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Standards Development Related to Fuel Use of Fast Pyrolysis Bio-Oil

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IEA Bioenergy – Task 34 - Pyrolysis

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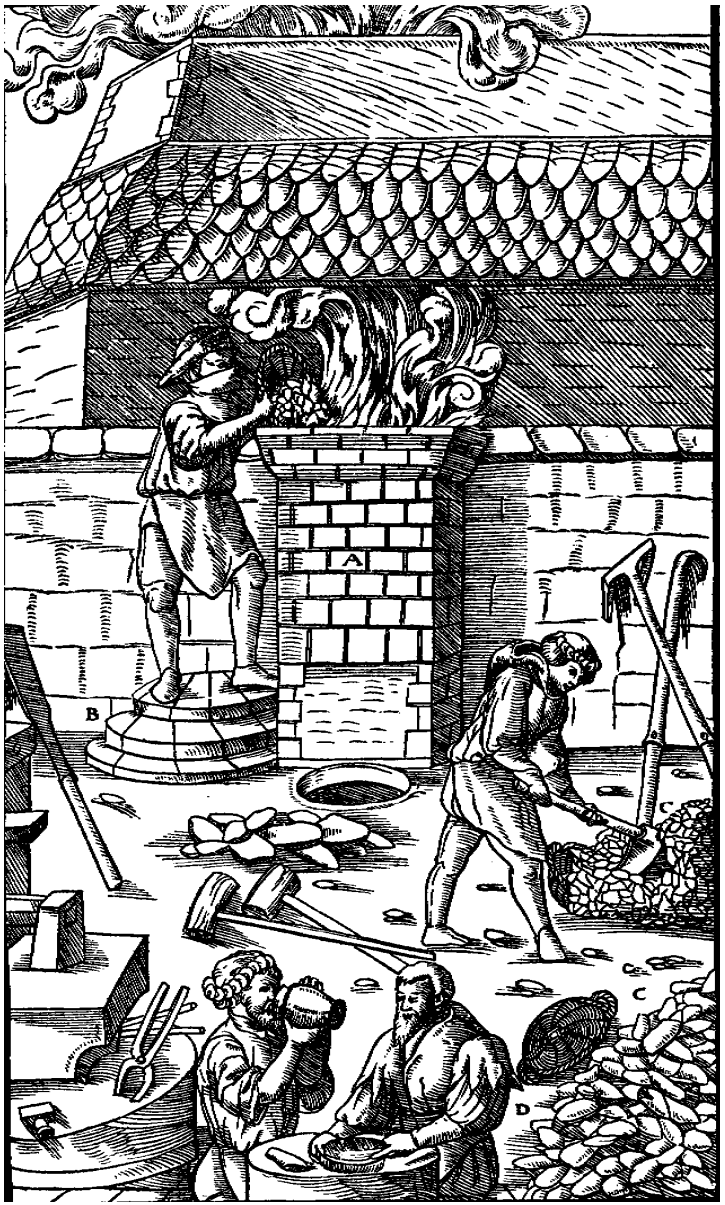
What is Biomass Pyrolysis?

Pyrolysis is thermal decomposition occurring in the absence of oxygen

Lower temperature and longer vapour residence times favour the production of charcoal.

High temperature and longer residence time increase the biomass conversion to gas.

