195	7.1	3.6
Mg	32	0.5	1.6	30	0	0.0

Pyrolysis liquid = Ensyn pyrolysis liquid, hardwoodVTT batch 6/95 (water 23.7 wt%)

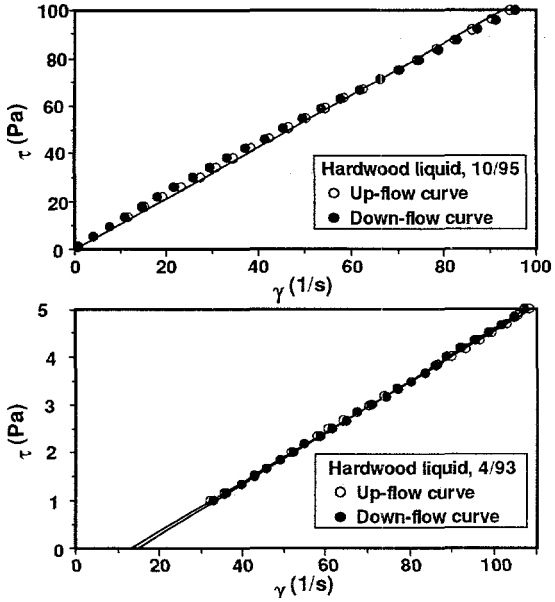
ELEMENTAL ANALYSES

Accuracy of CHN analysis.

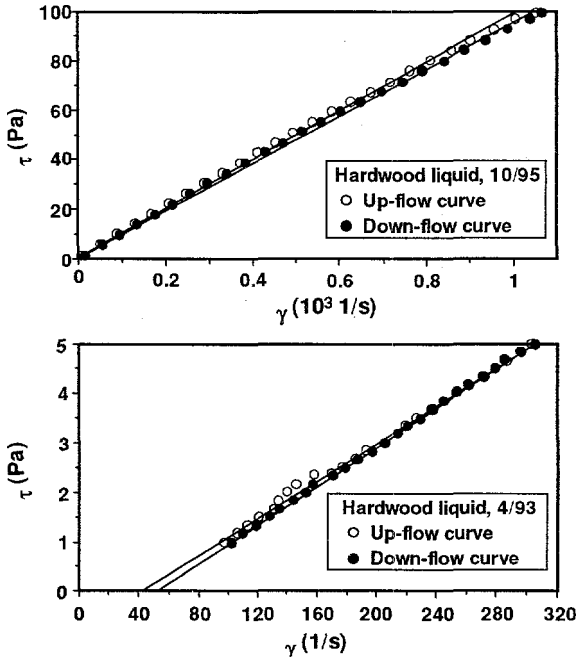
	Pyrolysis liquid						Residual oil standard		
	Hardwood 1			Hardwood 2					
Element	C	H	N	C	H	N	C	H	N
Concentration, wt%	49.2	7.0	0.06	39.5	7.3	0.02	87.0	11.4	0.18
	49.1	7.0	0.13	39.5	7.2	0.03	87.4	11.6	0.18
	48.9	7.0	0.07	38.9	7.1	0.01	87.5	11.5	0.18
	49.0	7.1	0.05	39.4	7.4	0.01	86.9	11.6	0.20
	49.2	7.1	0.07	39.4	7.3	0.03	87.4	11.5	0.22
	49.3	7.0	0.08	39.5	7.3	0.01	87.3	11.5	0.19
	49.4	7.0	0.06	-	-	-	86.9	11.6	0.21
	49.6	7.1	0.04	-	-	-	86.5	11.6	0.20
	-	-	-	-	-	-	87.5	11.4	0.22
Average, wt%	49.2	7.0	0.07	39.4	7.3	0.02	87.2	11.5	0.20
Stdevp, abs.	0.2	0.0	0.03	0.2	0.1	0.01	0.3	0.1	0.01
Stdevp, %	0.4	0.7	36.4	0.5	1.3	49.0	0.4	0.6	7.2

