Norms and Standards for Pyrolysis Liquids. End-User Requirements and Specifications

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The commercialization of biomass-derived pyrolysis liquids for use in heat and power applications is dependent on the ability to successfully provide a fuel of acceptable quality to an end user at a competitive price. One of the intentions of the European Union (EU) Altener 4.1030/C/00-015/2000 project was to derive standards for biomass-derived pyrolysis liquids, based on a consensus between providers of the equipment (boilers, engines, and turbines) and the producers of the liquids. Five basic properties (homogeneity, water content, solids content, stability, flash point) for the liquids are used as the primary criteria for pyrolysis liquid evaluation. Specific values are proposed to ensure that pyrolysis liquids meet a minimum grade that is acceptable for use as a fuel oil in boilers and engines. Data on emissions from boilers, engines and turbines are presented. Preliminary long-duration test data from boiler use are available to allow more-detailed specifications on secondary properties to be made. The purpose of this work is to ensure that a realistic set of specifications is determined, to allow the introduction of pyrolysis liquids into existing fuel infrastructures and markets.

Introduction

The work presented in this paper was conducted mainly as a part of an European Union (EU)-funded ALTENER II project (Contract No. 4.1030/C/00-015/2000), with the primary objective of determining norms and standards for biomass-derived fast pyrolysis liquids. The work was continued in the IEA−EU PyNe Network. For the purpose of updating the information, results from other studies, such as EU COMBIO, were included. The tasks within the EU ALTENER project included the following:

(1) The review of fast pyrolysis technologies and description of processes at pre-commercial and commercial scale suitable for heat and power production in the short term (1−4 years) to medium term (5−10 years) (also the review of incentives to develop pyrolysis technologies at a national and EU level).

(2) Derivation of the norms and standards for biomass fast pyrolysis liquids. Review of end-user requirements and specifications for biomass fast pyrolysis liquids to obtain specifications and standards in liquid fuel quality.

(3) The creation of sector and market strategies for the power production from pyrolysis liquids.

(4) The performance of analyses of long-term cost/benefit by comparing biomass fast pyrolysis to traditional forms of energy and other alternative renewable energy sources and comparing the overall conversion efficiencies to electricity.

(5) The quantification of benefits obtained in improving the producer−converter−user interface and improving the energy/environmental balance in pyrolysis liquids production.

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Table 1. Specifications Set by Ensyn, Wärtsilä, and Birka in the Early 1990s

	Diesel Engine Tests by Wärtsilä		Tests at Birka
	specifications	allowable variation for a container (surface/bottom)	combustion specifications
homogeneity	7-day storage	no phase separation	
water (wt %)	max. 26	max. 10% difference, max 26	max. 25
higher heating value, HHV (MJ/kg)	min. 18	max. 10% difference	min. 19
lower heating value, LHV (MJ/kg)	min. 16		min. 17
ash (wt %)	max. 0.1		max. 0.1
solids (wt %)	max. 1		max. 1
size distribution			
<50 μm (%)	100		
<25 μm (%)	min. 90		

Task 1 has been discussed in recent publications;[1,2] hence, it is addressed here only briefly. This publication mainly focuses on describing the results from task 2. Relevant results from other tasks will be incorporated as appropriate. Pyrolysis liquids offer some distinct advantages over gasification and combustion for power production:

(a) They have high energy density (more than 2.5–3.5 times the energy density of softwood, based on the lower heating value (LHV)).

(b) They are transported and handled more easily than raw biomass or producer gas; the transportation of liquids is more cost-effective than that for bulky biomass.

(c) The possibility to decouple solid biofuel handling from utilization; this advantage also includes the storability of liquid fuels for intermittent use (comparison to gaseous fuels).

(d) The use of pyrolysis liquid in existing boilers with modest retrofitting; fewer emissions in boiler use can be obtained, compared to solid fuels, because of better control of the combustion process.

(e) Intermittent power-plant operation is feasible (comparison to gasification and combustion power plants) with power production at peak times, to improve electricity revenues.

(f) Pyrolysis liquids can replace heating fuel oil, which, along with diesel oil, are middle distillates; this permits additional middle distillates to be used for transportation.

To introduce pyrolysis liquids into widespread markets, nationally and internationally accepted liquid fuel standards and norms are needed. Currently, there are no national or internationally recognized standards or fuel specifications for biomass-derived fast pyrolysis liquids. This makes the development of applications problematic, because there has been considerable variation in product quality. Based on the preliminary diesel engine[3–5] and boiler tests,[6] an engine manufacturer (Wärtsilä NSD Oy in Finland), a potential bio-oil user (Birka Energi (formerly Stockholm Energi AB) in Sweden), and a liquid producer (Ensyn, Ltd. in Canada) set the requirements that are presented in Table 1. This formed the basis for further discussions with Oilon Oy (Finland) and Fortum Oy (Finland), who also input their boiler experiences to the liquid specifications. Considering these specifications, the particle size distribution determined by filtration[7] was inaccurate. Presently, microscopic methods[7] are suggested for particle size measurement. However, there is still no accurate method for determination of the particle size distribution of solids in pyrolysis liquid.