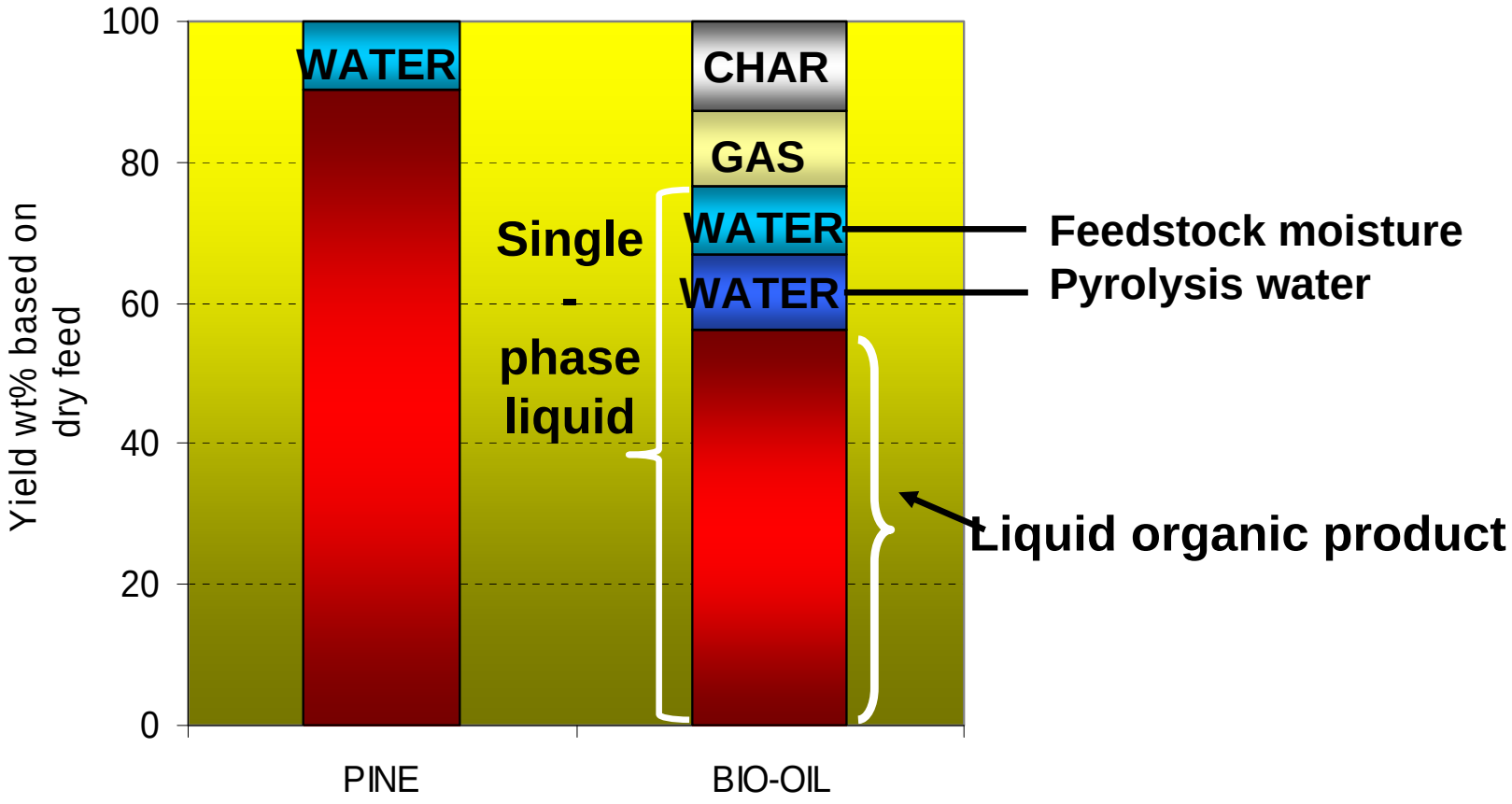
Moderate temperature and very short vapour residence time are optimum for producing liquids.



Pyrolysis in late medieval foundry processes
Georgius Agricola, De Re Metallica Libri XII, MDLVI

Fast Pyrolysis Of Biomass

Rapid (1-2 s) thermal (about 500 C) degradation of biomass under inert atmosphere into bio-oil as main product and into side-products gases, and char

