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Pyrolysis Oil:
An Innovative Liquid Biofuel for Heating
The COMBI O Project

Silvia Vivarelli, Gianluca Tondi
ETA Renewable Energies - Piazza Savonarola, 10
I-50132 Florence, Italy
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  • Specifications for pyrolysis oil
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  • Pyrolysis oil upgrading

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Pyrolysis oil from biomass

Biomass thermal conversion processes
Pyrolysis oil from biomass

**Fast Pyrolysis main advantage**

- In one step converts biomass into a liquid product, which can be easily transported, handled and stored.
- Energy density increased about four times compared to biomass feedstock

**Other advantages**

- PO can be used in conventional boilers with minor modifications (under investigation)
- Lower emissions in boiler use compared to solid fuels
- Liquid fuels from biomass are a fundamental RE source
- Suitable to decentralised generation
Pyrolysis oil from biomass

Fast pyrolysis process - General Layout
Pyrolysis oil from biomass

Fast pyrolysis key features

Pre-treatment
- Feedstock drying to less than 10% is necessary (by-product gas or char combustion can be employed)
- Feedstock grinding as small particle size (i.e. <200 µm for rotating cone reactor, <2 mm for fluidized bed, <6 mm for transported or circulating fluid bed) necessary to obtain high heating rates
- Additives for chemicals production

Process of thermal degradation in absence of oxygen (pyrolysis)
- Wide range of reactor configurations: fluid beds and circulating fluid beds are the most diffused
- Very high heating rates (up to 1000°C/s or even 10000°C/s) limited by wood conductivity
- High heat transfer rate (sand can help)
- Moderate and carefully controlled temperature (about 500°C to maximise liquid yield)
- Atmospheric pressure but also vacuum reactors existing

Products collection
- Short residence time between vapours formation and cooling to limit secondary cracking (few hundreds of milliseconds in case of chemicals and food additives production, up to 2 seconds for fuels)
- Liquid collection is difficult: temperature control is needed to avoid blockage from heavy ends condensation and light ends recovery is important
- Char removal is a main issue: fine char is carried over from cyclones and can be removed by means of hot vapour filtration (under development) or by liquid filtration (cartridge or rotary filters or centrifuges)

Pyrolysis products: char, liquid and gas.

Liquid yields in the range 65-75% wt on dry feedstock in most processes.
Pyrolysis oil from biomass

Pyrolysis oil (also bio-oil or bio-crude oil)

A dark brown liquid is obtained having typical properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>15-30%</td>
</tr>
<tr>
<td>pH</td>
<td>1.5-3</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.2 kg/dm³</td>
</tr>
<tr>
<td>HHV as produced</td>
<td>16-21 MJ/kg</td>
</tr>
<tr>
<td>Viscosity (at 40°C and 25% water)</td>
<td>40-100 cp</td>
</tr>
</tbody>
</table>

Source: Bridgwater 2000

Compared to conventional fuels:

<table>
<thead>
<tr>
<th>Fuel property</th>
<th>Unit</th>
<th>Pyrolysis oil</th>
<th>Diesel oil</th>
<th>HFO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density @ 15°C</td>
<td>kg/dm³</td>
<td>1.22</td>
<td>0.85</td>
<td>0.96</td>
</tr>
<tr>
<td>Kinematic viscosity @ 50°C</td>
<td>cStoke</td>
<td>13</td>
<td>2.5</td>
<td>351</td>
</tr>
<tr>
<td>Lower heating value</td>
<td>Mj/kg</td>
<td>17.5</td>
<td>42.9</td>
<td>40.7</td>
</tr>
<tr>
<td>Ash</td>
<td>% wt</td>
<td>0.13</td>
<td>&lt; 0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Water content</td>
<td>% wt</td>
<td>20.5</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Elemental analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>%</td>
<td>48.5</td>
<td>86.3</td>
<td>86.1</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>%</td>
<td>6.4</td>
<td>12.8</td>
<td>11.8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>%</td>
<td>42.5</td>
<td>0.9</td>
<td>0</td>
</tr>
<tr>
<td>Sulphur</td>
<td>%</td>
<td>0</td>
<td>0.15-0.30</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Not miscible with hydrocarbon fuels
Pyrolysis oil from biomass

Pyrolysis oil utilisation

**Chemicals production**
- Potentially attractive due to chemicals high value.
- Currently commercial application is for food flavourings (liquid smoke)
- Other possibilities: pharmaceuticals, fertilizers, etc..

**Transport fuels production**
Hydrotreating/hydrocracking is necessary to upgrade as a diesel or zeolite cracking to aromatics, but both processes are expensive.

