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Quality Control in Fast Pyrolysis Bio-Oil Production and Use

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Introducing a new fuel, fast pyrolysis bio-oil, into the market is not without its challenges. Fast pyrolysis bio-oil is different from conventional liquid fuels, and therefore must overcome both technical and marketing hurdles. To standardize the bio-oil quality on the market, specifications are needed and in order to promote its acceptance as a fuel, the methodology should be as similar to that for mineral oils as possible. In the EU a new chemical regulation system is being implemented. The regulation applies to substances manufactured in or imported to the EU in annual quantities of one tonne or more per company.

This article will focus on norms and standards for fast pyrolysis bio-oils. It will include the present status and address what still has to be done on bio-oil specifications and relevant test methods. The article will address industrial needs in commercialization of the fuel oil use of bio-oil, including the registration application to the REACH program, as well as development of a standard within ASTM. The article will discuss the most important properties of bio-oil and the variation in these properties. It will address the issue of quality follow-up in bio-oil production, including the properties to be followed and the laboratory and on-line monitoring methods. The article will provide a state of the art of fuel oil specifications, test methods, and testing procedures as they are applied to bio-oil. It will review the effort in support of the implementation of an ASTM standard including the methods validation work. © 2009 American Institute of Chemical Engineers Environ Prog, 28: 404–409, 2009

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INTRODUCTION

A new fuel, biomass fast pyrolysis bio-oil, is coming into the market. Bio-oil is different from conventional liquid fuels, and therefore must overcome both technical and marketing hurdles. To standardize bio-oil quality on the market, specifications are needed. For promoting the acceptance of bio-oil as a fuel into markets, the methodology should be as similar to that for mineral oils as possible. Development of appropriate specifications and standard methods of analysis is challenging.

BACKGROUND OF STANDARD METHODS DEVELOPMENT

Since the 1980s several researchers have characterized the physical properties of fast pyrolysis bio-oil using various standard methods developed for mineral oils [1–5]. Fast pyrolysis bio-oils are less stable than mineral oils. The viscosity of the fast pyrolysis bio-oils increases over time, especially when heated. In order to predict the increase in viscosity during the storage, an accelerated aging test was developed [4, 6, 7].

In the 1990s standard fuel oil analyses were systematically tested for fast pyrolysis bio-oils at VTT [4, 8, 9] and modifications to the methods have been developed when needed. The suitability of various methods has been verified by analyzing several fast pyrolysis bio-oils produced from various feedstocks and using different pyrolysis processes. Some new analytical methods for fast pyrolysis bio-oils have been developed, like for solids content [4]. For chemical characterization, a water extraction method was developed [10].

The first IEA (International Energy Agency) Round Robin for biomass liquids in 1988 was carried out by

Elliott, McKinley and Overend [11]. It was found out that xylene distillation EN 95, which is used for mineral oils, cannot be used for the determination of water content of fast pyrolysis bio-oils because these oils contain a high amount of water-soluble compounds. Karl-Fischer titration was recommended as a suitable method for fast pyrolysis bio-oils.

Two separate round robin tests were initiated in 1997: one [12] within EU PyNe (Pyrolysis Network) and the other [13] within IEA PYRA (Pyrolysis Activity). From both of them it was concluded that the precision of carbon, hydrogen, density, and water by Karl-Fischer titration was good. High variations were obtained for nitrogen, viscosity, pH, and solids. The conclusion was also that clear instructions for analyses are needed.

In 2001 a round robin was organized within the IEA-EU PyNe (Pyrolysis Network) cooperation. Analyses were carried out by 12 laboratories for four different fast pyrolysis bio-oils (originating from pine, spruce, hardwood mix, and bark) produced by different large-scale pyrolysis processes. Water, solids content, pH, viscosity, stability test, and CHN determinations were included. Instructions based on VTT's physical analyses [8] were given. In general, the accuracy of physical analyses, except the stability test, was good. This round robin included also chemical characterization of bio-oils. In general, the results of chemical characterization were not very consistent. The variation in quantitative GC/MSD was unacceptable. A standard reference sample was suggested [14].

Specifications for standard fuel oils have been established by ASTM and similar organizations in their respective countries. Elliott [1] has suggested the specification standards for various fast pyrolysis bio-oils in the IEA BLTF (International Energy Agency Biomass Liquefaction Test Facility) project. The classification was based on ASTM standards D-396 for fuel oils, D-975 for diesel fuels, and D-2880 for gas turbine fuels. A decade later similar kind of classification [15] was proposed by the IEA PYRA (Pyrolysis Activity) project.

In the EU in 2002, CEN's Technical Board created the working group CEN/BT/WG 149 "Liquid and Gaseous Alternative fuels" [16]. In 2005 the results of WG 149 were included in CEN/TC 19 "Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin" workplan including standardization of fast pyrolysis bio-oil in longer term. The main result of the work in BT/WG 149 was an overview of priorities in standardization of liquid and gaseous alternative fuels before 2010.