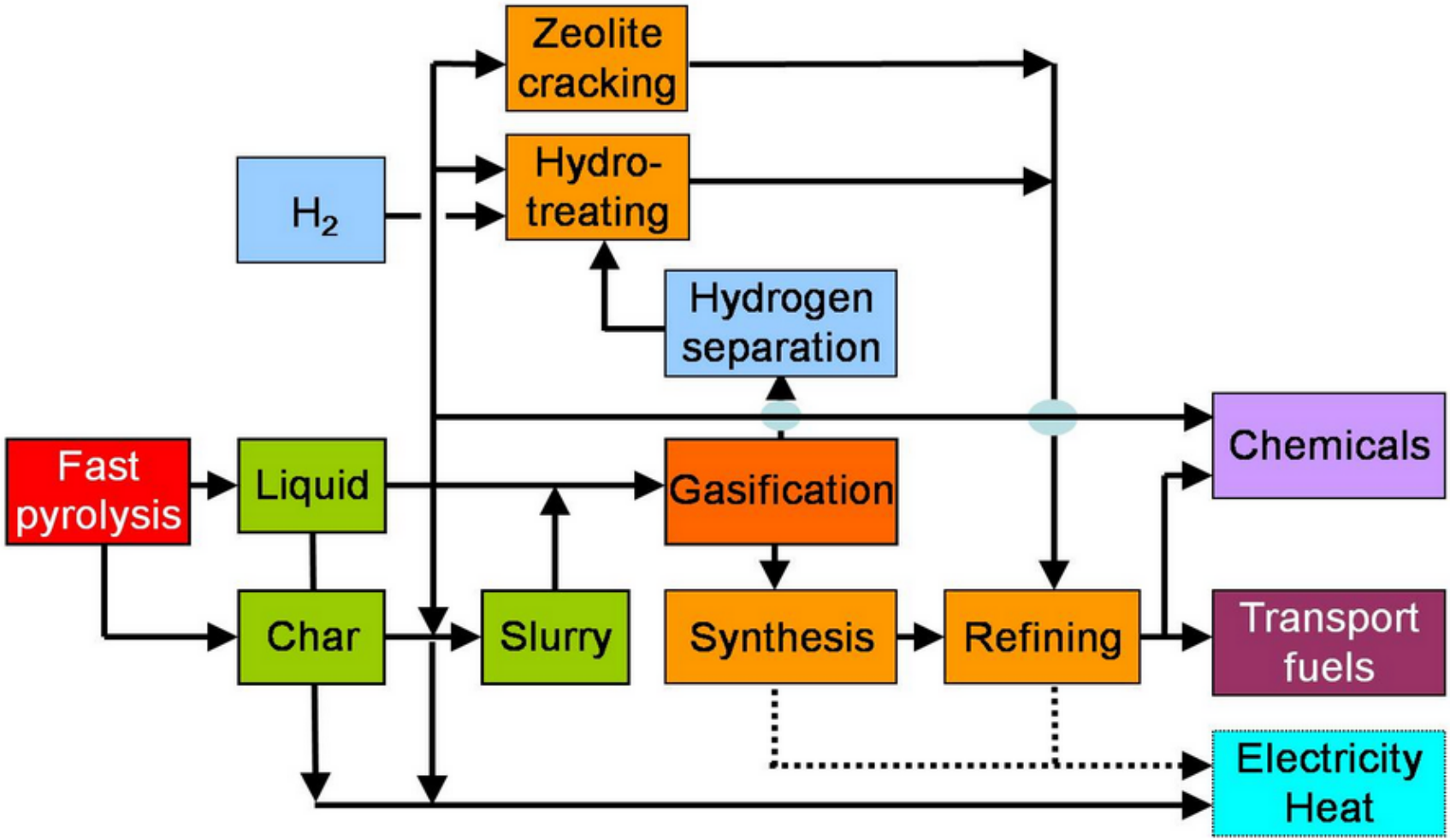


Energy & Fuels, 2010, 24, ss. 1380-1388

Why Fast Pyrolysis Bio-oil?