Orenda (Canada) specified the critical properties of biofuels (Table 2), based on their gas-turbine experience.[8] Considering pyrolysis liquids, some comments to the guidelines in Table 2 are given:

(A) The presented thermal stability (item 9(ii) in Table 2) cannot be obtained without a significant addition of alcohol. The average increase in viscosity (measured at 40 °C) for pure pyrolysis liquid in the test 24 h at 80 °C is 100%, which can be a problem for firing in an engine.

(B) Based on present knowledge, the pH (item 8 in Table 2) cannot be increased to a value above 4 without causing phase separation. Some amines can be used to increase the pH above 4, but the introduction of nitrogen into the liquid would cause an increase in NO_x emissions.

(C) The meaning of Ramsbottom carbon (item 11 in Table 2) for pyrolysis liquids is unclear, and this value cannot be significantly influenced.

(D) The solids content must be reduced to <0.1 wt % for all applications, to reduce particulate emissions, prevent fouling of heat transfer surfaces in boilers, and reduce erosion in nozzles, valves, and pumps. The methods used to measure the solids content are not consistent in the industry, and, therefore, values can vary appreciably. This was also stated[9] after recent gas-turbine tests.

The work on establishing standards includes (1) collecting feedback from liquid producers and end-users on fuel oil quality of pyrolysis liquids, (2) defining fuel oil quality and fuel oil specifications for pyrolysis liquids, (3) defining norms and standards for sampling and test methods, and (4) standardization of pyrolysis liquid as a fuel.

The focus of this publication is to provide data for the first two mentioned tasks. The third task will be

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(6) Hallgren, B. Test Report of Metlab Miljö Ab. Skelleftehamn: Metlab Miljö Ab, 1997, 17 p.
(7) Oasmaa, A. Fuel Oil Quality Properties of Wood-based Pyrolysis Liquids, Academic Dissertation, University of Jyväskylä, Jyväskylä, Finland, 2003; 32 p. + app. 251 p. (Research Report Series, Report 99.)
(8) Button, F. Orenda Aerospace Corporation, Canada; personal correspondence, 2003.
(9) Ashmore, C. *Gas Turbine World* **2004**, *4* (34).

Table 2. Preliminary Biofuel Property Guidelines for the OGT 2500 Turbine

ID	fuel parameter	test method	guidelines
1	lower heating value, LHV	ASTM D240/5291	15−25 MJ/kg
2	pour point maximum	ASTM D97	15 °C
3	kinematic viscosity at 80 °C	ASTM D445 mod.	4−7 cSt
4	surface tension at 80 °C, maximum	D971 mod.	30 MN/m
5	specific analysis, maximum		
	Na + K	AA or ICP[a]	5 ppm_w
	Ca	AA or ICP[a]	5 ppm_w
	V	AA or ICP[a]	3 ppm_w
	Pb	AA or ICP[a]	5 ppm_w
	Cl	ASTM D240	1 ppm_w
	S	ASTM D4294	0.02 wt %
	ash	ASTM D482	0.05 wt %
6	density at 80 °C, maximum	ASTM D4052	1.20 G/mL
7	solids content of >0.1 μm, maximum[b]	ASTM D2276 (Millipore Membrane Filtration)	0.25 wt %
8	pH	Accumet 925 pH meter	2.5−7.0
9	thermal stability:[c] parameters at 80 °C		
	(i) solids creation, maximum	NA[d]	0.1 wt % increase in solids content
	(ii) viscosity, maximum	NA[d]	5% increase in viscosity
	(iii) phase stability	NA[d]	no phase separation permitted
10	water content	ASTM D95, followed by D1744	15−25 wt %
11	Ramsbottom carbon residue on 10% distillation residue, maximum	ASTM D5245	10 wt %

[a] AAS = atomic absorption spectroscopy. ICP = inductively coupled plasma spectroscopy. [b] Note: 90% of the solids should be <5.0 μm in size. [c] Exposure for 24 h at 80 °C. [d] Not analyzed.

Table 3. Operational Fast Pyrolysis Plants (>20 kg/h) in 2004 for Liquid Fuels

organization	country	plant capacity (kg/h)	liquid end-use
Ensyn Red Arrow	United States	2000	internal energy use
Dynamotive	Canada	400	gas-turbine and boiler tests
BTG	The Netherlands	250	boiler tests
PyTec	Germany	20	motor tests
VTT Processes	Finland	20	boiler tests

addressed in a separate publication.[12] The fourth task has been reviewed in the final report of the CEN CEN/TC 343/W63 working group.[13]

Fuel Oil Production

Over the past 20 years, developments in fast pyrolysis technologies have led to the construction and operation of many plants, ranging from laboratory scale to demonstration scale.[2,14] A summary of current plants in operation is given in Table 3.

Ensyn/Red Arrow plants produce primarily chemicals; however, the remaining liquids are combusted for energy. Ensyn has also supplied large quantities of pyrolysis liquid for use as fuel oil.[10,15]

Dynamotive and Orenda are close to commissioning[9] a 2.5-MW biomass-based cogeneration project that will supply electricity and steam for a wood processing facility in West Lorne, Ontario, Canada. The plant is expected to process 100 tons per day (100 tpd) of wood waste that will be converted to produce 70 tons of pyrolysis liquid, 20 tons of char, and 10 tons of noncondensable gases. The feedstock is dried to reduce the moisture content to <10 wt %. The dried biomass is subsequently shredded to a small particle size before being fed into the pyrolysis reactor, which consists of a deep bubbling fluidized bed system. At a base load output of 2.5 MW, the gas turbine will consume about 50 tons of pyrolysis liquid. In effect, this means a surplus of 20 tpd will be available for sale to commercial users. Excess electricity generated will be sold into the Ontario energy grid. In addition to the West Lorne cogeneration plant, Dynamotive has announced several other bio-oil power projects.[9] These include a planned 2.5-MW distributed generation cogeneration plant that would supply district heating and power for the Public Utility Commission of Sault Sainte Marie in Ontario. The plant is planned to operate on a combination of waste wood and other solid biomass feedstock.

