Bio-oil ≠ Bio-oil - Major differences in properties and use of fast pyrolysis bio-oil compared to fossil fuels and other bio-oils

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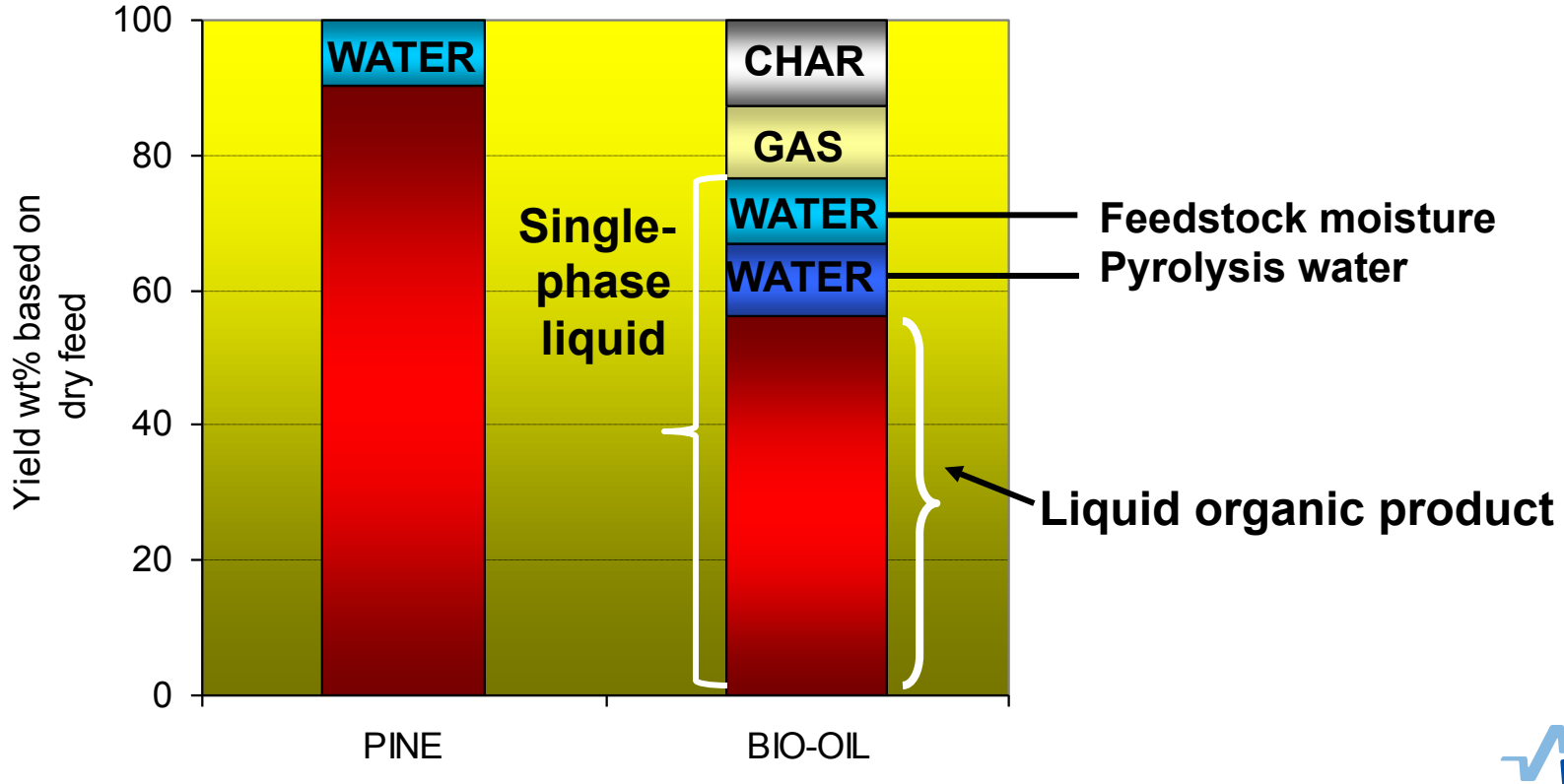
Contents

- Fast pyrolysis of biomass
- Chemical composition of fast pyrolysis bio-oils
- Fuel oil analyses
- Behaviour
- Comparison to other bio-fuels
- Conclusions

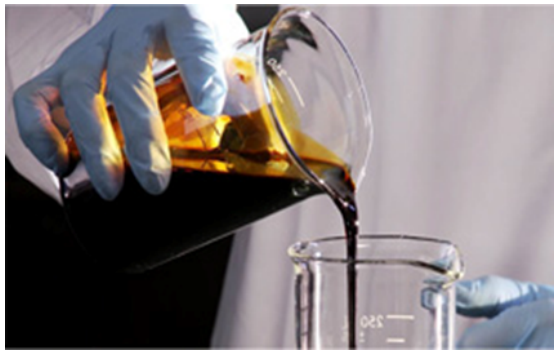
Fast pyrolysis of biomass

- 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
- Slow pyrolysis (long residence time) will produce more char, gas, and water with less organic and the condensates will be in two phases