Hardwood 1 = Ensyn pyrolysis liquid, VTT batch 8/94 (water 18.6 wt%). Hardwood 2 = Union Fenosa bio-oil, VTT batch 10/94 (water 27.9 wt%). Residual Oil Standard AR 100, LOT 1621: C 87.28 wt%, H 11.49 wt% ,N 0.193 wt% (no water). Alpha Resources, Inc., Certificate of Analysis,

NEWTONIAN BEHAVIOUR OF PYROLYSIS LIQUIDS



The flow curve of pyrolysis liquid (Ensyn hardwood) at 25 °C. Viscosities 53 mPas for VTT batch 4/93 (water 25.5 wt%) and 1075 mPas for VTT batch 10/95 (water 23.3 wt%).



The flow curve of pyrolysis liquids (Ensyn hardwood) at 50 °C. Viscosities 19 mPas for batch 4/93 and 95 mPas for batch 10/95.

Comparison of kinematic viscosity determined by using Cannon-Fenske and Ubbelohde methods. Sample: Ensyn pyrolysis liquid, hardwood, VTT batch 11/96 (water 20.6 wt%).

Method	Cannon-Fenske			Ubbelohde		
Temperature, °C	20	50	80	20	50	80
Equilibration time, min	30	30	20	30	30	20
Viscosity, cSt	666	52	11	649	52	12
	674	52	11	651	52	12
	671	52	11	649	52	12
	678	52	11	-	52	12
Average, cSt	672	52	11	650	52	12
Stdevp,abs.	4.4	0.1	0.1	1.1	0.0	0.0
Stdevp,%	0.6	0.3	0.5	0.2	0.1	0.0

Dynamic viscosity at different temperatures by using a rotaviscotester (Haake VT 550 equipped with a cover, NV cup of 8 ml). Sample: Ensyn pyrolysis liquid, hardwood, VTT batch 11/96 (water 20.6 wt%). Kinematic viscosities have been calculated by dividing with the density of the liquid. Densities for batch 11/96: 1.240 kg/dm^3 @ 20°C, 1.214 kg/dm^3 @ 50 °C, 1.180 kg/dm^3 @ 80 °C.

Temperature, °C	20	50	80
Equilibration time, min	15	15	10
Shear rate, 1/s	100	800 - 1 000	2 500
Viscosity, mPa s	839	70	16
	837	70	17
	840	71	18
	838	71	-
	838	70	-
	-	70	-
Average, mPa s	838	70	17
Stdevp,%	0.12	0.67	4.8
Viscosity, cSt	676	58	14

INFLUENCE OF EQUILIBRATION TIME ON VISCOSITY

Sample: Ensyn pyrolysis liquid, hardwood, VTT batch 1/94 (water 32.9 wt%)

Method: ASTM D 445

Results:

	Viscosity, cSt		
Equilibration time[a], min	20 °C	50 °C	80 °C
30	19.15	5.06	2.16
50			2.19
80			2.21
140			2.27

[a] *Equilibration time for a sample in a measuring capillary in the viscometer bath.*

