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Bioolja, pridobljena s hitro pirolizo, za nepremične motorje z notranjim zgorevanjem - Specificiranje kakovosti

Fast pyrolysis bio-oil for stationary internal combustion engines - Quality determination

Pyrolyseprodukte - Schnell Pyrolyse-Bio-Öle für stationäre Verbrennungsmaschinen - Qualitätsbezeichnung

Pétrol et produits rélatives - Huiles biologique de pyrolyse rapide pour application en moteurs stationés avec combustion interne - Désignation de qualité

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Petroleum and related products - Fast pyrolysis bio-oils for stationary internal combustion engines - Quality determination

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European foreword

This document (CEN/TR 17103:2017) has been prepared by Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin”, the secretariat of which is held by NEN.

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This document has been prepared under a mandate [1] given to CEN by the European Commission and the European Free Trade Association.

Introduction

The European Union is promoting the use of renewable energy. Liquid biofuels have rarely been used for CHP applications with the exception of vegetable oils which in some cases have been used in combined heat and power (CHP) applications and several boiler manufacturers promote its use. However, given the demand for biodiesel for the transport sector little uptake has been reported for biodiesel in the CHP sector. Hence the European Commission (EC) requested CEN to develop a 'Technical Specification for a quality specification for pyrolysis oil replacing fuel oils in stationary internal combustion engines' [1].

Fast pyrolysis bio-oils (FPBO) or fast pyrolysis liquids are completely different from conventional fossil fuels both in their physical properties and chemical composition. They are brownish liquids with a distinct and smoky odour. They can be produced from woody biomass [3] and agrobiomass (herbaceous [3]) and there is a wide range of reactor types suitable for fast pyrolysis bio-oil production. Contrary to fossil fuels, they are highly polar, mainly water-soluble containing typically about 25 % (*m*/*m*) (on wet basis) water, are acidic in nature, dense, and viscous liquids, very poorly or not miscible with hydrocarbons [4].

CEN adopted work item 00019499 for the requested work and installed CEN/TC 19/WG 41 'Pyrolysis oil' to develop the CEN Technical Specification. During its work the group encountered the following:

- FPBO is not yet commercialized for stationary internal combustion engines (ICE) and there is neither enough data on the properties for FPBO for ICE use and parameters to determine combustion properties are not fully understood. Also the long-duration tests in ICE have not yet been carried out.

- WG 41 performed an enquiry within the leading engine manufacturers to collect data and proposals for threshold values. Most of the manufacturers did not have experience with FPBO. Several comments made by the manufacturers was that further research and development work was required on several issues (e.g. type of fuel injection system, chemical resistance, effect of solids/char content of bio-oil on erosion/corrosion at fuel nozzles, and ignition properties).

- There are several important properties (e.g. combustion properties, flash point and chlorine) that should be incorporated as grade criteria, but no established test methods for fast pyrolysis bio-oil are available. Research and development is needed to develop these methods to be used for specification of FPBO for ICE.

WG 41 thus proposed to CEN/TC 19 to draft a Technical Report (TR) instead of a Technical Specification, which was approved [2] and thereafter adopted by the CEN/BT and accepted by the EC. This document is laying down the outcome of the study and the quality that so far has been found acceptable for ICE. Further investigations and market application should be continued in order to decide to eventually revise this document into a deliverable originally requested by the EC.

1 Scope

This Technical Report describes the key properties of fast pyrolysis bio-oils and their importance to the fuel quality for use in stationary internal combustion engines.

Internal combustion engine (ICE) in the scope of this document means a type of engine in which heat energy and mechanical energy is produced inside the engine. ICE include compression ignition engines (diesel engines) and gas turbines.

Attention is drawn to differences especially in those properties, which can have an effect on the required engine performance, such as ash, acidity, viscosity, combustion properties, and sulfur content.

In addition to the quality requirements and related test methods for FPBO, further instructions on storage (Annex A), sampling (Clause 4), and materials compatibility (Annex B) are given.

NOTE For the purposes of this Technical Report, the terms "% (*m*/*m*)" and "% (*V*/*V*)" are used to represent the mass fraction (μ) and the volume fraction (φ) of a material, respectively.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 16476, *Liquid petroleum products - Determination of Sodium, Potassium, Calcium, Phosphorus, Copper and Zinc contents in diesel fuel - Method via Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES)*

EN 16900:2017, *Fast pyrolysis bio-oils for industrial boilers - Requirements and test methods*

EN ISO 2719, *Determination of flash point - Pensky-Martens closed cup method (ISO 2719)*

EN ISO 3104, *Petroleum products - Transparent and opaque liquids - Determination of kinematic viscosity and calculation of dynamic viscosity (ISO 3104)*

EN ISO 3170:2004, *Petroleum liquids - Manual sampling (ISO 3170:2004)*

EN ISO 6245, *Petroleum products - Determination of ash (ISO 6245)*

EN ISO 8754, *Petroleum products - Determination of sulfur content - Energy-dispersive X-ray fluorescence spectrometry (ISO 8754)*