In 2007 a pyrolysis oil standard initiative for ASTM within D02 Petroleum Products and Lubricants committee was initiated. In June 2007 the ASTM Initiative received the Work Item Number 15564 within D02.E0.1 (Burner Fuels subcommittee) for development of a burner fuel standard for Pyrolysis Liquid Biofuel. After several draft iterations and votes, the standard is approaching final approval.

PROPERTIES AND TEST METHODS OF FAST PYROLYSIS BIO-OILS

Biomass fast pyrolysis bio-oils differ significantly from petroleum-based fuels in both physical properties (Table 1) and chemical composition. Bio-oils are acidic, unstable, polar, mainly unvolatile liquids containing a large amount of chemically dissolved water [1]. Light fuel oil consists mainly of aliphatic and aromatic hydrocarbons (C_9—C_{25}) that are not miscible with bio-oil. The unusual properties of the bio-oils must be taken into account in the determination of fuel oil qualities and in applications. Table 1 shows the variation in fuel oil properties of bio-oil compared with light fuel oil. The variation in bio-oil properties is mainly due to variation in water content.

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

Analysis	Typical bio-oil	U.S.#4 FO
Water, wt %	20–30	0.5 (water and sediment)
Solids, wt %	0.01–0.5	—
Ash, wt %	0.01–0.2	0.1 max
Nitrogen, wt %	0–0.4	—
Sulfur, wt %	0–0.05	Varies
Stability	Unstable*	—
Viscosity (40 °C), cSt	15–35	5.5-24
Density (15 °C), kg/dm^3	1.10–1.30	—
Flash point, °C	40–110	55 min
Pour point, °C	−9 to −36	−6 min
LHV, MJ/kg	13–18	—
pH	2–3	—
Distillability	Not distillable	—

*Unstable at high temperatures or for prolonger periods of time.

Water and Solids

Water is recommended to be analyzed according to ASTM E 203 by Karl-Fischer titration and solids as insolubles in methanol-dichloromethane (Table 2). The use of the latter solvent ensures also the solubility of extractives in softwood liquids [8].

Homogeneity

To have a homogenous liquid water content should not increase above 30 wt %. Feedstock moisture and yield of organics are the main parameters affecting the water content of the liquid [17, 18]. Homogeneity of fast pyrolysis bio-oil can be checked by analyzing water content from different depths of the liquid [8].

Viscosity

Kinematic viscosity according to ASTM D445 (Table 2) can be used for fast pyrolysis bio-oils [8].

Stability

Fast pyrolysis bio-oils react by time and temperature, which is seen as an increase in viscosity espe-

Table 2. Test methods for fast pyrolysis bio-oils [8]

Analysis	Method	Comment
Water, wt %	ASTM E 203	1
Solids, wt %	Methanol-Dichloromethane insolubles	2
Ash, wt %	EN 7, ASTM D 482	3
CHN, wt %	ASTM D 5291	4
Density (15°C), kg/dm^3	ASTM D 4052	5
Viscosity (20, 40°C), cSt	ASTM D 445	6
Pour point, °C	ASTM D 97	7
Heating value, MJ/kg	DIN 51900, ASTM D 240	8
Flash point, °C	ASTM D 93	9

1, Karl-Fischer titration. Methanol-Chloroform (3:1) as a solvent. Water addition method for calibration. HYDRANAL K reagents (Composite 5 K and Working Medium K) in case of a fading titration end-point. Totally, 50 mL solvent for two determinations. Sample size about 0.25 g (water content >20 wt %). Stabilization time 30 s; 2, For example Millipore one place or Scleicher & Schuell (AS 600/2) multiplace filtration system, 1-μm filter, sample size 1–15 g in order to obtain 10–20 mg residue, sample:solvent = 1:100; 3, Controlled evaporation of water to avoid foaming; 4, Proper homogenization. For forest residue liquids careful rolling of the sample bottle. Large sample size as possible. Triplicates; 5, Careful mixing of foam-prone forest residue liquids in order to avoid air bubbles; 6, It is recommended to use Cannon-Fenske viscometer tubes because the flow direction in these tubes compared to Ubbelohde tubes ensures more accurate results with dark coloured liquids. No prefiltration of the sample if visually homogenous. Elimination of air bubbles before sampling. Equilibration time 15 min; 7, No preheating of the sample; 8, Use of a fine cotton thread for ignition; 9, Elimination of air bubbles before sampling.