VTT has continuously produced liquid fuel for boiler tests[16] and fuel oil quality studies.[7,10,17] Fortum Oy and Vapo Oy have constructed a 500-kg/h pyrolysis plant in 2001 and operated the plant in 2002−2003, producing more than 40 m^3 of liquids for testing. Development work was stopped at the end of 2003, primarily because of an increase in feedstock costs but also due to a change in taxation in Sweden on fossil fuels in combined heat

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(14) Bridgwater, A., Ed. *Fast Pyrolysis of Biomass: A Handbook*; CPL Press: Newbury, U.K., 2002; Vol. 2, 424 p.
(15) Oasmaa, A.; Kytö, M.; Sipilä, K. Pyrolysis Liquid Combustion Tests in an Industrial Boiler. In *Progress in Thermochemical Biomass Conversion*; Bridgwater, A., Ed.; Blackwell Science: Oxford, U.K., 2001; Vol. 2, pp 1468−1481.
(16) Gust, S. Combustion Experiences of Flash Pyrolysis Fuel in Intermediate Size Boilers. In *Developments in Thermochemical Biomass Conversion*; Bridgwater, A., Boocock, D. G. B., Eds.; Blackie Academic & Professional: London, U.K., 1997; Vol. 1.
(17) Oasmaa, A.; Peacocke, C. *A Guide to Physical Property Characterisation of Biomass-Derived Fast Pyrolysis Liquids*; VTT: Espoo, Finland, 2001; 65 p + appendices (34 p).

Table 4. Pyrolysis Liquids Properties from Different Feedstocks Produced in Pyrolysis Units of >80 kg/h

analysis	Dynamotive	Dynamotive	Dynamotive	Forestera	Ensyn	
feedstock	pine/spruce (100% wood)[a]	pine/spruce (53% wood, 47% bark)[a]	bagasse[a]	spruce (100% wood)[b]	oak/maple[b]	LFO No. 2
moisture (wt %)	2.4	3.5	2.1	6−9		
particle size (mm)	<1.2	<1.2	<1.2	3−5		
ash (wt %)	0.42	2.6	2.9			
pyrolysis liquids						
water (wt %)	23.3	23.4	20.8	23.8	22	max. 0.05
solids (wt %)	<0.1	<0.1	<0.1	0.05	0.045	0
ash (wt %)	<0.02	<0.02	<0.02	<0.02	0.01	0
nitrogen (wt %)	<0.1[21]	0.3−0.4[21]	0.7[22]	0.04	0.2	
sulfur (wt %)	<0.01[17]	<0.05[17]	<0.1[22]	<0.01[17]	<0.01	0.5
viscosity (cSt)						
@ 20 °C	73	78	57		650	
@ 40 °C				15	50 at 50 °C	3.4
@ 80 °C	4.3	4.4	4		12	
density @ 15 °C (kg/dm³)	1.20	1.19	1.20	1.19	1.18	0.876
flash point (°C)				38	55	min. 38
pour point (°C)					−25	min. −6
higher heating value, HHV (MJ/kg)	16.6	16.4	15.4	17.6	17	
lower heating value, LHV (MJ/kg)				16.0	15.7	40
pH	2.3	2.4	2.6	2.4	2.5	
distillability	not distillable	not distillable	not distillable	not distillable	not distillable	distillable
water insolubles (wt %)	25	25	24	21	50	100

[a] Taken from ref 20. [b] Taken from ref 10.

power (CHP) plants, which reduced the competitiveness of Forestera.

In Europe, the main barrier to the commercialization of pyrolysis technologies is the poor availability of inexpensive biomass and the relatively low consumer price for heating oils, compared to transportation fuels. One of the challenges facing the industry is the fact that pyrolysis liquids will have to compete with conventional fuel oils, which are well-established and well-known to the end user (utility, local grid, on-site use for heat and power, etc.). Some of the main problems in the large-scale application of pyrolysis liquids have been (1) high solids content (>0.5 wt %) and no standardized or commonly agreed method for accurate determination of its components; (2) an unacceptably wide range of physical and chemical properties (viscosity, LHV, water content, the number of phases, and pH) from different suppliers, making application development problematic; (3) the lack of handling (transferring, pumping, storage) instructions and health and safety data (some toxicological testing is currently ongoing); (4) the lack of industry-recognized quality specifications and poor fuel quality (relative to conventional fuel oils); and (5) low pH, which is not acceptable in conventional fuel handling systems (most components are not acid-resistant).