**Heat and/or electricity production**
The most investigated and promising application.
Pyrolysis oil from biomass

Pyrolysis oil applications

Heat production in large thermal plant (>1 MW\textsubscript{th}) replacing heavy fuel oil (HFO)
- Due to the low price of HFO the replacement of HFO with PO does not seem a realistic target.

Heat production in medium and small boilers replacing light fuel oil (LFO)
- PO utilisation in substitution of LFO (rather high cost fuel) is one of the most promising routes, economically viable.
  - Several tests have been carried out. Some problems reported: high viscosity and polymerization causing blocking, clogging of nozzles and bad atomisation. Solutions were addition of alcohol or in line pre-heating.
  - Due to high ignition point chamber pre-heating with conventional fuels before switching over to bio-oil and a more complex start up sequence is required.
  - Other major issues are the adoption of acid resistant materials (especially for valves, nozzles, pressure regulators and pump) and the solid content reduction to avoid erosion and bad combustion.

Electricity/heat production in diesel engines, replacing light fuel oil
- Due to the high price of electricity it has attracted attention.
  - Utilisation is possible only if the system is significantly modified or with PO/diesel emulsions; pilot ignition is necessary.

Utilisation of PO for electricity/heat production in gas turbines
- Research activity started more than 20 years ago → same problems as reported above

Long-term operational experience and further research necessary to optimize the system

The COMBIO project

Bioenergy for a sustainable development, Viña del Mar 9 November 2004
The COMBIO Project

Overview

The COMBIO project is supported by the European Commission, DG Research within the Fifth Framework Programme, EESD.

General aim of the project: Verify a new liquid biofuel chain for heat production in existing boilers currently fired with mineral oils.

Duration: 36 months

01/01/2003 → now → 31/12/2005

Project coordinated by: VTT Processes

Project partners:
- Fortum
- Fortum Oil and Gas
- CSGI-University of Florence
- Fortum Värme
- Vapo
- Istituto Motori-CNR
- ETA-Renewable Energies

Finland
Italy
Italy
Sweden
Finland
Italy
Italy
The COMBI O Project

Overview

Objectives

• Generation of process performance data of a pilot scale pyrolysis oil (PO) production

• Defining three classes of preliminary oil specifications: replacing HFO in large boilers (2-10 MWth), LFO in medium size (0.2-1 MWth) and small (< 100 kWth) boilers

• Generating and reporting of performance and emission data of boilers in long term test for the three sizes. Generation of fundamental combustion data to assist in developing higher quality fuels

• Improving pyrolysis oil quality in PDU (Process Development Unit)-scale. Two main technologies are studied: emulsions and hot vapour filtration

• Improving economic competitiveness of the bioenergy chain. The target is to be able to produce at close to fuel oil prices and compete with other renewable alternatives (i.e. chips, wood, pellets).
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Overview

Renewable Heating Oil - COMBIO

CO₂ neutral = no CO₂ tax
Liquid biofuel = simple, easy to use
Efficient processes = economical heating
Low emissions = use in urban areas

Forest industry residues and wastes

Foresteram™ plant

CO₂ Emission Reduction

Heating

Forest industry residues and wastes

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The COMBIO Project

Overview

The biomass chain

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Harvesting</th>
<th>Processing</th>
<th>Transport</th>
<th>Utilisation</th>
</tr>
</thead>
</table>

It is necessary to study all steps in the chain simultaneously in order to fulfil quality specifications required by users:

- Feedstock collection, transport, pretreatment (grinding & drying)
- PO production in a pyrolysis unit
- PO storage and transport
- PO upgrading (Emulsions and Hot Vapour Filtration)
- PO utilisation in boilers
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Overview

Feedstock collection, transport and pretreatment (grinding and drying)

Selected feedstocks:
• Chips of white wood (no bark)
• Forestry residues

Feedstocks are mechanical harvested, then transported by trucks to the pyrolysis production plant.
Transport typically accounts for 30-50% of the delivered feedstock cost.

Delivered raw material has to be treated:
• Crushing / grinding → particles have to be very small to fulfil the requirements of rapid heating to achieve high liquid yields
• Drying to a moisture content < 8% wt → essential as all the feed water is included in the liquid product (by product gas and char combustion used)
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Pilot plant production

In 1998 Fortum Oil& Gas, Fortum Power&Heat and Vapo entered into an agreement developing a proprietary pyrolysis process

FORESTERATM realized at the Technology Centre of the Porvoo refinery, Finland.