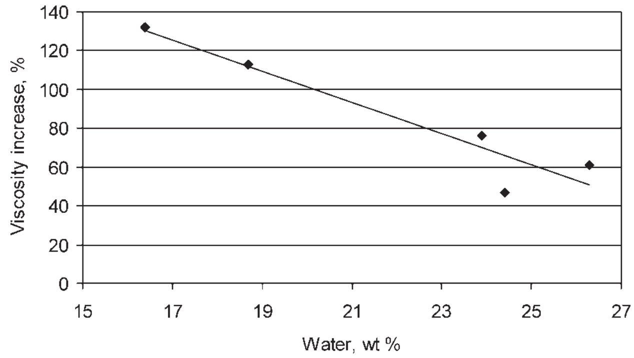

Figure 1. Correlation of water content to the stability of fast pyrolysis bio-oils. Samples produced from softwood from various test runs in a VTT's 20 kg/h pyrolyzer.

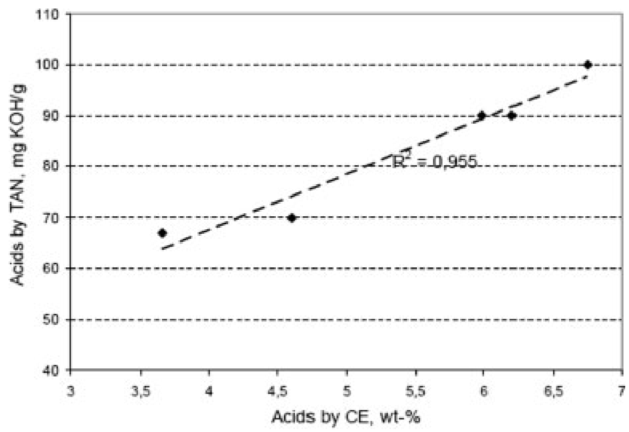

Figure 2. Correlation of TAN (total acid number) with the amount of volatile acids by CE (Capillary Electro Phoresis). [To be published in VTT Publication series 2009, **http://www.vtt.fi/publications/**].

cially when heated [19]. The water content and added solvent, if applicable, affects to the stability of bio-oil (see Figure 1). Stability of the bio-oils can be determined by an ageing test using fixed conditions [6, 8]. The temperature, holding time, and viscosity measurement in the method should be standardized. A standard reference sample is recommended to be included.

Acidity

pH gives the acidity level of fast pyrolysis bio-oils. For more precise determination total acid number (TAN) can be measured. Although there are other acidic compounds than the acids in fast pyrolysis bio-oils TAN correlates well with the total amount of volatile ($C \leq 6$) acids and a calibration curve (see Figure 2) may be drawn.

Flash Point

Flash point of fast pyrolysis bio-oil according to ASTM D 93 does not correlate with its ignition properties like with mineral oils. However, the flash point is acquired by authorities for storage and transportation classification. A flash with bio-oil is caused because of presence of easily volatile compounds but the water evaporated will right away distinguish the flame. This gives bio-oil a low flash point although it is ignited above 500°C. To get a proper safety classification for bio-oil its ignition properties should be tested in certified laboratory.

Pour Point

Pour point can be measured by ASTM D 97 and it gives the lowest temperature at which the oil can be pumped. For fast pyrolysis bio-oils produced from softwood the pour point is typically below −30°C.

Table 3. Expected parameters for pyrolysis liquid biofuels in ASTM burner fuel standard,

Property	Test method	Specification	Units
Gross Heat of combustion	D240	15 min	MJ/kg
Water content	E203	30 max	mass %
Pyrolysis solids content	Annex A1	2.5 max	mass %
Kinematic viscosity at 40°C	D445*	125 max	mm^2/s
Density at 20°C	D4052	1.1–1.3	kg/dm^3
Sulfur content	D4294	0.05 max	mass %
Ash content	D482	0.25 max	mass %
pH	E70-07	Report	
Flash point	D93 Procedure B	45 min	°C
Pour point	D97	−9 max	°C

*Without filtering.

QUALITY CONTROL IN FAST PYROLYSIS BIO-OIL PRODUCTION AND USE

Quality follow-up during fast pyrolysis bio-oil production both ensures the production of constant quality product and helps in avoiding possible problems during production [19].

Feedstock

Feedstock moisture is the main parameter to be followed. Too moist feedstock causes formation of multiphase liquid product. VTT has good experience with fast Sartorius MA 45 Moisture Analysis device. A rough indication of expected organic liquid yields [19] can be obtained by analyzing the volatiles/fixed carbon of the feedstock to be pyrolyzed. Standardization of biomass analyses [20] are under development in CEN/TC 335.

Product Gas

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

Liquid Product

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

There are on-line analyzers available for determination of water and solids. Some of these may be applicable also for analyzing fast pyrolysis bio-oils. Water may be analyzed on-line by volumetric Karl-Fischer titration. For solids follow-up online particle measurements are available [19], which can be used as indicative tools for rapid change in solids concentration. Both these on-line methods need sample dilution unit.