MATERIAL TESTING FOR STORING, TRANSPORTATION, AND USE OF PYROLYSIS LIQUIDS

Material	Composition	Test conditions	Weight loss wt%
PTFE (Teflon)	Polytetrafluoroethylene	6 weeks at room temperature	0.000
AISI 01	97.3% Fe, 0.9% C, 1.2% Mn, 0.5% W, 0.1% V	24 h at 60 °C	0.823
AISI 316 *	69.75% Fe, 0.05%C, 17% Cr, 11% Ni, 2.2% Mo	6 weeks at room temperature 6 weeks at 50 °C 3 months at 50 °C	0.000 0.000 0.000
AISI 420	84.7% Fe, 0.4% C, 13.6% Cr, 0.8% Si, 0.5% Mn	6 weeks at room temperature 6 weeks at 50 °C	0.191 2.2
HASTELLOY X	48.5% Ni, 21% Cr, 19% Fe, 9% Mo, 2% Co, 0.5% W	6 weeks at room temperature	0.012
NIMONIC 80A	71.9% Ni, 19.5% Cr, 4% Mo, 2.25% Ti, 1.4% Al, 1% Co	6 weeks at room temperature 1 week at 80 °C 3 weeks at 80 °C	0.002 0.109 0.226
HAYNES 188	39.4% Co, 22% Cr, 22.9% Ni, 14.5% W, 1.2% Fe	6 weeks at room temperature 1 week at 80 °C	0.000 0.000
ARCLOK	80.8% Fe, 12.7% Cr, 4.2% Ni, 1% Mo, 1% Mn, 0.02% C, 0.3% Si	6 weeks at room temperature	0.006
Copper	99.9% electrolytic Cu	1 month at room temperature 1 month at 50 °C	0.000 0.000
Brass	78% Cu, 19% Si, 3% Zn	1 week at 80 °C 3 weeks at 80 °C	0.005 0.009
Chromium as a coating on AISI01		6 weeks at room temperature 1 week at 80 °C	0.000 1.0
Nickel	99.5% Ni, 100 ppm Co	6 weeks at room temperature	0.004
NIKROTAL 80	80% Ni, 20% Cr	6 weeks at room temperature	0.005

** Werkstoff no. 1.4401, SS 2347, Avesta 832SF*

WATER EXTRACTION OF PYROLYSIS LIQUID - METHOD DESCRIPTION

30 November 1996

PYROLYSIS LIQUID : WATER = 1:10

1. 400 g of distilled water is weighed in a 500 ml Erlenmeyer or 500 ml Schott flask.
2. 50 g of pyrolysis liquid (A, water content wt%) is mixed to the water as slowly as possible stirring continuously (e.g. by a magnetic stirrer).
3. The bottle is closed and placed to a mixer at least for two hours. The solution may stand overnight.
4. The solution is filtered through a Büchner funnel (blue ribbon filter paper, filter pore size about 2 μm) into a suction flask. An intermediate flask, e.g., Wulff flask, is used for water suction. Should the filtrate not be clear it is filtered again through a 0.1 μm filter to remove tiny particles disturbing the water analysis. If a weighable amount of precipate remains on the filter paper, it is dried and added to the total amount of solids.
5. The precipitate in the Erlenmayer/Schott flask and in the Büchner funnel are rinsed with 100 g of distilled water.
6. The filtrate is weighed, and its pH and water content (K-F) are measured. The wet precipitate is also weighed prior to drying.
7. The Büchner funnel with precipitate is dried in a vacuum oven at 40 °C overnight.
8. The precipitate in the Büchner funnel is cooled in the desiccator and weighed immediately after cooling (B). The precipitate is ground in a mortar or with a clean grinder to avoid water absorption. The precipitate (substance insoluble in water) is stored in the desiccator for analysis.
9. If a weighable amount of precipitate remains on the walls of the sample flask, the flask is dried in the vacuum oven at 40 °C for three hours, cooled in an desiccator and weighed. The weight of this precipitate (C) is added to the amount of the precipitate dried in the Büchner funnel (B).

Analyses:

- pyrolysis liquid - water, pH, CHN
- filtrate - water, pH, TC+TOC (volatile acids)
- substances insoluble in water- CHN, moisture (due to absorption of water during preparing the sample for CHN analysis)

Substance insoluble in water (dry basis), wt% =

(B+C)*100/[((100-a)*A)/100]

WATER EXTRACTION OF PYROLYSIS LIQUID - MASS, WATER, CARBON BALANCES

Hardwood liquid[a].