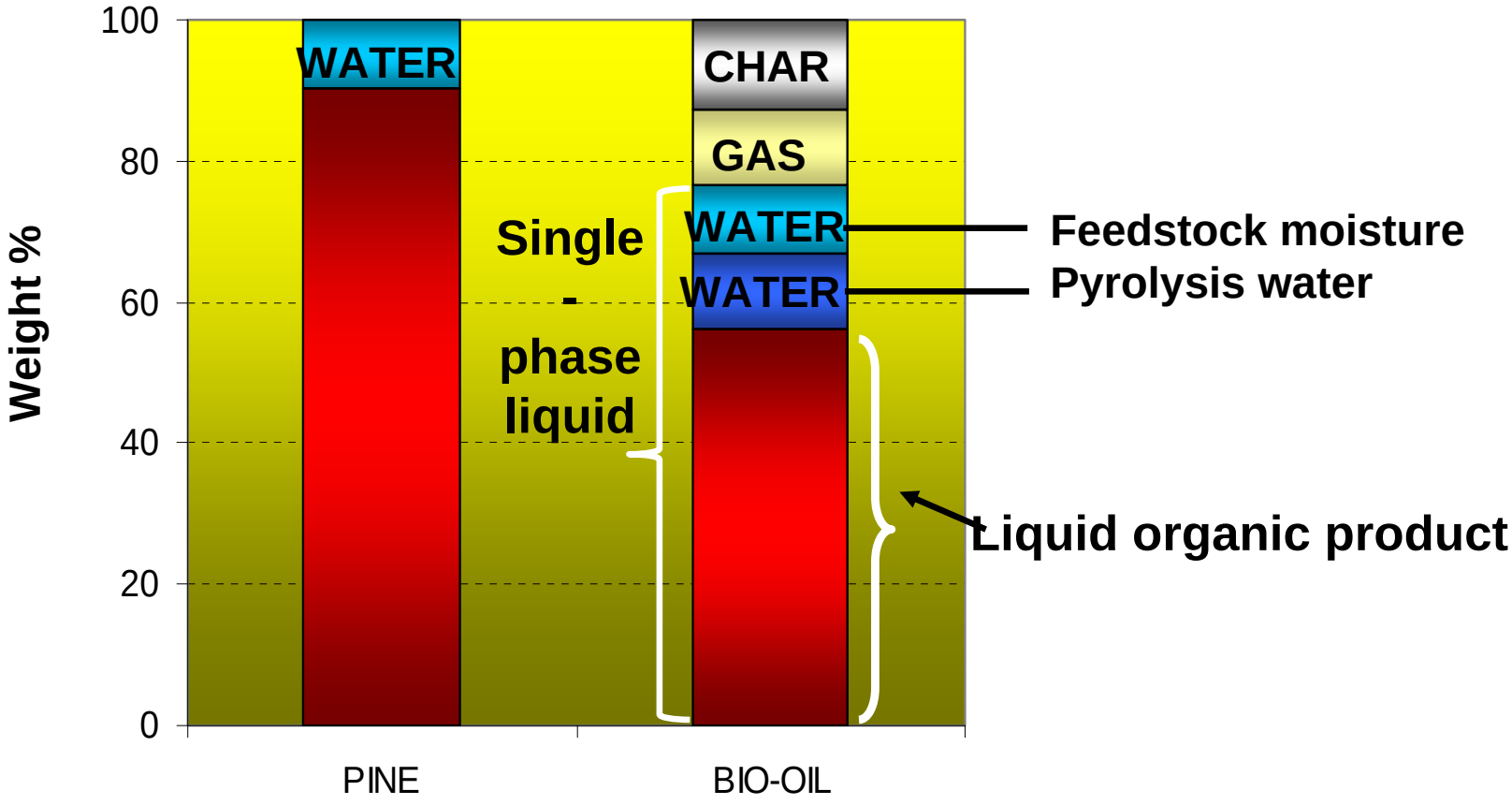
- Relatively simple process offers potentially lowest cost liquid bio-fuel
- Feasible at relatively small scale and readily integrated with existing industry
- Increased energy density
- Process is relatively feedstock insensitive
- Fluid product for easy transport, storage and utilization
- Potential for upgrading to higher value products

Potential Applications of Bio-oil



http://www.pyne.co.uk/

Bio-Oil: Liquid Organic Product



Energy & Fuels, 2010, 24, ss. 1380-1388

Characteristics of Bio-Oil

Fast pyrolysis liquid has a higher heating value of about 17 MJ/kg as produced with about 25 wt% water that cannot readily be separated.