The plant includes:

- Size reduction crusher
- Flue gas drum dryer
- Pyrolysis reactor- fluidized bed technology
- Cyclones
- Vapour recovery units (quencher)
- Aerosol removal units
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Pilot plant production

Main process performance parameters

- Plant capacity
- Product yield

Main criteria for determining the product quality

<table>
<thead>
<tr>
<th>Solids content</th>
<th>Feedback from field tests → even a very small amount of inorganics (mainly silicates) in the liquid could lead to erosion in the nozzles (combustion problems) and pump</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Requirement → solid content &lt;0.05% wt</td>
</tr>
<tr>
<td></td>
<td>Cyclone could remove up to 0.1% wt solids content (grew at 0.3% when char and tar blocking occurred)</td>
</tr>
<tr>
<td></td>
<td>A centrifuge was used</td>
</tr>
<tr>
<td>Water content</td>
<td>In the range 23-25% wt</td>
</tr>
</tbody>
</table>

Also viscosity and stability are quite important.
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Pilot plant production

The Forestera™ product

During 2003 more than 30 m³ (36 tonnes) of pyrolysis oil were produced.

<table>
<thead>
<tr>
<th>Typical properties of FORESTERA™ product</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower heating value (MJ/kg)</td>
<td>15</td>
</tr>
<tr>
<td>Lower heating value (MJ/l)</td>
<td>19</td>
</tr>
<tr>
<td>Viscosity (cSt) at 0 C⁰</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>30 C⁰</td>
</tr>
<tr>
<td></td>
<td>50 C⁰</td>
</tr>
<tr>
<td></td>
<td>80 C⁰</td>
</tr>
<tr>
<td>Flash point (C⁰)</td>
<td>45-65</td>
</tr>
<tr>
<td>Water content (wt%)</td>
<td>23-28</td>
</tr>
<tr>
<td>Solids content original (wt%)</td>
<td>&lt;0,1</td>
</tr>
<tr>
<td>Solids content improved (wt%)</td>
<td>&lt;0,05</td>
</tr>
<tr>
<td>Density (kg/l)</td>
<td>1,2</td>
</tr>
</tbody>
</table>
Conclusions

- The reaction conditions were very stable with small reaction temperature variations;
- Process could be run on a continuous basis for 4-5 days
- Main reason for coming off-line was coking and deposits formation in some transfer piping
  → Better insulation and changes in the demisters
- Commercial centrifuges were used and a high quality product could be obtained
- Nominal capacity of 500 kg/hr feed could not be reached
- Liquid yield was approximately 65±2% slightly lower than expected 70-72 % wt probably due to a larger mean average particle size of the fed fuel
- The process requires some optimization work in order to permit very long duration runs, to achieve maximum capacity and to process wet feedstock.
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Specifications for pyrolysis oil

• Specifications for mineral oils established by ASTM and similar organizations in respective countries
• No national or international standards for biomass derived pyrolysis liquids
• Currently a standardization work is ongoing under CEN

Most important properties for boiler use

• Calorific value
• Solids content
• Water content
• Viscosity
• Stability
• Homogeneity
• Flash point

Specifications are expected by the end of the project.
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Utilisation in boilers

Laboratory scale combustion

Different pyrolysis oil and PO-light oil emulsions have been studied in order to characterize their combustion behaviour with specific attention to ignition, emissions and influence of ageing.

Experiments in SDCC (single droplet combustion chamber)

To define ignition quality and residual formation tendency

- Higher ignition temperature for PO (580°C) than emulsion (420°C)
- Light oils <1%wt carbonaceous residuals while PO very prone to form
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Utilisation in boilers

Laboratory scale combustion

Experiments in DTF (drop tube furnace)

To study the overall combustion quality and the emissions

Procedure to produce calibrated droplets in the range 70-200 µm was defined.
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Utilisation in boilers

Medium size (200 kWth – 1 MWth) boilers

Field trials carried out in a Fortum Oil&Gas-Oilon Oy boiler at Saarijärvi, Thermia Oy. More than 12000 liters of Forestera™ combusted of which 4000 litres were for the COMBIO project.

Start up and shut down operations run with light fuel oil being system totally automated.

Tested pyrolysis oil → Forestera™ from wood chips, having a 0.04 % solid content, a 22% water and viscosity 24 cSt at 40°C.

Results

• Emissions very low, approaching those of a light fuel oil boiler
• Any inclusion of hard solid would cause erosion due to high pressure, 17-20 bar, necessary to have small drops → good combustion
• Solids content lowered to 0.05%wt
• Technically a success; high costs for the special applications pump required.
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Utilisation in boilers

Small (<100 kWth) boilers - pump test rig

A test rig was designed and built by CSGI to analyse the effect of PO in standard diesel oil pump typically used in domestic burners/heaters.

Equipment basically composed by:
• Gear pump (9 bar, 42 l/h)
• Electrical motor
• Nozzle or valve
• 2 transparent tanks.