Fuel Oil Quality

The production of consistent high-quality liquid has been demonstrated by Dynamotive in Canada and by Fortum[18] in Finland. Properties of pyrolysis liquids produced in large-scale (> 80 kg/h) units are presented in Table 4. Ensyn has produced 100 tonnes of constant-quality[10] pyrolysis liquid, which has been successively combusted[15] in 8-MW boilers at Oilon (Finland) and in 10-MW boilers at Fortum Värme (Sweden). Problems with the liquid combustion in diesel engines have been reported by Ormrod.[19] Note that the liquid was not

(18) Gust, S. Fortum Oil and Gas, Finland; personal correspondence, 2004.

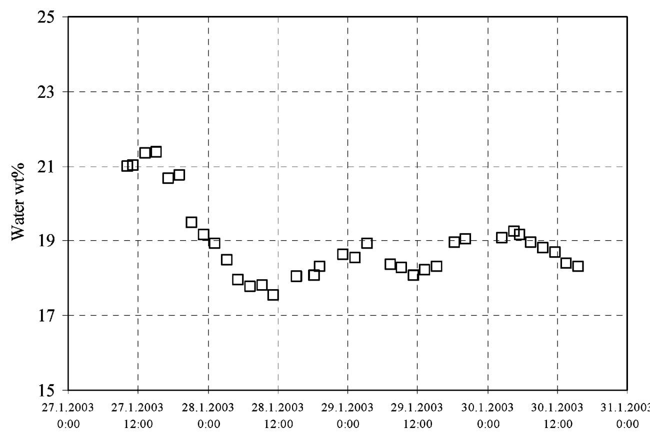

Figure 1. Follow-up of water content of the product liquid during the pyrolysis experiment (after the replacement of the seed oil (pyrolysis liquid from earlier run) in scrubbers).

whole liquid, but rather a heavy fraction of pyrolysis liquid, after a fraction of water-soluble compounds was removed. Properties of pyrolysis liquids produced in plants >80 kg/h are presented in Table 4.

The main variable that affects the quality of pyrolysis liquid is the biomass feedstock but also the post-production processing techniques. To gain a better understanding of the effect of feedstock on product quality, feedstocks should be compared. The main factors affecting fuel oil quality are water (Figure 1) and solids.[7,23] Variations in water content indicate a change

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(20) Morris, K. W.; Johnson, W. L.; Thamburaj, R. Fast Pyrolysis of Biomass for Green Power Generation. In *First World Conference and Exhibition for Energy and Industry*, Sevilla, Spain, 2000; pp 1519−1524.

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(22) Garcia-Perez, M.; Chaala, A.; Roy, C. *J. Anal. Appl. Pyrolysis* **2002**, *65*, 11−136.

(23) Solantausta, Y.; Oasmaa, A. Fast Pyrolysis of Forestry Residues and Sawdust, Production and Fuel Oil Quality. In *Proceedings of Bioenergy 2003. International Nordic Bioenergy Conference*, Jyväskylä, Finland, September 2−5, 2003; Finbio: Jyväskylä, Finland, 2003; pp 424−427.

in feedstock moisture, process parameter, or oxygen leak. An increase in the solids content can result from low gas velocities (<15 m/s) in the cyclones, or it can be due to a large portion of "fines" <10 μm in size, which are not collected by the cyclones. In addition, the liquid homogeneity should be observed during operation.

Water content is measured by Karl Fischer titration, according to the standard ASTM E 203. To verify the use of another sample solvent or reagent, the water addition method for calibration is recommended. In solids determination, ethanol is suggested as the washing solvent for liquids produced from clean wood from softwood or hardwood. For extractive-rich liquids[21] produced from forest residue and bark, a methanol–dichloromethane (1:1) mixture should be used. Microscopic examination of the liquids gives information on possible phase separation or presence of solid material (e.g., extractives, inorganics) in the liquid. Therefore, the homogeneity of the liquid can be verified by microscopic determination and/or by sampling from different depths in a storage container and analyzing the moisture content by Karl Fischer titration.[17] Criteria for a poor-quality liquid product are as follows: a water content of >30 wt % and/or duplicates differing by >1 wt %. The principal criterion for a good-quality liquid product is a solids content of <0.1 wt %.

Presently, both water and solids contents are performed in the laboratory as separate analyses, but online methods are being developed.[24,25] Water content has good correlations with density and heating value; consequently, a density meter based on the Coriolis effect has been tested at VTT to allow a continuous method to be used. The results are promising, but more work is needed. For a more-detailed assessment of the liquid quality, the following analyzes are suggested: microscopic examination for solids, stability, inorganics in solids, water-insoluble material, and extractives content.

Fuel Oil Applications

The majority of efforts in applications have been on pyrolysis liquids produced by Union Fenosa (1992–1996, ~40 t), Ensyn (1991–2003, ~500 t), BTG (1999–2004, ~50 t), Fortum (2002–2003, ~30 t), and Dynamotive (2004, ~10 t), because these have been the only companies producing significant (tonne) quantities for supply tested by various organizations. Problems in the 1990s often arose because of inconsistent liquids quality, as it was found that aged liquids underwent phase separation. It is expected that increasing the availability of liquids in significant quantities will lead to more boiler, engine, and turbine manufacturers offering to test liquids for combustion applications.