The “thick, heavy” liquid widely referred to as ‘bio-oil” is composed of a complex mixture of oxygenated compounds.

Bio-oil is miscible with polar solvents such as methanol, acetone, etc. but totally immiscible with petroleum-derived fuels.

Bio-oil exhibits ageing behaviour resulting in increased viscosity

Chemical Composition of Bio-Oil

Fast pyrolysis bio-oil is comprised of hundreds of various compounds. The main groups are:

4 – 6 wt-% carboxylic acids

15 – 20 wt-% aldehydes, ketones, furans, pyrans, monomeric phenols, etc.

25 – 35 wt-% carbohydrates, “sugars”

20 – 30 wt-% water

20 – 25 wt-% pyrolytic lignin, extractives, solids (incl. ash), polymerisation products

Energy & Fuels, 2003, vol. 17, 2, ss. 433 – 443
Energy & Fuels, 2008, vol. 22, 6, ss. 4245 – 4248

Characteristics of Bio-Oil (contd)

Physical property		Typical value
Water content		20 - 40%
pH		2 - 3
Specific gravity		1.15 - 1.20
Elemental analysis	C	56%
	H	6%
	O	38%
	N	0–0.1%
HHV as produced		13 - 19 MJ/kg
Viscosity		50–150 cP
Solids		0.1 – 0.25%
Vacuum distillation residue[1]		up to 50%

1: If bio-oil is heated to 100ºC or more to try to remove water or distill off lighter fractions, it rapidly reacts and eventually produces a solid residue of around 50 wt% of the original liquid and some distillate containing volatile organic compounds and water

Anja Oasmaa & Cordner Peacocke

Properties and fuel use of biomass-derived fast pyrolysis liquids

A guide

http://www.vtt.fi/inf/pdf/publications/2010/P731.pdf

Challenges

Identify the technical knowledge gaps that need to be closed order for industry to establish the infrastructure to address wide-spread utilization of pyrolysis oils:

- **compatibility (blending) with existing hydrocarbon fuels**
- **long term storage stability**
- **containment, handling and corrosivity**
- **fouling and plugging**
- **burner design and combustion performance**

Infrastructure-related requirements and/or regulations must also be addressed:

- **technical standards including WHMIS issues: hazard identification and product classification; MSDS**
- **spillage and emissions monitoring/regulations**

etc …

IEA Bioenergy

IEA Bioenergy was set up in 1978 by the International Energy Agency (IEA) with the aim of improving cooperation and information exchange between countries that have national programmes in bioenergy research, development and deployment.

Task 34 Pyrolysis of Biomass

Improve the rate of implementation and success of fast pyrolysis of biomass for fuels and chemicals. Programme of work which addresses the following priority topics:

- **norms and standards;**
- **analysis – methods comparison, developments;**
- **country updates and state-of-the-art reviews;**
- **and fuels and chemicals from pyrolysis**

IEA Bioenergy

Task 34 - Pyrolysis

- **Task Leadership**
  - U.S.A. – Doug Elliott
- **National Team Leaders**
  - Germany: Dietrich Meier
  - Finland: Anja Oasmaa
  - Canada: Fernando Preto
  - UK: Tony Bridgwater
  - Netherlands: Bert van de Beld

http://www.pyne.co.uk/

Task 34 Norms and Standards

Areas of collaborative activities include:

- **Refining pyrolysis oil fuel oil specifications in cooperation with establishing the ASTM D7544 bio-oil standards (Ensyn Technologies Inc played a lead role)**
- **Testing of analytical methods in independent laboratories according to ASTM/CEN directions (solids content has been standardised as ASTM D7579)**
- **CAS Registry # 1207435-39-9; CAS # defined as an "RN" meaning that it is a defined chemical mixture, not a true compound; an additional physical descriptor of viscosity of 5-200 cSt @ 50° C was provided**
- **Input to the CEN and REACH process for registering bio-oil for commercial use in Europe**