Mass, g	Material	Water	Carbon	Solutes
PL[b]	20.03	4.71	8.97	15.32
Water	201.41	201.41	0.00	0
In, total	221.44	206.12	9.0	15.32
Water insoluble	15.42	7.71	4.90	7.71
Aqueous	206.02	196.67	4.25	9.35
Out, total	221.44	204.38	9.1	17.06
In-out, g	0	1.74	-0.2	-1.74
Mass loss, %	0	0.8	-1.9	-11.4
Water insoluble, wt%				
of original liquid	**38.5**			**38.5**
dry basis	**50.3**			**50.3**

[a] *Ensyn pyrolysis liquid, VTT batch 10/95.* [b] *PL = pyrolysis liquid*

Straw liquid[c].

Mass, g	Material	Water	Carbon	Solutes
PL	39.8	7.92	17.55	31.9
Water	441.3	441.3	0.00	0
In, total	481.1	449.2	17.6	31.9
Water insoluble	17.0	7.93	6.17	9.07
Aqueous	464.1	444.35	10.99	19.75
Out, total	481.1	452.3	17.2	28.8
In-out, g	0	-3.1	0.4	3.1
Mass loss, %	0	-0.7	2.2	9.7
Water insoluble, wt%				
of original liquid	**22.8**			**22.8**
dry basis	**28.5**			**28.5**

[c] *VTT pyrolysis liquid AFPB 1/7, 2/96*

APPENDIX 10

LUBRICITY

Results of a four-ball test. Weight 40 kp (392 N), temperature 22 °C, time one hour. Ball diameter 12.7 mm. Ensyn pyrolysis liquid (PL), hardwood mix, VTT batch 10/95 (water 23.3 wt%).

Sample	Average wear, mm	Viscosity (@ 50 °C), cSt
Pyrolysis liquid (PL)	0.7	50
Rape seed oil[a]	0.5	24
PL + 1 wt% rape seed oil[a]	0.6	56
Raw tall oil	1.5	47
DIKC[b]	1.6	2.5
Pyrolysis liquid (PL)	0.5	-
PL + 5 wt% rape seed oil[a]	0.6	-
PL + 5 wt% white oil[c]	0.5	-
PL + 5 wt% castor oil	0.5	-
PL + 5 wt% polyglygol[d]	0.5	-

[a] Mildola SDG, [b] "City"-Diesel fuel, summer grade, [c]Shell Ondina 15 (viscosity 15 cSt @ 40 °C), [d] Polyethylene glycol 200

STABILITY TESTS

Material and methods

The raw materials of the stability test were an eucalyptus pyrolysis liquid (Union Fenosa) and a hardwood pyrolysis liquid (Ensyn). 80 - 90 ml of the original liquid was placed in 100 ml glass bottles. The bottles were firmly closed and protected from light. The eucalyptus liquid samples were stored at room temperature (23 °C), and at elevated temperatures (35, 60, 80 °C) in ovens over various time periods. The hardwood liquids were stored at room temperature and at temperatures of 50, 60, and 80 °C for various time periods. After the certain time the samples were cooled rapidly and analyses were performed.

The viscosity of the eucalyptus liquid at 50 °C was measured at the Finnish Pulp and Paper Research Institute (KCL) by Haake's closed-cup rotaviscometer. The viscosity of the hardwood liquid samples was analysed as a kinematic viscosity by a standard method (ASTM D 445). The water content was analysed by Karl Fischer titration according to ASTM D 1744.

Results

Viscosity change and water analyses for the eucalyptus liquid

Sample	Storing conditions	Viscosity (50 °C), mPa s	Water, wt%
Reference	20 °C (fresh)	67	19.2
1	20 °C, 3 months	82	20.0
2	6 months	86	19.6
3	12 months	-	20.0
4	35 °C, 1 month	96	20.2
5	2 months	121	-
6	3 months	144	20.3
7	6 months	194	20.8
8	12 months	375	21.9
9	50 °C, 24 hours	70	19.6
10	72 hours	76	19.8
11	1 week	90	19.9
12	1 month	144	-
13	2 months	220	21.4
14	80 °C, 3 hours	68	19.6
15	24 hours	96	20.3
16	72 hours	151	21.2
17	1 week	280	21.0

Raw material: Ensyn RTP liquid from oak-maple, produced 7-10/95.