EN ISO 9038, *Determination of sustained combustibility of liquids (ISO 9038)*

EN ISO 12185, *Crude petroleum and petroleum products - Determination of density - Oscillating U-tube method (ISO 12185)*

EN ISO 20846, *Petroleum products - Determination of sulfur content of automotive fuels - Ultraviolet fluorescence method (ISO 20846)*

ISO 3016, *Petroleum products — Determination of pour point*

ASTM D93, *Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester*

ASTM D4294, *Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry*

ASTM D5291, *Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants*

ASTM D5453, *Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence*

ASTM D7579, *Standard Test Method for Pyrolysis Solids Content in Pyrolysis Liquids by Filtration of Solids in Methanol*

ASTM E70, *Standard Test Method for pH of Aqueous Solutions With the Glass Electrode*

ASTM E203, *Standard Test Method for Water Using Volumetric Karl Fischer Titration*

DIN 51900-1:2000, *Testing of solid and liquid fuels — Determination of gross calorific value by the bomb calorimeter and calculation of net calorific value — Part 1: Principles, apparatus, methods*

DIN 51900-3, *Testing of solid and liquid fuels — Determination of gross calorific value by the bomb calorimeter and calculation of net calorific value — Part 3: Method using adiabatic jacket*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
agrobiomass
biomass obtained from energy crops and/or agricultural by-products (agricultural residues)

[SOURCE: FAO unified bioenergy terminology [UBET]; modified]

3.2
fast pyrolysis
thermal treatment of lignocellulosic biomass at short hot vapour residence time (typically less than 5 s) typically at between 450 °C–600 °C and at near atmospheric pressure or below, in the absence of oxygen, using small (typically less than 5 mm) dry (typically less than 10 % *(m/m)* water) biomass particles

Note 1 to entry: Under REACH it is defined as “lignocellulosic biomass, at short hot vapour residence time (typically less than about 10 s) typically at between (450-600) °C at near atmospheric pressure or below, in the absence of oxygen”.

3.3
fast pyrolysis bio-oil
FPBO
liquid produced by fast pyrolysis from biomass

Note 1 to entry: The typical yield of bio-oil is 60 % (*m*/*m*) - 75 % (*m*/*m*) on wet basis (energy basis) and 55 % (*m*/*m*)– 65 % (*m*/*m*) of organic matter. Other products are char and non-condensable gases.

3.4
solids
solid particles which are not soluble in methanol-dichloromethane (1:1), possibly containing inorganic elements including sand, char, and additional insoluble organic material

Note 1 to entry: The solids will in time settle to the bottom or raise up to the surface depending on their density and the fast pyrolysis bio-oil composition.

3.5
stability
situation in which physico–chemical properties remain unchanged during handling and storage

Note 1 to entry: FPBOs are not chemically or thermally as stable as conventional petroleum fuels due to the high content of reactive oxygen containing compounds and low-boiling volatiles. The instability of FPBOs can be observed via an increase in viscosity ("aging") and possible phase-separation by time and temperature. A stability test based on viscosity increase at 80 °C in 24 h may be used to predict if the bio-oil will stand for a year's storage at room temperature without phase-separation [4].

Note 2 to entry: Physico-chemical properties remain unchanged during handling and storage at a temperature close to 20 °C (storage stability) for a long time (i.e. a few months) or when heated at moderate temperature, i.e. lower than 100 °C, for a short time, i.e. less than one day [23].

4 Sampling and sample handling

It is strongly advised to review all intended test methods prior to sampling to understand the importance of sampling technique, and special handling requirements for fast pyrolysis bio-oils.

Samples shall be taken as described in EN ISO 3170 and/or in accordance with the requirements of national standards or regulations for the sampling of FPBO.

Some procedures in EN ISO 3170 are not relevant with fast pyrolysis bio-oils; FPBO is mostly water-soluble (approximately 80 %) and hence does not include any free water:

— sampling methods described in EN ISO 3170:2004, Clause 8 are not relevant for FPBO;

— for verification of mixing efficiency application of the procedure as described in EN ISO 3170:2004, 9.3.2 is not recommended;

— water content determination should only be carried out according to ASTM E203.

The samples shall be taken immediately after mixing (see Annex A for further instructions).

If bio-oil samples are not analysed immediately, samples should be stored in a freezer [4, 5, 6, 15, 16, 17].

It is pointed out that the sampling devices, sample bottles, and other devices in contact with bio-oil shall be compatible with bio-oil (see Annex B). Bio-oil shall be well mixed when transferring from the primary sampling process and/or container to another container and/or analytical apparatus. Minimum of two samples should be taken and the maximum difference of the viscosity shall not exceed ± 5 % at 40 °C [6]. A minimum of 0,1 L sample size is recommended.

The bio-oil shall be properly mixed and analysed according to the recommended standard methods. The bio-oil shall not be filtered or preheated above 40 °C for more than 30 min even though mentioned in some of the analysis standards. FBPO can typically be analysed like single-phase bio-oils because the separation of extractive-rich layer is very slow. However, the sampling and analyses should be carried out immediately after sample homogenization.