Task 34 Preparation of Guidelines Transportation, Handling and Use

- **A number of MSDS for pyrolysis oils are available, however the experiences and claims from commercial producers need to be assessed and incorporated into a comprehensive MSDS.**
- **Flammability – flash point, ignition and sustained combustibility**
- **Detailed toxicological data is required for exposure to liquids and vapours - acute toxicity, mutagenicity and ecotoxicology**
- **Further work is required to develop procedures for dealing with spills.**
- **Quality Control and Quality Assurance**

Task 34: Round Robin(s) for Analytical Method Development

- **15 laboratories from five participating countries**
- **2 bio-oils – filtered and unfiltered**
- **Viscosity measurement and accelerated aging tests**
- **Kinematic viscosity measurement was found to provide more consistent results compared to dynamic viscosity.**
- **Application of the ageing tests was found to be highly variable and a more precisely defined and performed method is needed.**
- **The presence of suspended solids (char) in the bio-oil was found to lead to higher variability in the measurements, generally.**

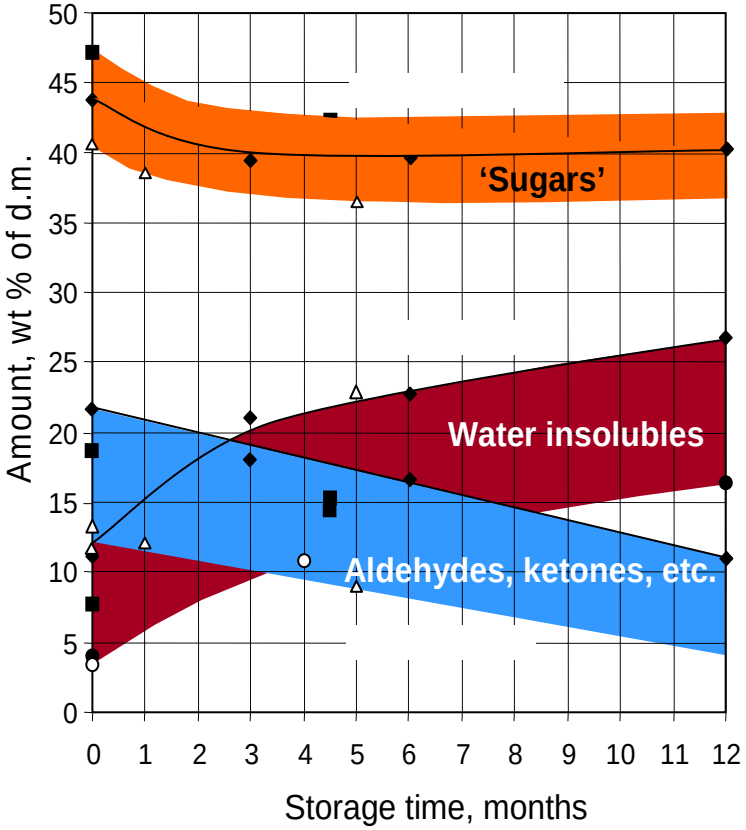
Reference:

Results of the IEA Round Robin on Viscosity and Stability of Pyrolysis Bio-oils, Energy & Fuel 26, 3769-3776 2012

Results of the IEA Round Robin on Viscosity and Stability of Pyrolysis Bio-oils: Long-Term Tests and Repeatability, Energy & Fuel, in press

Stability

- Bio-oils are not as stable as conventional petroleum fuels
- The instability can be observed as increased viscosity over time, particularly when heated
- In extreme cases phase separation can occur
- Aging effects can be reduced or controlled by the addition of alcohols such as ethanol or methanol
- Aging effects are exacerbated or accelerated by the presence of fine char
- Major changes in ageing happens in carbonyl and water insoluble fractions. Changes in these product groups can be used as stability indicators



Diebold, J.P. A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils. In: Fast Pyrolysis of Biomass: A Handbook, Vol. 2., Bridgwater, A.V. (Ed.), CPL Press, Newbury, UK, 2002, 424 p.