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

Chemical composition of fast pyrolysis bio-oils



Hundreds of various compounds main groups being:

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, etractives, solids (incl. ash), polymerisation products

→ ***Chemical composition determines physical properties***

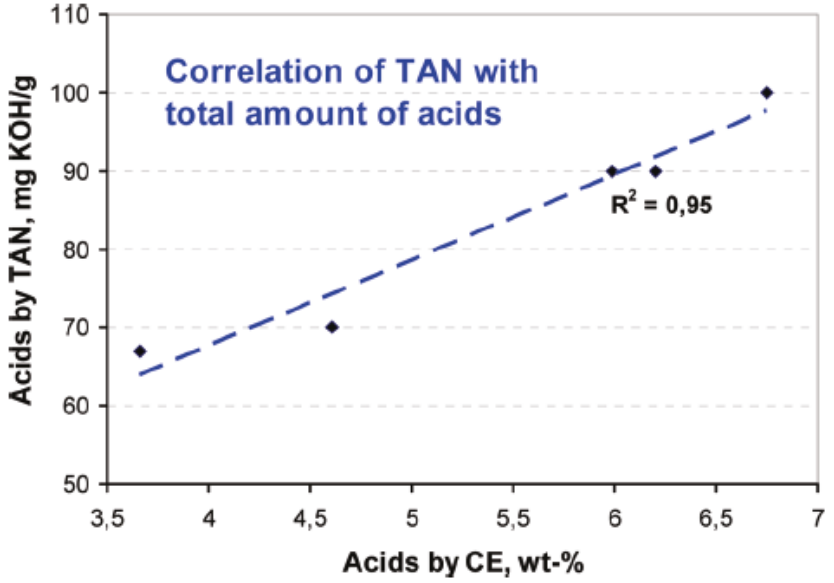
Energy and fuels, 2003, vol. 17, 2, ss. 433 – 443
Energy Fuels, 2008, vol. 22, 6, ss. 4245 – 4248

Acids in fast pyrolysis bio-oil

COMPOSITION
2 - 6 wt-% acetic acid
< 2 wt-% formic acid
< 1 wt-% glycolic acid
< 1 wt-% propionic acid
< 1 wt-% lactic acid
traces of other acids

ANALYSIS
Capillary Electro Phoresis (CE)
Total Acid Number (TAN) or pH

EFFECT
Material corrosion



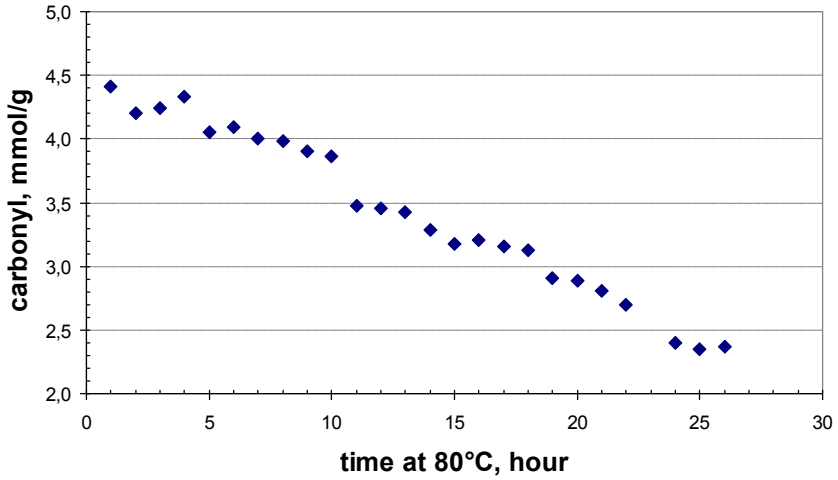
acid (wt %)	storage time at room temperature (months) 0	3	6	stability test (80 °C, 24 h)
acetic	2.2	2.5	2.5	2.5
glycolic	0.4	0.5	0.5	0.5
formic	1.2	1.4	1.3	1.3
total	3.8	4.4	4.3	4.3
TAN	70	73	71	74

Energy & Fuels, 2010
VTT Publication 731. 2010 http://www.vtt.fi/inf/pdf/publications/2010/P731.pdf