Viscosity change and water analyses for the pyrolysis liquid from oak and maple.

No.	Temperature, °C	Time, h	Viscosity @ 50 °C, cSt	Water, wt%
Test 0A	20	0	49	23.5
Test 0	20	0	51	22.7
Test 1A	20	672	52	23.5
Test 2A	20	672	51	23.4
Test 7A	50	24	53	24.0
Test 8A	50	48	61	24.5
Test 9	50	72	60	23.1
Test 10	50	168	69	23.6
Test 11	60	6	52	22.9
Test 12	60	25	64	23.2
Test 13	60	72	90	-
Test 14	60	120	131	23.1
Test 15	60	336	205	-
Test 21	80	1	46	23.4
Test 22	80	2	47	23.2
Test 23	80	3	48	23.5
Test 24	80	4	49	22.9
Test 25	80	6	58	22.8
Test 26A	80	8	66	24.4
Test 27	80	18	92	23.8
Test 28	80	24	108	24.9
Test 28A	80	24	124	26.7
Test 29	80	48	334	27.1
Test 30	3	6	52	23.1
Test 31	3	24	50	22.8
Test 32	3	48	50	23.2
Test 33	3	168	49	22.2
Test 34	3	336	48	22.5
Test 35A	3	672	47	23.5
Test 36	9	6	52	23.1
Test 37	9	24	50	23.6
Test 38	9	48	49	23.2
Test 39	9	168	49	22.4
Test 40	9	336	48	21.6
Test 41A	9	672	48	23.7
Test 42	-14	24	49	23.7
Test 43	-14	168	48	22.6
Test 44A	-14	672	47	23.7
Test 44	-14	672	48	23.2
Test 45	-14	4 320		

A = Same batch of pyrolysis liquid, but different container.

STABILITY TEST METHOD

Method description

The 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. 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 50 °C is measured as kinematic viscosity by a standard method (ASTM D 445). The water content is analysed by Karl Fischer titration according to ASTM D 1744.

$$\Delta \text{ Viscosity } (50\ ^{\circ}\text{C})\ [\%] = \frac{(\nu_2 - \nu_1)}{\nu_1} \times 100$$

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

ν_1 = viscosity of the original sample, cSt
ν_2 = viscosity of the sample aged at 50 °C, cSt
ω_1 = water content of the original sample, wt%
ω_2 = water content of the sample aged at 50 °C, wt%

Test producibility

Sample: Ensyn pyrolysis liquid, hardwood, VTT batch 11/96
Analyses: water 20.8 wt%, viscosity @ 50 °C 52 cSt

	1	2	3	4	5	6	7	8
N_2 purge	no	no	no	no	yes	yes	yes	yes
Aging temp., °C	80	80	80	80	80	80	80	80
Aging time, h	25	25	25	25	25	25	25	25
Weight change, wt% of original liquid	0.04	0.02	0.03	0.04	0.02	0.04	0.02	0.06
Viscosity @50°C, cSt	129	127	126	136	126	131	130	125
Average		129.5				128		
Stdevp,%		3.0				2.0		
Water, wt%	21.6	21.6	21.7	21.5	21.5	21.6	21.4	21.7
Average		21.6				21.6		
Stdevp,%		0.33				0.52		
Δ Viscosity @50 °C, %		149				146		
Δ Water, %		4				4		