Results

• Under high speed motion PO, even in emulsion regardless the percentage, attacks carbon steel
• Most affected items were: driven shaft and pressure regulating valve.
• Solutions: valve in PVDF and for shaft stainless steel too expensive → possible solution is the application of surface treatments
• Niploy process coating (electrochemical nickel coating about 50 µm) under investigation.
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Utilisation in boilers

Large (2-10 MWth) boilers

The combustion test was carried out in a 9 MW boiler at the Årsta District Heating Plant in Stockholm by Fortum Värme in April 2004.

The boiler has forced circulation with temperature regulated at 160 °C and no flue gas cleaning equipment.

Having the PO a low heating value it was necessary to co-fire it with a support fuel. Fatty acid was used having an heating value of 45 MJ/Kg.

Boiler started up with 100% support fuel then PO was added decreasing the amount of fatty acid.

Duration of the test: about 6 hours
Total PO consumption: 4 m³

Results

Handling of the PO was easy and test worked out well.

Emissions measurements indicated a dust content higher than expected while other emissions showed low values.

⇒ Further tests needed
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Pyrolysis oil upgrading

Aim → make a product comparable with conventional fossil fuels

Improvement through:
- Emulsions production
- Hot vapour filtration

Hot vapour filtration

PO is affected by the presence of small char particles that can be removed by hot vapour filtration.

An hot vapour filter is installed at VTT Process Development Unit in Finland. Tests are ongoing.
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Pyrolysis oil upgrading

Emulsions production from PO

Two different pyrolysis oil were studied during the first 18 months of the project:

- FORTUM oil from saw dust
- VTT oil from forestry residue

Emulsification plant production capacity → 50 l/h dealing with a range 5-50% wt pyrolysis oil.

FORTUM oil has high viscosity and density → more stability.

VTT oil higher tendency to separation in different phases (no dispersion through agitation) and higher alkali content.

More than one hundred surfactant tested. Amount: 1.5% wt of emulsion.

Aged FORTUM oil emulsion had density depending sedimentation (can be re-dispersed), while VTT oil emulsion showed also droplets growing.

<table>
<thead>
<tr>
<th></th>
<th>VTT</th>
<th>FORTUM</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O content (% w/w)</td>
<td>25.8</td>
<td>26.1</td>
</tr>
<tr>
<td>Viscosity at 40°C</td>
<td>17 cSt</td>
<td>25 cSt</td>
</tr>
<tr>
<td>Solid Contentb (%w/w)</td>
<td>0.17</td>
<td>0.20</td>
</tr>
<tr>
<td>Ash Weigth (%w/w)</td>
<td>0.099</td>
<td>0.035</td>
</tr>
<tr>
<td>Density at 20°C</td>
<td>1.12 kg/dm³</td>
<td>1.22 kg/dm³</td>
</tr>
<tr>
<td>pH</td>
<td>2.5-3</td>
<td>2.5-3</td>
</tr>
<tr>
<td>Alkali/ Ash (mg g⁻¹)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>4.59</td>
<td>0.55</td>
</tr>
<tr>
<td>K</td>
<td>16.44</td>
<td>3.94</td>
</tr>
<tr>
<td>Mg</td>
<td>11.44</td>
<td>1.67</td>
</tr>
<tr>
<td>Ca</td>
<td>31.87</td>
<td>4.1</td>
</tr>
<tr>
<td>Pb</td>
<td>0.003</td>
<td>0.048</td>
</tr>
</tbody>
</table>
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Techno-economic assessment

A cost and performance analysis will be carried out in order to assess the market potential for pyrolysis oil.

The whole bioenergy chain will be taken into account.

One of the case studies: Italy

A GIS (Geographic Information System) based tool will be used.
Conclusions

• Pyrolysis process has been shown to be able to produce high yields of liquid products which can be easily shipped and stored and then utilised in small and medium size boilers ($50 \text{ kW}_{\text{th}}$-$1 \text{ MW}_{\text{th}}$)

• However no long term experiences have been carried out

• Pyrolysis oil seems not yet economically competitive to enter into heating fuel market; competitive when compared to LFO

• It is expected that implementation of directives regarding liquid biofuels, RES and CHP, decreasing CO2 emission target of Kyoto Protocol and certificate trade will generate many attractive markets

• Further technological development is needed for commercial use

• Investigation is ongoing on the whole bioenergy chain to assess the techno-economic feasibility.
Thank you for your attention!

Further information on the COMBIO Project (update in the next days)

www.combio-project.com

Any question?

Contacts in ETA Renewable Energies:
Silvia Vivarelli silvia.vivarelli@etaflorence.it
Gianluca Tondi gianluca.tondi@etaflorence.it
Tel +39-055-5002174
Fax +39-055-573425