Boiler Application. Boiler work has been performed predominantly in the EU by Fortum Oy (Finland), VTT/Oilon (Finland), and Birka Energi (Sweden). An interesting application test of BTG (The Netherlands) involves the co-firing of 15 tons of bio-oil (>1% bio-oil of the feed) in the gas-fired power station in Harculo, The Netherlands.[26] The only commercial system that has been operating for over 10 years, where pyrolysis liquid is used for heat generation, is located at the Ensyn Red Arrow Products pyrolysis plant in the United States. A 5-MW_{th} swirl burner is used for combustion of the pyrolysis liquid fractions and char and gas from the plant, with average emissions of 17% CO, 1.2% NO_x, and 0.2% formaldehyde of the permitted levels.[1] The liquids were also co-fired at a local utility; however, this was subsequently discontinued.[27,28] Some work has been conducted in Canada, and limited results are available.[2] Other work has been discussed in a recent review by Czernik and Bridgwater.[1]

In 2003, Fortum successfully performed field tests with their product Forestera in a 400-MW_{th} heating fuel boiler. The burner was provided by Oilon Oy[29] of Finland, which was the result of their joint development work during the period of 2000–2002. It was found that emissions could be reduced to the level of heating oil, provided that the existing burner was replaced by a burner that had been modified[29] and solids content was reduced to low levels. More than 12 m^3 of Forestera have been combusted (Table 5), in over 1500 cycles. The combustion system was fully automated and operated under the control of a thermostat. Field tests were performed to verify critical components and to determine the required fuel quality. One of the more important findings of the work was the necessity to reduce solids to <0.1 wt % and to ensure that inorganics in the form of ash and sand left over from the feedstock are present in concentrations of <0.03 wt %. The conclusion of these tests was that emissions could be reduced to acceptable levels, provided that a fuel of sufficient quality is provided and flame characteristics are modified. However, it was also found that the combustion system must be more complex and costly than for conventional heating fuels. This would require a lower-cost pyrolysis liquid to compensate for the higher installation costs to get customers to be willing to test this option.

The combustion of pyrolysis liquids in boilers of varying capacities has identified a variety of problems and issues, as detailed later in Table 8. Some of these can be addressed by improving the liquid quality, whereas others will necessitate modifications to the equipment itself.

Therefore, for pyrolysis liquids to be used or to be acceptable for boiler applications, the following minimum requirements must be achieved: (a) preheating to 70–80 °C immediately prior to combustion, to reduce the viscosity to 2–4 cSt, and no recirculation of heated product back to the storage tank (because this can cause

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(28) Mullaney, H.; Farag, I. H.; LaClaire, C. E.; Barrett, C. J. Technical, Environmental and Economic Feasibility of Bio-oil in New Hampshire's North Country, Final Report, Project No. 14B316 UD-KEIF. University of New Hampshire Industrial Research Center, Durham, NH, 2002.

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Table 5. Examples of Some Boiler Emissions for Various Liquid Sources

	Ensyn		Union Fenosa[a]		Ensyn			Ensyn	Dynamotive	Fortum
feedstock	hardwood		eucalyptus		hardwood			hardwood	pine	spruce
solids content (wt %)	0.5		0.7					~0.4	0.17	0.05
type of boiler	Arimax Eetta 200 kW boiler		Arimax Eetta 200 kW boiler		water-wall utility boiler, 10 MW_{th}			10 MW_{th} boiler, Oilon Lenox GRT-5L	10 MW_{th} boiler, Oilon Lenox GRT-5L	300 kW_{th} LFO boiler
analysis										
O_2 (vol %)	4	6	5	6				3.3–3.6	3.3–3.4	3–4
CO (ppm)	32	28	40	20	32	32	67	1–2	10–25	10–20
NO_x (ppm)	142	137	170	150	195	198	208	159–164	108	100–150
THC					0.8	1.0	1.4			
particulate (mg/MJ)					105	144	161	15	92	
Bacharach No.	5	5	2.5	2.8				2	2.8	1–2[b]
reference	ref 26		ref 26		ref 25			ref 10	ref 10	ref 15

[a] With an additional 3 wt % of ethanol and 3 wt % of water, modified refractory in boiler to ensure complete combustion, bubbling fluidized bed (BFB). [b] Particulate emissions contain only inorganic materials. No tars found. Amount is dependent on the ash content of the oil.

polymerization); (ii) startup and shutdown on conventional fuel, to avoid deposition and coking of nozzles; and (iii) ensuring a sufficiently low concentration of solids (<0.1 wt %).

Engine Application. The first work on engines was conducted by VTT on a 55-kWe Valmet engine that was equipped with a pilot injection.[30] It was observed that, although pyrolysis oil was hard to ignite, it burned readily after the combustion had begun. Pyrolysis oil with 5% ignition improver gave, more or less, the same exhaust performance as conventional diesel fuel and better emission performance than the reference fuel (RF35) with poor ignition quality.

Further tests were performed with a 60-kWe standard four-cylinder Valmet 420 DS-engine that was equipped with pilot injection. Main conclusions were as follows:[4,5] modifications for the injection pump are needed; more-resistant elements are needed; injectors manufactured from a material resistant toward corrosion proved more tolerant toward pyrolysis oil than ordinary injectors; the combustion of pyrolysis oil was rapid, even though fairly high CO and HC emissions were measured; and an oxidizing catalyst may have decreased the emissions to an acceptably low level.

