
BIOLIQUIDS-CHP PROMOTION PACK

# BIOLIQUIDS

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## INTRODUCTION

This summary describes the technologies for power and heat production from biomass derived liquids.

## BIOLIQUIDS SELECTION, PRODUCTION AND PROPERTIES

A number of different bioliquids have been evaluated for use in prime movers.

### Primary fuels

The 'primary' liquids are biodiesel, sunflower oil and pyrolysis oil. The latter has been produced from pine wood and wheat straw. The biodiesel has been purchased in Germany and is produced from rapeseed. The sunflower oil has been collected in Italy by the University of Florence. Bio-ethanol has been added because this fuel is used as a rinsing fuel to switch from diesel to pyrolysis oil and vice versa. Bio-butanol and bio-ethanol are included as it was used to create blends of bio-oil and biodiesel. Additionally, bio-ethanol has been used in a few cases to improve pyrolysis oil properties. In Table 1 an overview is given of the properties of these primary liquids.

### Modified fuels

From Table 1 it is clear that the properties of pyrolysis oil deviate quite substantially from biodiesel, and direct fuelling might be complicated. Therefore, five different techniques have been investigated to improve specific properties of pyrolysis oil. An overview of the methods is given in Table 2. These modified fuels have been produced and analysed. The results of the fuel analysis are given in Table 3.

**Table 1 Properties of the primary liquids**

| Property | unit | Bio-diesel | Sun-flower Oil | Pyrolysis Oil | | | Bio-Ethanol [A] | Bio-Butanol |
|---|---|---|---|---|---|---|---|---|
| | | | | Pine I | Pine II | Straw | | |
| C | wt% | 77.3 | 77.5 | 42.8 | 45.5 | 48.6 | 50.9 | 64.9 |
| H | wt% | 12.1 | 11.9 | 7.6 | 5.8 | 7.9 | 12.7 | 13.5 |
| N | wt% | <0.01 | <0.01 | <0.01 | <0.01 | 0.4 | <0.01 | <0.01 |
| O (Balance) | wt% | 10.6 | 10.6 | 49.6 | 48.8 | 43.0 | 36.4 | 21.6 |
| Water | wt% | - | - | 21.7 | 25.4 | 21.2 | - | - |
| Ash | wt% | - | - | 0.047 | 0.016 | 0.053 | - | - |
| Solids | wt% | - | - | 0.27 | 0.04 | 1.28 | - | - |
| Density | $kg/m^3$ | 871 | 910 | 1207 | 1170 | 1184 | 780 | 810 |
| LHV | MJ/kg | 27.1 | 37.4 | 17.1 | 16.1 | 20.1 | 27.1 | 34.4 |
| HHV | MJ/kg | 40.2 | 40.0 | 18.7 | 18.8 | 21.9 | 30 | 37.4 |
| LHV | MJ/L | 32.7 | 34.0 | 20.6 | 18.8 | 23.8 | 21.4 | 27.9 |
| pH | - | - | - | 2.85 | 2.85 | 3.3 | - | - |
| MCRT | wt% | - | 0.06 | - | 15.1 | - | - | - |
| Kinematic viscosity 20°C | cSt | 6.9 | 80.7 | 65.1 | - | 80.4 | 1.5 | 3.6 |
| 40°C | cSt | 4.2 | 40.6 | 20.0 | 13.0 | 21.2 | 1.1 | 2.8 |
| Cetane Number | - | ~60 | ~40 | ~10-25 | - | - | ~8-10 | 17 |
| Aging Index | % | tbd | | | | | - | - |
| Contaminants | ppm | | | | | | | |
| Cl | | <10 | <10 | <10 | n.d. | 240 | n.d | n.d. |
| Fe | | 1.3 | 2.2 | 11 | | 11 | | |
| Mg | | 3.7 | 4.4 | 6 | | 37 | | |
| Mn | | <1 | <1 | 1.2 | | 12 | | |
| Ca | | 1.3 | 5.2 | 15 | | 135 | | |
| Sr | | <1 | <1 | <1 | | 1.3 | | |
| Sn | | <1 | >1 | <1 | | 2.6 | | |
| Si | | 2.0 | 42.9 | 6.6 | | 83 | | |
| P | | <1 | 2.3 | <1 | | 15 | | |
| Al | | 5.3 | 6.6 | 35 | | 48 | | |
| K | | 14.4 | 13.4 | 21 | | 254 | | |
| Na | | 18.4 | 17.8 | 20 | | 22 | | |

[A] 3 wt% of Beraid (Cetane improver) is added to the fuel;

Abbreviations
HDO Hydro-deoxygenation
PO Pyrolysis oil (bio-oil)

**Table 2 Modified fuels from pyrolysis oil**

| | Upgrading process | Treatment | Reason for specific treatment |
|---|---|---|---|
| 1 | Emulsion | Emulsification of 95 wt% pyrolysis oil with 5 wt% of biodiesel. 0.025 wt% Athlox 4912 is added as emulsifier. | Improving the ignition properties. |
| 2 | PO-Ester | Reactive distillation of pyrolysis oil with butanol in the presence of a catalyst (Nafion); Acidic components will form an ester with the butanol. Water will be removed during the process. | Reduce acidity and water content. Increase heating value of the oil. |
| 3 | Mild-HDO | Mild hydrotreatment of the pyrolysis oil in the presence of a catalyst, a hydrogen atmosphere and at high pressure. | Reduced acidity, increase heating value, improve ignition properties & thermal stability. |
| 4 | PO-Sugar | Fractionation of pyrolysis oil, and separation of the sugar fraction. This is diluted with 20 wt% of ethanol to reduce viscosity and used as engine fuel. | Reduce lignin fraction, less sedimentation, less water and increased heating value. |
| 5 | Blend | Mixing pyrolysis oil with 10 wt% of biodiesel and adding 30 wt% of 1-butanol to obtain a single phase mixture. | Homogeneous fuel, improve ignition properties, decrease viscosity. |

**Table 3 Properties of modified oils**

| Property | Unit | Emulsion | PO-Ester | Mild HDO | PO-Sugar | Blend |
|---|---|---|---|---|---|---|
| C | wt% | 44.4 | 58.2 | 67.6 | 47.1 | 54.5 |
| H | wt% | 6.4 | 7.1 | 8.1 | 7.1 | 8.7 |
| N | wt% | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| O (balance) | wt% | 49.2 | 45.9 | 24.2 | 43.8 | 36.8 |
| Water content | wt% | 22.8 | 4.5 | 6.7 | 2.2 | 17.2 |
| Ash content | wt% | 0.298 | 0.055 | 0.017 | 0.016 | 0.01 |
| Solids content | wt% | - | - | - | - | 0.02 |
| Density | $kg/m^3$ | 1,198 | 1,168 | 1,106 | 1,151 | 998 |
| LHV, calculated | MJ/kg | 16.3 | 18.4 | 27.0 | 18.7 | 23.8 |
| LHV | MJ/ltr | 19.5 | 21.5 | 29.9 | 21.5 | 23.8 |
| pH | - | 2.1 | 3.5 | 3.1 | 3.6 | 3.0 |
| MCRT | wt% | 18.0 | 17.6 | 11.0 | 18.0 | 7.7 |
| Kinematic viscosity at 40°C | cSt | 35.6 | 55.6 | 149.1 | 91.0 | 6.9 |
| Acid number | mg KOH/g | - | 78.5 | - | 47.9 | 53.1 |
| Carbonyl number | mg BuO/g | 133.4 | 157.0 | 9.7 | 148.4 | |
| Aging Index | % | tbd | | | | |