5 Requirements and test methods

5.1 General

FPBO is not yet commercialized for stationary internal combustion engines (ICE) and there is not enough data on properties for neither engine use nor the long-duration tests in internal engines.

Contrary to fossil fuels, FPBOs are highly polar, mainly water-soluble containing typically about 25 (% *(m/m)* on wet basis) of water, acidic in nature, dense, and are viscous liquids with a moderate to high level of viscosity at 40 °C, very poorly or not miscible with hydrocarbons [4]. A typical range for FPBO characteristics is shown in Table 1.

Table 1 — Typical range of characteristics of fast pyrolysis bio-oils

Property	Typical range	Unit
Gross calorific value, wet basis [8]	14–19	MJ/kg
Net calorific value, wet basis [8]	13–18	MJ/kg
Water content, wet basis [8]	20–30	% *(m/m)*
pH [8]	2–3	-
Total acid number (TAN) [8]	70–100	mg KOH/g
Kinematic viscosity at 40 °C [8]	15–40	mm^2/s
Density at 15 °C [8]	1,11–1,30	kg/dm^3
Pour point [8]	-9–-36	°C
Carbon, d.b.[a] [8]	50–60	% *(m/m)*
Total hydrogen, d.b. [8]	7–8	% *(m/m)*
Nitrogen, d.b. [8]	< 0,5	% *(m/m)*
Sulfur, d.b. [8]	< 0,05	% *(m/m)*
Oxygen, d. b. [8]	35–40	% *(m/m)*
Solids, wet basis [8]	< 1	% *(m/m)*
Carbon residue, wet basis [8]	17–23	% *(m/m)*
Ash, wet basis [8]	< 0,3	% *(m/m)*
Flash point [8]	40–110	°C
Sustain combustibility [8]	does not sustain combustion	-
Na, K, Ca, Mg. d.b.	0,05–0,2	% *(m/m)*
Chlorine	75–500	ppm

[a] d.b. is on dry basis. The change from wet basis (ar) to dry basis (d.b.) follows: $\frac{100}{100 - M_{ar}}$

Dry basis (d.b.) to wet basis (ar): $\frac{100 - M_{ar}}{100}$ where M_{ar} is water content on wet basis (% *(m/m)*).

WG 41 carried out enquiry within leading engine manufacturers to collect data and proposals for threshold values. Most of the manufacturers do not have experience of FPBO.

Several comments stated by manufacturers expressed that further research and development is requested before fuel quality specification can be drafted. The following issues were given as examples (see also Tables 2 and 3):

- type of fuel injection system,
- chemical resistance,
- effect of solids/char content of bio-oil on erosion/corrosion at fuel nozzles.

There are several important properties (e.g. combustion properties, flash point and chlorine) that should be incorporated as grade criteria that do not have established test methods for FPBO. Research and development is needed to develop these methods to be used for specification of fast pyrolysis bio-oil for ICE.

5.2 FPBO properties affecting internal combustion engines

5.2.1 Water content

Typically, the water content of the bio-oils is high (>20 % (*m/m*), on wet basis). Many of quality parameters correlate inversely with the water content, such as density, viscosity, and net calorific value. The density, viscosity, and net calorific value increase, when water content decreases. Water content also informs about the stability and phase separation tendency of FPBO [15]. A 30 % (*m/m*) limit for water content is recommended to ensure that no phase separation takes place. However, some bio-oils with water content above 30 % (*m/m*) are in one phase due to different chemical composition. A minimum water content is not needed as the maximum viscosity is proposed to specify. For ICE, a lower water content limit (≤25 % (*m/m*)) is proposed to avoid phase separation [18].

5.2.2 Net calorific value

Net calorific value is analysed according to DIN 51900-3 and the calculation of net calorific value at constant pressure ($H_{u,p}$) for moist fuel is specified in DIN 51900-1:2000, Clause 15 (see Formula (1)):

$$H_{u,p} = H_{o,v} - [k^{*}\cdot H + 0{,}8\,^{*}(\mathrm{N} + \mathrm{O}) + k_1{}^{*}\omega] \tag{1a}$$

$$N + O = 100 - [\omega + A + C + H + S] \tag{1b}$$

where

$H_{o,v}$ is gross calorific value at constant volume

k is the heat of evaporation taking account of the volumetric work performed by the water formed by the hydrogen during combustion at 25° C (23,7 J/g (as water) or 212 J/% (as hydrogen), or more exactly 23,7278 J/g and 212,1265 J/% respectively

k_1 is the specific heat of evaporation of water at constant pressure at 25 °C (24,4 J/%)

ω is analytical moisture content of the moist fuel, as a percentage of mass;

A is the ash content of the moist fuel, as a percentage by mass

C is the carbon content of the moist fuel, as a percentage by mass

H is the hydrogen content of the moist fuel (excluding hydrogen in water part of fuel), as a percentage by mass

S is the sulfur content of the moist fuel, as a percentage by mass

N is the nitrogen content of the moist fuel, as a percentage by mass

O is the oxygen content of the moist fuel, as a percentage by mass