Wärtsilä performed single-cylinder tests[31] in a Vasa 18V32 engine, as well as material testing.[32] The main conclusions were as follows: a pilot injection is needed; pyrolysis oil burns fast; emissions were acceptable; pyrolysis liquid specifications should include low solids contents and tight heating value controls; and injection equipment of corrosion-resistant materials can be produced to operate with pyrolysis liquid. Results indicated fast heat-release characteristics, along with an encouraging thermal efficiency of 44.9%. The relatively lower heating values and the batch-to-batch variations have indicated that the capacity within the traditional camshaft-driven injection pumps are insufficient. To avoid dramatic camshaft changes and complete engine reconstructions, the concept using the electronically controlled pressure amplifier system has been developed.

Wärtsilä stopped the development work mainly because of the poor quality (i.e., high solids content) of pyrolysis liquids of that time.

Ormrod Diesels have developed significant experience on pyrolysis liquids since 1993 using a 250-kWe modified dual fuel diesel engine.[33] Liquids from Union Fenosa, BTG, Dynamotive, and Ensyn have been tested. The thermal efficiency of the engine was 34.3 wt % when operating on diesel fuel and 32.4 wt % when operating on pyrolysis liquid with pilot diesel injection. The exhaust emissions (Table 6) indicate a characteristic rise in CO and a reduction in NO_x when operating on pyrolysis liquid.[19] Problems and possible solutions are included in Table 8, which is presented later in this paper.

In 2004, PyTEC (Hamburg, Germany) performed a 12-h continuous diesel-engine test in a CHP plant using a Mercedes-Benz motor (type OM 444 LA) that had 12 cylinders and a volume of 22 L. Filtered bio-oil made at Fortum, Finland was used without any further modification. A special on-line mixing system provided the addition of 4 vol % of diesel fuel. Bio-oil consumption was 120 L/h, producing ca. 305 kW/h of electricity, which was fed into the grid. Injection nozzles and pump were adopted to acid media. Slightly increased exhaust emissions of CO were encountered; all other emissions were within the acceptable range. Further test series are being performed in 2005.

University of Florence conducted engine tests with pyrolysis liquid emulsions.[34] They concluded that, compared to the straight use of pyrolysis liquid, the use of pyrolysis liquid emulsions in diesel engines requires fewer modifications to the engines. The most important results from the tests were (i) the injector, as well as the fuel pump, should be made of stainless steel or a similar material and (ii) much more research in the erosion–corrosion properties of emulsions is needed.

For engine applications, the minimum property specifications required are as follows: (1) solids content of <0.1 wt %; (2) viscosity in the range of 10–20 cSt; (3) maximum physical and chemical property variation

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Table 6. Engine and Burner Emissions[a]

	250 kWe Mirrlees, Six Cylinders, Ormrod Diesels, U.K.			25 kWe Stirling Engine, FLOX[b] Burner, ZSW, Germany
	7 wt % pilot fuel[c]	17 wt % pilot fuel[c]	100 wt % pilot fuel[c]	no pilot fuel
liquid source		BTG		BTG
feedstock		mixed hardwood		
solids (wt %)				0.35
O_2 (wt %)	15	15	15.8	6−10
CO (ppm)	3475	2057	271	<35−125
CO_2 (vol %)	4.4	4.6	3.9	
NO (ppm)	240	313	510	
NO_2 (ppm)	41	77	76	
NO_x (ppm)	384	266	586	20−95
SO_x (ppm)	0	33	86	
THC (mg/m^3)				20−40
particulate (mg/Nm^3)				
reference		ref 31		ref 34

[a] Taken from ref 11. [b] Flameless oxidation. [c] Diesel fuel was used as the pilot fuel.

within 10% of specification; and (4) improved lubricity, which currently is poorly defined for pyrolysis liquids.

Turbine Application. Most of the research with turbines has been conducted in Canada and the United States. There has been very little turbine development work in the EU1. The University of Rostock[35] has tested pyrolysis liquids in a small commercial gas turbine (Type T 216, Klöckner-Humboldt-Deutz AG, Germany) with a rated electric power output of 75 kW. Pretreatment of the liquids was required to remove solids >20 μm in size. The gas turbine combustion behavior was examined in numerous tests during the 1999−2000 period. The emissions were measured for both pyrolysis liquid and diesel fuel operation. When compared to diesel fuel, characteristically, the emissions of CO and NO_x were higher for pyrolysis liquid at partial load operation (0.56 g/kWh CO, compared to 0.13 g/kWh for diesel fuel, and 0.37 g/kWh NO_x compared to 0.18 g/kWh for diesel fuel).

Since 1995, Orenda Aerospace Corporation, Canada, has actively worked on the application of pyrolysis liquid in gas turbine combustion in a 2.5-MWe Class GT2500 engine designed and manufactured by Zorya−Mashproekt in the Ukraine and further modified for the alternative fuels application. Main modifications of the turbine have been in the hot section and combustion system.[36] The hot section was provided with an on-line cleaning system. The modifications[9] to the fuel system include preheating the fuel and a complete re-design of the nozzle to improve spray characteristics. A high-pressure flow has been provided and the start-up system uses diesel fuel flowing through the primary channel in the fuel nozzle. Following a warm-up period, pyrolysis liquid is fed into the secondary channel at an increasing rate while the diesel fuel flow is reduced until complete switchover is achieved. After operation on pyrolysis liquid, ethanol is used to wash the internal path of the fuel system. Because of acidic exhaust gas from the gas turbine, 300-series stainless steels are used in conjunction with high-density and fluorinated polyethylene for polymeric components.