Scholze B. 2002. Long-term Stability, Catalytic Upgrading, and Application of Pyrolysis Oils -Improving the Properties of a Potential Substitute for Fossil Fuels. Dissertation zur Erlangung des Doktorgrades im Fachbereich Chemie der Universität Hamburg vorgelegt von Britta Scholze aus Hamburg.

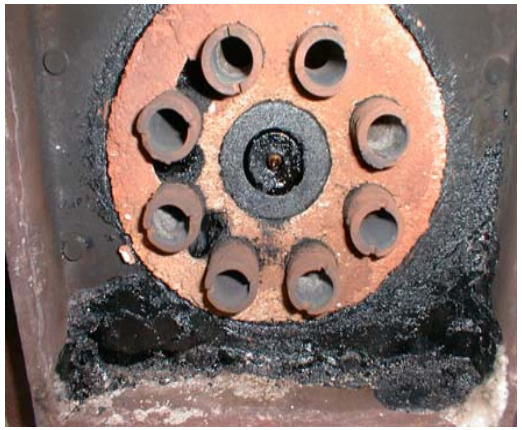
Oasmaa, A. 2003. Fuel oil quality properties of wood-based pyrolysis liquids. Academic dissertation. Jyväskylä. Department of Chemistry, University of Jyväskylä. 32 p. + app. 251 p.. Research Report Series, Report 99. Doctoral thesis

Oasmaa, A. et al. 2010. Acidity of Biomass Fast Pyrolysis Bio-oils. Energy & Fuels. American Chemical Society, vol. 24, ss. 6548-6554

Oasmaa, A. et al. 1011. An approach for stability measurement of wood-based fast pyrolysis bio-oils. Energy & Fuels. ACS Publications, vol. 25, 7, ss. 3307-3313

Liquid Fuels Comparison

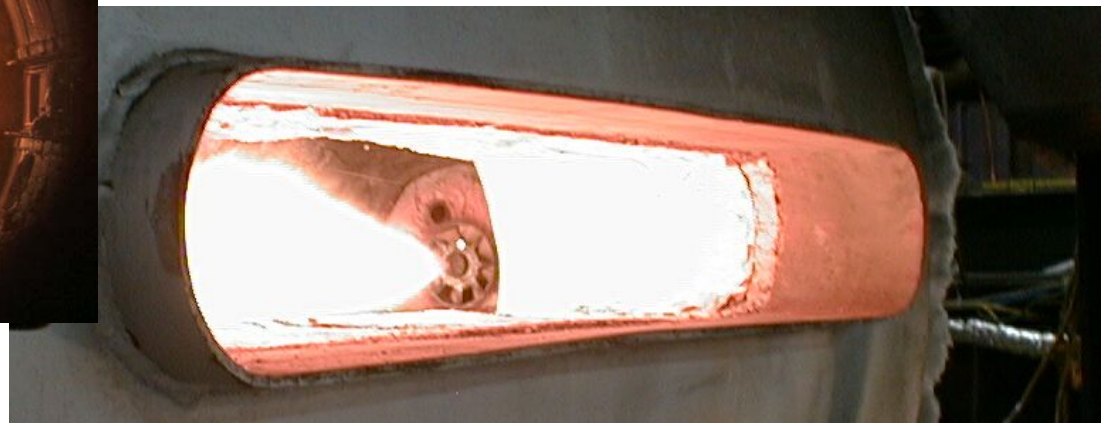
	FT Diesel	Low Sulphur Diesel	# 2 fuel oil	Biodiesel	Fast pyrolysis bio-oil
Water, wt%	0	0	0	< 0.1	25 - 30
Density (at 15°C), kg/dm3	0.797	0.847	0.93	0.888	1.15 - 1.2
HHV (MJ/kg)	45.5	45,6	44.2	40.2	13 - 19
LHV (MJ/kg)	43.2	42,6	41.1	37.5	11 - 17
Viscosity, cP (@20°C)	1.9-3.6	1,6	2.8-6.9	3.1-4.4	50 - 150
Flash point, °C		>62	38	>130	Not relevant



