**Development of Stability Test for Fast Pyrolysis Bio-oils**
12 November 2013, Anja Oasmaa, VTT, Finland

An international Round Robin study of the stability of fast pyrolysis bio-oil was undertaken in 2012 (Elliott et al.2012a,b). Fifteen laboratories in five different countries contributed. Two bio-oil samples were distributed to the laboratories for stability testing and further analysis. The stability test was defined in a method provided with the bio-oil samples. Viscosity measurement was a key input. The change in viscosity of a sealed sample of bio-oil held for 24 h at 80°C was the defining element of stability. The results showed that kinematic viscosity measurement was more generally conducted and more reproducibly performed versus dynamic viscosity measurement. The variation in the results of the stability test was great and a number of reasons for the variation were identified. One of the key factors was to improve the heat transfer by use of a water bath instead of the heating oven.

## Method description using a water bath

The pyrolysis liquid sample is mixed properly and left to stand until the air bubbles are removed. Two sample bottles can be used: Pyrex (VWR, number 215-1513) or borosilicate glas (VWR, bottle, silicon cork and aluminium ring: 216-3009, WHEA224100-178, WHE224191) bottles. At VTT the water bath used is Julabo TW12 WATER BATH, Order no.: 9550112 (http://www.labnet.fi/doc/tw12.pdf), but other water baths with accurate temperature controls can be used.

The volume of the bottles may vary and hence the inner volume of the sample bottles should be measured by water and mark the level for 10 vol% air volume. The new bottles are treated at 80°C for a few hours before use to remove moisture. The bottles are firmly closed and pre-weighed before being placed in a water bath at 80°C (± 1°C) for exactly 24 hours. It is recommended to use the same number of bottles every time. A reference sample of known pyrolysis liquid is included in the series. The Pyrex bottles are re-tightened after 15 minutes.

After a certain time, the closed sample bottles are cooled at room temperature for 1.5 hours, weighed and analysed. The samples are mixed and measured for viscosity and water. The viscosity of the liquid at 40°C is measured as kinematic viscosity by a standard method (ASTM D 445). The water content is analysed by Karl Fischer titration according to ASTM D 1744.

$$\Delta \text{ viscosity @ } 40°\text{C } [\%] = \frac{\nu_2 - \nu_1}{\nu_1}$$

$$\Delta \text{ water } [\%] = \frac{\omega_2 - \omega_1}{\omega_1}$$

$\nu 1$ = viscosity of the original sample, measured at 40°C, cSt
$\nu_2$ = viscosity of the aged sample, measured at 40°C, cSt
$\omega_1$ = water content of the original sample, wt%
$\omega_2$ = water content of the aged sample, wt%

**Note 1:** The test is recommended for use in internal comparisons of liquid stability for pyrolysis liquids from one process. The test is more reliable if the initial viscosities of the tested samples are similar.

**Note 2**: The possible difference in weights before and after the test is an indication of leakage. The test should be repeated if the net weight loss is above 0.1 wt% of the original weight.

**Note 3:** The reference sample is a good quality pyrolysis liquid that has been freshly divided into sample bottles and stored in a freezer below –9°C.

**Stability test (24 hours at 80°C) with a forest residue pyrolysis oil using water bath and heating oven**

| | Water bath | | Heating oven |
|---|---|---|---|
| | Pyrex bottles | Serum bottles | Pyrex bottles |
| Viscosity increase, % | 24,8 | 24,2 | 23,7 |
| Viscosity increase, % | 24,8 | 24,2 | 23,7 |
| Viscosity increase, % | 25,0 | 24,3 | 23,9 |
| Viscosity increase, % | 24,9 | 24,3 | 24,0 |
| Average | **25** | **24** | **24** |

## References


Elliott, D.C., Oasmaa, Anja, Preto, F., Meier, D., Bridgwater, A.V.. 2012. Results of the IEA Round Robin on Viscosity and Aging of Fast Pyrolysis Bio-oils. Energy & Fuels, Vol. 26, Nr. 6, Pp. 3769 – 3776 doi:10.1021/ef300384t

Elliot, D.C., Oasmaa, Anja, Meier, D., Preto, F, Bridgewater, A.V.. 2012. Results of the IEA Round Robin on Viscosity and Aging of Fast Pyrolysis Bio-oils: Long-Term Tests and Repeatability. Energy & Fuels, Vol. 26, Nr. 12, Pp. 7362 – 7366 doi:10.1021/ef301607v

Oasmaa, Anja, Peacocke, Cordner. 2010. A guide to physical property characterisation of biomass-derived fast pyrolysis liquids. A guide. Espoo: VTT. 79 p. + app. 46 p. (VTT Publications; 731) ISBN 978-951-38-7384-4 http://www.vtt.fi/inf/pdf/publications/2010/P731.pdf