Aldehydes and ketones

COMPOSITION

5 – 10 wt-%	hydroxyacetaldehyde
2 – 3 wt-%	hydroxypropanone
< 5 wt-%	other aldehydes and ketones
3 – 4 wt-%	furans, pyrans
2 – 5 wt-%	monomeric phenols



REACTIONS IN OIL

Gradual decrease in carbonyl compounds during storage

ANALYSIS

Total amount by solvent fractionation

Compound identification by GC-FID, GC-MSD

Carbonyl titration

EFFECT

Instability

Energy & Fuels. 2911, vol. 25, 7, ss. 3307-3313

“Sugars”

COMPOSITION
3 – 6 wt-% levoglucosan
< 1 wt-% cellobiosane, cellotriosane
Hydroxy acids
Anhydrosugar oligomers
Totally 25 – 35 wt%

ANALYSIS
Amount by solvent extraction as ether-insolubles of water soluble fraction
Amount by BRIX based on density
Compounds by HPLC or GC-MSD with derivatisation or by LC-MS

EFFECT
Stickyness
Instability

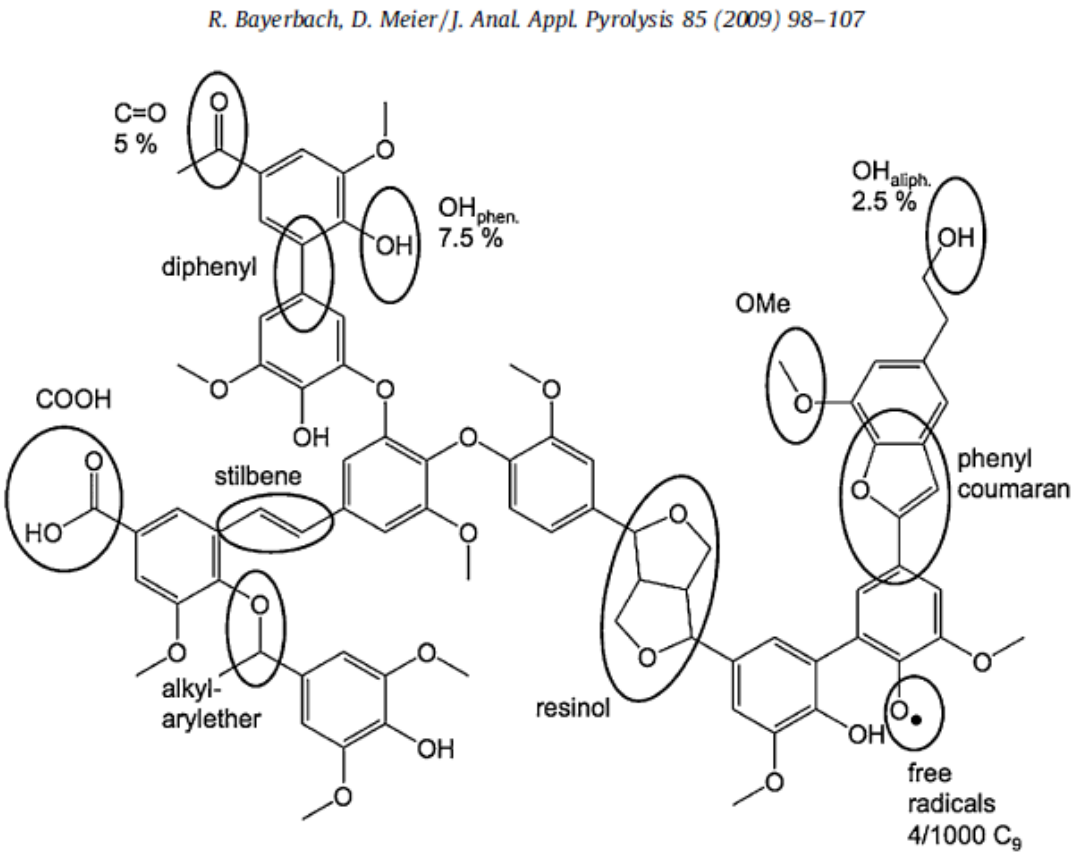
Energy and fuels, 2008, 22 (6), pp 4245 – 4248
Energy and fuels, 2003, vol. 17, 2, ss. 433 – 443.