Chemical characterization depends on the need. For quality follow-up the amount of water and water-insolubles typically provide enough information of product composition for quality control when used in conjunction with the other tests described in this document. Additional information is easily obtained by analyzing the water-soluble fraction for acids by Capillary Electro Phoresis (CE) or by TAN (total acid number) and for “sugars” (total amount of carbohydrates) by BRIX [21].

STANDARDIZATION OF FAST PYROLYSIS BIO-OILS

Ensyn is now leading the ASTM standard development effort for fast pyrolysis bio-oil under the title of Pyrolysis Liquid Biofuel. After several draft iterations and votes, the standard has passed balloting in D02-E0 Burner Fuels subcommittee and the D02 main committee and publication is pending. To achieve approval, the solids separation method (note #2 in Table 2) required a laboratory validation involving tests of two bio-oils at two laboratories over a 10-day period. The focus is to get one grade of bio-oil approved in burner applications, as specified in Table 3, and then work on the other grades of product, such as one with a low solids content. Subsequent standards for fast pyrolysis liquids (bio-oil) used as turbine fuel and diesel fuel will be the subjects of future evaluations, potentially leading to other standard developments.

There will be an IEA Bioenergy Task 34 on Pyrolysis for the 2010–2012 triennium. One of the main issues for the participants is standards development and registration efforts for bio-oil. As a group, the participants will contribute to efforts in standards development and registration. The United States will be the Operating Agent and D.C. Elliott will serve as the Task Leader.

REACH

General

In the EU a new chemical regulation system REACH (Registration, Evaluation, and Authorization of Chemicals) is being implemented. The European Chemicals Agency (ECHA) will manage the registration, evaluation, authorization, and restriction processes for chemical substances to ensure consistency across the European Union.

The regulation applies to substances manufactured or imported to the EU in annual quantities of one tonne or more per company, unless the regulation indicates otherwise. REACH requires that chemical substances on their own, in preparations and those which are intentionally released from articles have to be registered to the European Chemicals Agency (ECHA). The chemicals currently on the EU market which meet the definition of phase-in substances were to be preregistered before December 1, 2008. A SIEF (Substance Information Exchange Forum) will be formed for each preregistered substance with the same identity. SIEF members need to nominate a "Lead Registrant". They will share and assess data and prepare common parts of the registration (joint submission). Compensation for sharing data is agreed among the respective SIEF members.

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

Registration of Fast Pyrolysis Bio-Oil

A total of 32 preregistrations in REACH has been filed under the CAS number 94114-43-9. Discussions will be made to evaluate if all preregistrants are in a right group. A SIEF will be formed for each preregistered substance with the same identity and a "Lead Registrant" will be nominated.

In EU-Biotox project completed in 2005, led by CIRAD (France), and sponsored by European Commission DG TREN toxicological, ecotoxicological, and physico-chemical properties as well as MSDS were created for registration of fast pyrolysis bio-oils under CAS number 94114-43-9 [22]. Additional data for REACH registration include modifications to the present MSDS, and preparation of a chemical safety report (CSR). The CSR documents the results of the entire chemical safety assessment (CSA). CSA is the documentation of the registrant's chemical safety assessment (CSA) for his substance (or of relevant substances if the chemical safety report has been developed for a category of substances having similar properties). This chemical safety report contains a detailed summary of information on the environmental and human health hazard properties of the substance, together with an assessment of exposure and risk where such an assessment is required [23].

Use of PPORD (Product and Process Oriented Research and Development)

PPORD is defined as any scientific development related to product development or the further development of a substance, on its own, in preparations or in articles in the course of which pilot plant or production trials are used to develop the production process and/or to test the fields of application of the substance. PPORD may be applied for fast pyrolysis bio-oils if registered as a new substance. It gives five years time for registration [24].

CONCLUSIONS

Work is going on in order to obtain ASTM standards for fast pyrolysis bio-oils as fuel. After getting approval to one fuel oil grade, other options will be considered. Most of the test methods for the bio-oils are available but testing validations needed by ASTM should be carried out. The stability test method has to be standardized and the real safety classification for fast pyrolysis bio-oil should be provided. The IEA Pyrolysis activity will further process the data in the project in 2010–2012. The needed standardization activity in EU under CEN will be evaluated.

For quality follow-up during pyrolysis oil production and use following analyses are recommended: moisture and volatiles for feedstock, CO and CO_2 on-line analyses for product gases, and water and solids for liquid product. For water and solids on-line methods are available, but they need testing.

REACH in EU is now in progress. Ten fast pyrolysis companies have preregistered fast pyrolysis bio-oil. Depending on the amount of annual production the registration dead-lines can be November 30, 2010 or May 31, 2013. If fast pyrolysis bio-oil will be registered as a new substance a PPORD application with five years registration time may be used. Much of the needed data is available. Additional data needed include changes in MSDS and preparation of a chemical safety report.

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