Table 7. Normalized Emissions of Various Fuel Types at a Maximum Load of 2.5 MWe[a]

	Emissions (%)[b]			
fuel	CO_2	CO	NO_x	SO_2
No. 2 diesel oil	4.2	1	321	7
biofuel[c]	4−6	49−55	58−60	1−2
crude oil blend	4.4	14.8	326	421
biodiesel	4.3	4.1	321	1.4
ethanol	4.5	3	101	2
Ontario emissions limit	60	189	86	

[a] Based on the Ontario Emissions Limits for Simple Cycle OGT2500 (MOEE Policy A-5). Data taken from ref 37. [b] All gaseous emissions have been normalized to 15% oxygen. [c] Pyrolysis liquids produced by Dynamotive and Ensyn.

This gas turbine is designed to fire multiple fuels: pyrolysis liquid derived from wood and wood waste products, ethanol, biodiesel, and bituminous crude oil. At full continuous output, the plant is design-rated to generate 2500 kW of electric power and ~5400 kg/h process steam at >80% cogeneration efficiency.

In 2004, Dynamotive provided the fuel for Orenda's gas-turbine tests. During 2004, Magellan Aerospace Orenda Corporation conducted emission tests on its OGT 2500 turbine, which was operating with DynaMotive pyrolysis liquid.[37] The main focus of the test program was to monitor gaseous emissions from the OGT 2500 accurately while firing biofuel and diesel fuel. The turbine performed very well with all fuels, under different load conditions and during fuel switching. The turbine stabilized quickly, following rapid load increases and decreases. It demonstrated stable operation and an impressive turndown ratio between idle and a maximum measured power output of 2.5 MWe, regardless of the fuel used. The fuel handling system, which is designed to preheat the fuel up to 90 °C, performed very well with diesel and biofuel. Total operating hours with 100% of biofuel were 50 h for Ensyn biofuel and 5 h for Dynamotive biofuel. Table 7 summarizes measured continuous emissions monitoring (CEM) emission data at a maximum turbine load of 2.5 MWe and normalized to 15% oxygen in the flue gas.

(35) Strenziok, R.; Hansen, U.; Künster, H. Combustion of Bio-oil in a Gas Turbine. In *Progress in Thermochemical Biomass Conversion*; Bridgwater, A., Ed.; Blackwell Science: Oxford, U.K., 2001; pp 1452−1458.

(36) Lupandin, V.; Thamburaj, R.; Nikolayev, A. Test results of the GT2500 Gas Turbine Engine Running on Alternative Fuels: Bio Oil, Ethanol, Bio Diesel and Heavy Oil. Presented at the ASME TURBO-EXPO-05 Congress in Reno−Tahoe, NV, 2005, ASME Paper No. GT2005-68488.

(37) Razbin, V.; Coyle, I. Emission Tests on Magellan Aerospace Orenda Corporation, OGT 2500 gas turbine. CETC Energy Technology Centre: Ottawa, Canada, 2004, CETC-O-ACT-04-043-1 (CF).

Table 8. Issues Related to Using Pyrolysis Liquids as a Fuel in Boilers, Engines and Turbines

property	specification to be met	current value by present technology	problem(s)	possible solution(s)
variation	max. 10%	>50%	changes in feed and process parameters	quality control system
water	<27 wt %	18−40	inhomogeneity, phase separation (>30 wt % water)	feedstock drying increase (<50 °C) of condensation temperature
total solids[a]	<0.01 wt %	≤0.5 wt %	wear of injectors, increased liquids instability, high CO emissions	homogeneous particle size distribution of the feed, hot vapor filter, three cyclones on reactor exit, liquids filtration/centrifugation
inorganics[b]	<0.01 wt %	<0.1 wt %		feedstock choice, hot vapor filter, three cyclones on reactor exit, liquids filtration/centrifugation
homogeneity	single-phase	variation	uneven liquid quality	feedstock moisture <12 wt % liquid water content <27 wt %
stability	max. 100% increase in viscosity in aging test (24 h 80 °C, viscosity measurement at 40 °C)	50%−150%	changes in liquid properties during storage and use	alcohol addition [methanol preferred, but ethanol/2-propanol safer to use]
flash point	dependent on country	>40 °C	safety regulations for transportation	adjusting the liquid condensation temperature
pH	FDS[c]	2−3	corrosion of fuel lines	all pipework, vessels, and gaskets must be acid resistant
LHV	FDS[c]	16−19 MJ/kg	50% lower than fuel oil, does not auto-ignite at start-up	increase pump pressure to injectors, increase diameter of fuel lines, dual fuelling (%), combustion chamber modification
viscosity	FDS[c]	>50 cSt at 20 °C	too high for most fuel injectors	preheat liquids to reduce viscosity, add cosolvent (alcohol), use of emulsions
lubricity	FDS[c]	not determined	buildup of lacquer on the injection needle and fuel pump plunger	improvement in lubricity/flow properties, additives

[a] Includes char, ash, and sand. [b] Includes ash and sand. [c] FDS cannot be influenced or specified. Value to be included in the Fuel Data Sheet.