SOME ROUTINE ANALYSES FOR LIQUID FUELS AND LUBRICANTS

VTT Energy
P.O.Box 1601
02044 VTT

4 November 1996

1. LUBRICANTS

Analysis	Method	Remarks
1. Emulsion characteristics	ASTM D 1401	
2. Air release properties	DIN 51381	
3. Pour point	EN 6 (ASTM D 97)	
4. Detecting of antifreeze (ethylene glycol)	ASTM D 2982 A	
5. Gasoline dilution of crankgase oils	ASTM D 322	
6. Corrosion-preventing characteristics:		
- rust corrosion	ASTM D 665 A	Destillated water
	ASTM D 665 B	Sea water
- copper corrosion	ASTM D 130	
7. Chlorine	ASTM D 803	Bomb method
8. Shear stability	DIN 51382	30 cycles 250 cycles
9. Flash point	ASTM D 92	Cleveland open cup
	ASTM D 93	Pensky-Martens closed cup
10. Insolubles	ASTM D 893	Pentane insolubles Toluene insolubles
11. Acid and base numbers	ASTM D 2896 =EN 55	Potentiometric perchloric acid titration
	ASTM D 664	
	ASTM D 974	Colour-indicator titration
12. Penetration*	ASTM D 217	For greases (standard cone)
	ASTM D 1321	for waxes (needle penetration)
	ASTM D 5	For bitumen
13. Interfacial tension*	ASTM D 971	
14. Saponification number	ASTM D 94 DIN 51559	Colour-indicator method
15. Sediment by pressure filtration		Diameter of filter pores 0.45 mm
16. Trace sediment	ASTM D 2273	By centrifuging

Analysis	Method	Remarks
17. Sulphated ash	ASTM D 874	For unused lubricating oils
18. Density	ASTM D 4052	By digital density meter
19. Density, correction	ASTM D 1250	
20. Dropping point	ASTM D 566	For greases
21. Ash	EN 7, (ASTM D 482)	
22. Foaming characteristics	ASTM D 892	
23. Water separation ability	DIN 51589	
24. Water content	ASTM D 95, ASTM D 1744 (Karl-Fischer), ASTM E 203 (Karl Fischer)	
25. Viscosity	ASTM D 445	
27. Viscosity index	ASTM D 2270	
28. Four ball test	ASTM D 2783 IP 239 (1 h)	
29. Elemental analysis	ASTM D 5373-93 LECO CHN-600	

2. LIQUID FUELS

1. Asphaltene content	DIN 51595	
2. Furfural test	Decision n:o 326/74 by the Finnish Ministry of State Funds	
3. Furfural content	DIN 51424	
4. Evaporation residue*	EN 5, ASTM D 381	
5. Oxidation stability	ASTM D 525	For gasoline
6. Conradson carbon residue	ASTM D 189	Direct for the sample For 10% distillation residue
7. Vapour pressure*	ASTM D 323	Reid method
8. Pour point	EN 6, ASTM D 97	
9. Lubricant content in fuels for two-stroke engines	DIN 51784	
10. Corrosion-preventing characteristics:		
- rust corrosion	ASTM D 665 A	Destillated water
	ASTM D 665 B	Sea water
- copper corrosion	ASTM D 130	
11. Flash point	DIN 51755	Abel-Pensky (flash point +5 -65 °C)
	ASTM D 93	Pensky-Martens closed cup
12. Calorific value	DIN 51900	
13. Sulphur content	EN 41 (ASTM D 4239)	Wickbold LECO SC 32 for solid samples
14. Sediment by pressure filtration		Diameter of filter pores 0.45 mm
15. Cloud point	ASTM D 2500	