Water-insoluble fraction

COMPOSITION
15 - 20 wt-% degraded lignin
< 1 wt-% solids
1 – 5 wt-% extractives
Polymerisation products in aged liquids

ANALYSIS
Water extraction
Increase in molecular weight by GPC

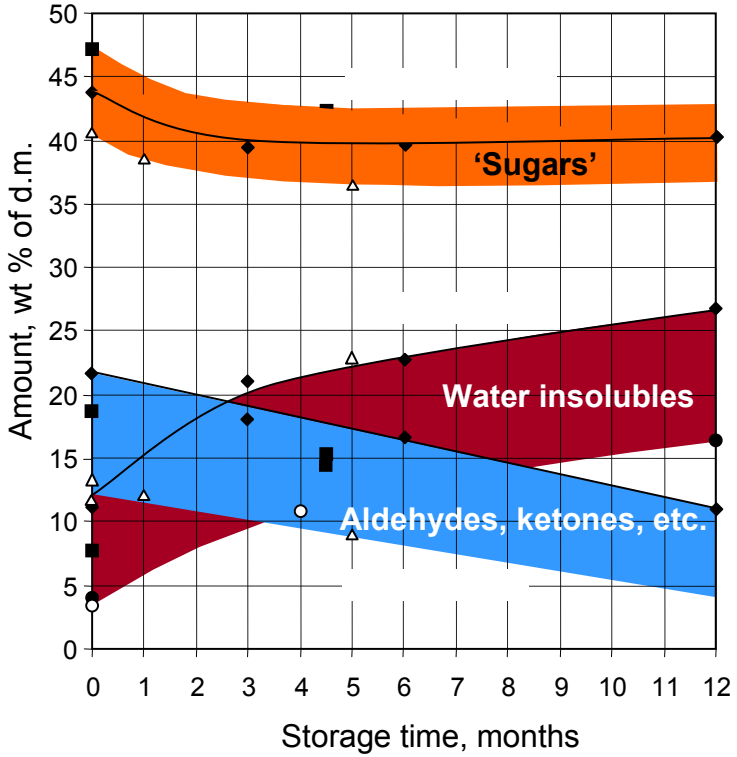
EFFECT
High non-volatile fraction
High viscosity



J. Anal. Appl. Pyrolysis 60 (2001) 41, J. Anal. Appl. Pyrolysis 58–59 (2001) 387, J. Anal. Appl. Pyrolysis 77 (2006) 95–101

Stability

- Not as stable as conventional petroleum fuels
- The instability can be observed as increased viscosity over time, particularly when heated
- Major changes in ageing happens in carbonyl and water insoluble fractions the changes in these product groups can be used as stability indicators
  - The changes in carbonyls can be measured by GC analyzing aldehydes and ketones, by carbonyl titration, or by FTIR
  - The changes in water-insolubles can be determined as changes in viscosity or in molecular weight
  - The change in carbonyl content correlates with the change in viscosity



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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

Fuel oil analyses

Water content 20 – 30 wt%

Acidic, pH 2 - 3

Heating value 13 - 19 MJ/kg (LHV)

Viscosity between that of light and heavy fuel oils

High ignition temperature

Density 1.15 - 1.2 kg/l

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

→ ***Water content of the oil affects to physical properties, like heating value, density, and viscosity***

Properties and fuel use of biomass-derived fast pyrolysis liquids: a guide. VTT Publication 731. 2010
Journal of Analytical and Applied Pyrolysis., vol. 73 (2005) 2, s. 323 - 334.
Energy & Fuels, 2005, vol. 19, 5, ss. 2155-2163
Environmental Progress & Sustainable Energy, 2009, 28, 3, pp. 404 - 409

Liquid fuels comparison

	FT Diesel	Low Sulphur Diesel	# 2 fuel oil	Ethanol	Butanol	Biodiesel	Vegetable oil (canola)	Tall oil	Fast pyrolysis bio-oil
Water, wt%	0	0	0	< 0.1	< 0.1	< 0.1	< 0.1	< 1	25 - 30
Density (at 15°C), kg/dm3	0.797	0.847	0.93	0.789	0.810	0.888	0.93	0.955	1.15 - 1.2
HHV (MJ/kg)	45.5	45,6	44.2	29,8	37.3	40.2	39,7		13 - 19
LHV (MJ/kg)	43.2	42,6	41.1	27	34.4	37.5	36,9	37	11 - 17
Viscosity, cP (@20°C)	1.9-3.6	1,6	2.8-6.9	1,07	3	3.1-4.4	30		50 - 150
Flash point, °C		>62	38	13	29	>130	220	>160	Not relevant

Fast pyrolysis bio-oils are not miscible with mineral oils or biodiesels
They are miscible with alcohols

Conclusions

- Fast pyrolysis bio-oils are physically and chemically completely different from fossil fuels or other “bio-oils” like biodiesels or bio-alcohols and cannot be used as drop-in-fuels without appropriate upgrading
  - Fast pyrolysis bio-oils are highly polar and hence completely unmiscible with mineral oils or biodiesels
  - About 80 wt.% of the bio-oil is water-soluble
- In the EU a new chemical regulation system REACH (Registration, Evaluation and Authorisation of Chemicals) is being applied. Registration under REACH has to be made if bio-oil is produced or imported to the EU.