Needs:

- New burner and fuel train designs
- Standardization of fuel properties

Pyrolysis Oil Combustion



- Numerous co-firing demonstrations
- Stand-alone firing under development

Standard Specification for Pyrolysis Liquid Biofuel

- D-7544
- This specification covers grades of pyrolysis liquid bio-fuel produced from biomass intended for use in various types of fuel-burning equipment under various climatic and operating conditions. These grades are described as follows:
- Grade G is intended for use in industrial burners equipped to handle the pyrolysis liquid bio-fuels meeting the requirements listed for Grade G in Table 1.
- Grade D is intended for use in commercial/industrial burners requiring lower solids and ash content and which are equipped to handle the pyrolysis liquid bio-fuels meeting the requirements listed for Grade D in Table 1.
- The pyrolysis liquid bio-fuel listed under in Table 1 is not intended for use in residential heaters, engines, or marine applications not modified to handle these types of fuels.

ASTM D-7544 Table 1

Property	Test Method	Grade G	Grade D
Gross Heat of Combustion, MJ/kg, min	D240	15	15
Water Content, % mass, max	E203	30	30
Pyrolysis Solids Content, % mass, max	D7579	2.5	0.25
Kinematic Viscosity at 40°C, mm^2/s, max	D445[A]	125	125
Density at 20°C, kg/dm^3	D4052	1.1–1.3	1.1–1.3
Sulfur Content, % mass, max	D4294	0.05	0.05
Ash Content, % mass, max	D482	0.25	0.15
pH.	E70	Report	Report
Flash Point,°C, min	D93, Procedure B	45	45
Pour Point,°C, max	D97	–9	–9

[A] Without filtering.

ASTM D-7579 Standard Test Method for Pyrolysis Solid Content In Pyrolysis Liquids by Filtration of Solids in Methanol

REACH

- **REACH is the European Community Regulation on chemicals and their safe use (EC 1907/2006). It deals with the Registration, Evaluation, Authorisation and Restriction of Chemical substances. The law entered into force on 1 June 2007.**
- **The aim of REACH is to improve the protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemical substances.**
- **Manufacturers and importers are required to gather information on the properties of their chemical substances, which will allow their safe handling, and to register the information in a central database run by the European Chemicals Agency (ECHA) in Helsinki.**

http://guidance.echa.europa.eu/guidance4_fi.htm

REACH: Bio-oil

- **Natural substances and derived monomers and chemicals do not have to be registered if they have not been chemically modified and if they are not classified as dangerous substances. Tar is an example of natural substances which have to be registered even though it is originated from nature.**
- **Task 34 consultations with Reach indicate that even though fast pyrolysis liquid is not tar and can be characterized as a collection of monomers derived from natural substances it most probably has to be registered.**
- **Registration under REACH has to be made if bio-oil is produced or imported to the EU.**

CEN

- The European Committee for Standardization (CEN) was officially created as an international non-profit association based in Brussels on 30 October 1975.
- CEN is a business facilitator in Europe, removing trade barriers for European industry and consumers.
- Its mission is to foster the European economy in global trading, the welfare of European citizens and the environment. Through its services it provides a platform for the development of European Standards and other technical specifications.

Task 34:2012 Mandate for CEN/TC 19

European Standard for a quality specification for pyrolysis oil:

A. **Replacing heavy fuel oil in boilers**
B. **Replacing light fuel oil in boilers**
C. **Replacing fuel oils in internal combustion engines**
D. **Suitable for gasification feedstock for production of syngas and synthetic bio-fuels**
E. **Quality specification for pyrolysis oil suitable for mineral oil refinery co-processing**

As bio-oil becomes more widely available, Task 34 will continue to participate in development of analytical methods and implementation of standard methods, particularly assessing the most suitable test methods for specifications.

Acknowledgements:
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