Analysis	Method	Remarks
17. Sediment	ASTM D 473	
	ISO 3735	
18. Cetane index	ASTM D 976	Density 15% + 50% dist.
	ASTM D 4737	Density 15% + 10% dist. + 50% dist .+ 90% dist.
19. Filterability	EN 116	
20. Density	ASTM D 4052	
21. Distillation < 370 °C	ASTM D 86	For gasoline, engine petrol
	ASTM D 86	For gas oil
22. Water	ASTM D 95	
	ASTM D 1744	Karl Fischer
23. Water and sediment	ASTM D 96	By centrifuging
24. Viscosity	ASTM D 445	
25. Elemental analysis	ASTM D 5291-92	
	LECO CHN-600	
26. Cetane number	ASTM D 613	
27. Octane number	ASTM D 2699	

* *Not in routine use*

BENCH-TEST

Sampling:

Pyrolysis liquid samples of 100 - 500 ml are taken at certain points (e.g. before the engine), e.g., every 30 - 60 minutes in plastic (PP, PTFE, HDPE) bottles. If possible the samples for analyses are selected by visual observations. Otherwise samples are selected including the first and last samples and a few samples evenly between these two. If the engine is connected to the test system, the material remained in the injection nozzle is dissolved in methanol if possible. All samples are kept at room temperature during the analyses.

Analytical procedure:

The first and last samples are analysed for viscosity and solids (Table 1). If there is a clear difference in results other samples are chosen for analyses. Additional analysis (Table 2) shall be carried out if needed. For example, if corrosion is suspected, Fe should be analysed. Material/solid char remained in the nozzle can be analysed (ash, metals, CHN, microscopy) if needed.

Table 1. Basic analyses.

Analysis	Method	Phenomena
Viscosity, cSt (50°C)	ASTM D 445[1]	Thickening of the liquid (polymerisation/condensation)
Solids, wt%	Ethanol insolubles[2]	Corrosion/polymerisation

[1] *No pre-filtration of the sample if visually homogenous. Elimination of air bubbles before analysis. Equilibration time 30 minutes.*
[2] *Millipore filtration system, 0.1 µm filter, solvent:sample = 100:1 (Appendix 3/3).*

Table 2. Additional analyses.

Analysis	Method	Phenomena
Fe, wt%	AAS[3]	Corrosion
Metals, wt%	ICP, AAS[3]	Corrosion
Water, wt%	ASTM D 1744[4]	Formation of water/ chemical reactions
Molecular weight distribution	GPC[5] + THF-solubility	Polymerisation
Microscopy		Phase change
GC-MSD, IR		Reactions

[3] *Wet combustion as a pretreatment method*
[4] *Karl-Fischer titration. Chloroform-methanol (3:1) as a sample solvent. 50 ml solvent for two determinations. Sample size about 0.25 g (water content above 20 wt%). Stabilisation time 30 s.*
[5] *GPC (Gel Permeation Chromatograph)/HPLC. Detector: RI (Refractive index) Erma 7510. Standard: polystyrene. Sample solvent: THF (tetrahydrofuran).*

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Title

Physical characterisation of biomass-based pyrolysis liquids

Application of standard fuel oil analyses

Abstract

The main purpose of the study was to test the applicability of standard fuel oil methods developed for petroleum-based fuels to pyrolysis liquids. In addition, research on sampling, homogeneity, stability, miscibility and corrosivity was carried out. The standard methods have been tested for several different pyrolysis liquids. Recommendations on sampling, sample size and small modifications of standard methods are presented. In general, most of the methods can be used as such but the accuracy of the analysis can be improved by minor modifications. Fuel oil analyses not suitable for pyrolysis liquids have been identified. Homogeneity of the liquids is the most critical factor in accurate analysis. The presence of air bubbles may disturb in several analyses. Sample preheating and prefiltration should be avoided when possible. The former may cause changes in the composition and structure of the pyrolysis liquid. The latter may remove part of organic material with particles. The size of the sample should be determined on the basis of the homogeneity and the water content of the liquid. The basic analyses of the Technical Research Centre of Finland (VTT) include water, pH, solids, ash, Conradson carbon residue, heating value, CHN, density, viscosity, pour point, flash point, and stability. Additional analyses are carried out when needed.

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