Orenda Aerospace Corporation[8,38] has set up preliminary specifications (Table 2), through which they evaluate the suitability of pyrolysis liquid for the gas turbine. For turbine applications, the minimum requirement is that the particle size must be <10 μm. For turbine applications, the minimum property specifications required is a solids content of <0.1 wt %.

Fuel Oil Specifications and Standards

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

Elliott[39] has suggested the specification standards for various pyrolysis liquids in the International Energy Agency Biomass Liquefaction Test Facility (IEA BLTF) project. The classification was based on ASTM standards D-396 for fuel oils, D-975 for diesel fuels, and D-2880 for gas turbine fuels. A decade later, a similar classification was proposed[40] by the IEA Pyrolysis Activity (PYRA) project. Based on feedback from potential end-users,[16,38,41−43] specifications were addressed to be tighter, with a maximum variation of ±10%. Stability, homogeneity, water, solids, and ignition are considered to be the most critical properties. Stability (measured as viscosity increase, relative to time) is necessary for the proper adjustment of pumps, nozzles, burners, and other equipment. Slight phase separation may result in poor combustion. High water content (>30 wt %) gives high particulate emissions.[15] These emissions can be decreased, to a certain extent, using a support fuel and optimizing the atomization viscosity by temperature adjustment. The solids content of the pyrolysis liquid is detrimental for the equipment, especially for injectors and turbine blades, and also results in higher particulate emissions. The limit for the flash point is defined according to legislation for transportation and storage.

In this paper, an approach was made to specify only the properties that can be influenced, as shown in Table 8. These include homogeneity, water and solids contents, stability, and flash point. Because fuel oil speci-

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Table 9. Preliminary Specifications for Pyrolysis Liquids

property or application	boiler	diesel engine	gas turbine
size class	0.2−1 MW_{th}		2.5 MW_e
variation	max. 10%	max. 10%	
homogeneity	single-phase	single-phase	single-phase
stability	single-phase	single-phase	single-phase
water content	max. 27 wt %	max. 27 wt %	max. 25 wt %
flash point	min. 40 °C	0 °C	
total solids	0.05 wt %		0.05 wt %
ash content	0.03 wt %	0	max. 0.05 wt %
SiO_2 content	max. 0.01 wt %	0	
particle size			90% <5 μm
viscosity @ 80 °C			max. 7 cSt
LHV			min. 15 MJ/kg
lubricity			

fications cover a range of applications from boilers to turbines, the grade of fuel required also increases, for a wider range of physical and chemical properties. This means that properties that are important for one application may not be as important for another. The size of a unit will also influence the properties of the liquids, because smaller domestic boilers require liquids with low viscosities, whereas larger commercial boilers may accept a liquid with a higher viscosity. Additional data have been included to address the wide spectrum of properties that may be required in different fuel applications, as well as to assist in the design of process equipment and power generation systems.

Based on all the feedback from end-users, as well as the research performed earlier, preliminary specifications are presented in Table 9.

Standardization

A recommendation on initiating standardization of alternative fuels including pyrolysis liquid under CEN has been submitted by CEN/TC 343/W63 working group13. The purpose was to collect information in the areas of (1) existing standards (for instance, on specifications, classification systems, and test methods) for liquid and gaseous alternative fuels; (2) ongoing and planned work on standards for specifications, classification systems, test methods, etc. for liquid and gaseous alternative fuels; and (3) setting priorities for future work and standards (for instance, on specifications, classification systems, and test methods) for liquid and gaseous alternative fuels.

WG 149 recommended to the CEN Technical Board and to CEN/TC 19 to take further necessary measures to establish standards on liquid and gaseous alternative fuels for stationary applications. In future work that involves the revision of existing standards or the production of new standards for alternative fuels, further research and development is necessary. This work, to a great extent, must be performed in combination with engine studies. To enable a market introduction of alternative fuels, they must be generally accepted by engine and vehicle manufacturers and fuel distributors.

Conclusions

There is encouraging operational experience on fast pyrolysis liquids in boilers and turbines, which creates confidence for the implementation of heat or combined heat power (CHP) plants. The production of quality liquids has been demonstrated by Dynamotive in Canada and Fortum in Finland. Long-term testing of liquids in boilers and turbines has been successively performed, and important engine development has been achieved. However, technical difficulties concerning the use of the liquids still remain, because of the small amount of long-term research and insufficient number of commercial pyrolysis plants producing liquids for long-duration testing. In regard to the fuel oil quality of pyrolysis liquids, some properties can be changed by improving the quality of the fuel, and adaptations are still required to the hardware for others (see Table 8).

Biomass fast pyrolysis technologies have experienced a slow growth over the past eight years, primarily because of low oil costs and low base electricity prices throughout most of Europe. Therefore, the demand for a renewable liquid fuel for heat and power generation has been reduced, and other competing technologies have come to the forefront, namely, for transport fuels, which have a higher market value (e.g., biodiesel). There are a range of incentives in the EU at the international and national level for renewable energy technologies, although the level and form of support vary significantly. In some cases, no distinction is made in the level of technological development in renewable energy technologies, with all being classed as commercially available, which is not the case. Some harmonization in support measures is required to improve technology development. There is not enough empirical data to allow full norms and standards for biomass-derived fast pyrolysis liquids to be determined at this time. There is a real need for bulk quantities of liquids to be supplied to boiler and power generation equipment developers, to enable standards for liquids to be fully assessed and specified.

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

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