# COMBIO

## A New competitive Liquid Biofuel for Heating

## PROJECT OVERVIEW

The COMBIO project, short term for "A New Competitive Liquid Biofuel for Heating", is supported by the European Commission, DG Research, within the Fifth Framework Programme under EESD (Energy, Environment, Sustainable Development).

The project is coordinated by VTT Processes (Espoo, Finland) and the partners are Neste Oil Corporation (Espoo, Finland), CSGI-University of Florence (Florence, Italy), Istituto Motori-CNR (Naples, Italy), Fortum Värme (Stockhom, Sweden), Vapo Oy (Jyväskylä, Finland) and ETA-Renewable Energies (Florence, Italy).

The duration of the project has been 42 months, from the 1st of January 2003 to the 30th of June 2006.

The aim of the project is to verify a new liquid biofuel, pyrolysis oil (PO), chain for heat production, to determine fuel specifications for PO in different applications and to carry out long-term combustion tests. Scientific objectives include modification of PO composition for improved stability by hot gas filtration and production of emulsions and cleaner combustion by increased understanding of fundamental phenomena.

It is estimated that implementation of liquid biofuel, RES and CHP directives, $CO_2$ decreasing objectives and certificate trade will generate many attractive markets for biofuels. The objectives of the project are compatible with the EU directives, with the targets of the Kyoto Protocol and with several national and international research programs.

The following specific scientific objectives have been defined to solve major technical problems and to address the principal economic uncertainties:

- Generation of process performance data of pilot-scale PO production;
- Definition of three classes of preliminary PO fuel specifications for the following applications: replacing heavy fuel oil in large boilers, replacing light fuel oil in intermediate and small size boilers;
- Generation and reporting of performance and emission data of large and medium size boilers in long term tests;
- Generation of fundamental PO combustion data to assist in developing higher quality fuels;
- Improvement in the PO fuel quality in pilot demonstration unit scale, in order to fulfil specifications required by users. The fuel properties, which need most development, are homogeneity, stability, solids content, pH, heating value and viscosity;
- Improvement in the economic competitiveness of the bioenergy chain. The target is to be able to produce close to fuel oil prices and to compete with other renewable alternatives.

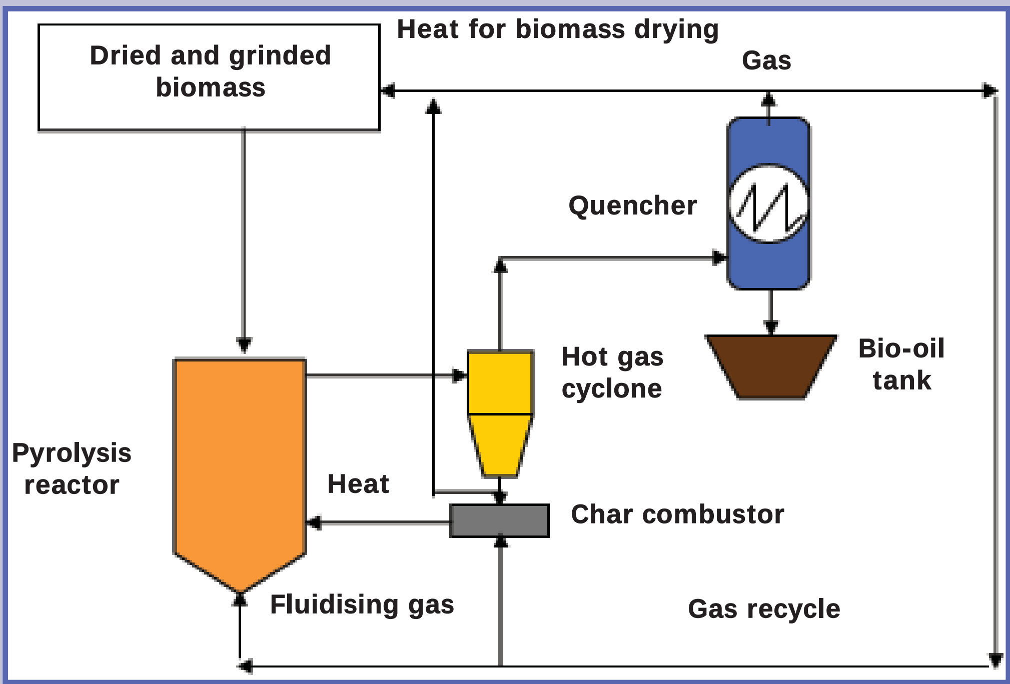
Pyrolysis oil has been produced in a partner (Neste Oil) pilot plant and it has been used in boiler (Fortum Värme and Neste Oil) and laboratory tests (IM). Biomass feedstock availability has been reviewed in Italy (ETA) and Finland (Vapo). Preliminary fuel specifications have been developed further (VTT). Laboratory facilities have been prepared and used to study fundamentals of pyrolysis liquid combustion (IM). Emulsions from PO and light fuel oil have been produced in laboratory to be tested in combustion (CSGI). An existing process development unit has been modified to include a hot vapour filter (HVF) (VTT). Competitiveness of PO production in Finland has been assessed (VTT) and a techno-economic assessment of the whole bioenergy chain from biomass sources to PO production, PO emulsion production, transportation and utilization in small scale boilers in Tuscany, Italy, has been carried out (ETA).

More information on the COMBIO project can be found at:
**www.combio-project.com**

## FAST PYROLYSIS AND PYROLYSIS OIL (PO)

Fast pyrolysis is a process to convert in one step biomass into a liquid product, pyrolysis oil (also bio-oil or bio-crude oil), which can be easily transported, handled and stored, increasing the energy density about four times compared to biomass feedstock.

Liquid fuels from biomass are a fundamental renewable energy source, they are suitable to decentralized generation and result in lower emissions in boiler compared to solid fuels.




Fast pyrolysis is a process to convert in one step biomass into a liquid product, which can be easily transported, handled and stored, increasing the energy density about four times compared to biomass feedstock.
Pyrolysis is a thermal degradation in absence of oxygen at a moderate and carefully controlled temperature, about 500°C in order to maximize the liquid yield.
Biomass is heated at very high heating rates (up to 1000°C/s or even 10000°C/s) and high heat transfer rates and it decomposes in vapour, gas and char. The vapour residence time should be very short (up to 2 seconds for fuel) to minimise secondary reactions and then a rapid quenching phase occurs in which the vapour condenses and the produced liquid is stored into a tank.
Biomass before being fed into the pyrolysis plant has to be pre-treated : feedstock has to be dried to a moisture content < 10%wt and to be chipped and grinded as small particle size are necessary to obtain high heating rates that is high liquid yields.
Common values for liquid yield are in the range of 65-75% wt on a dry biomass feed basis.

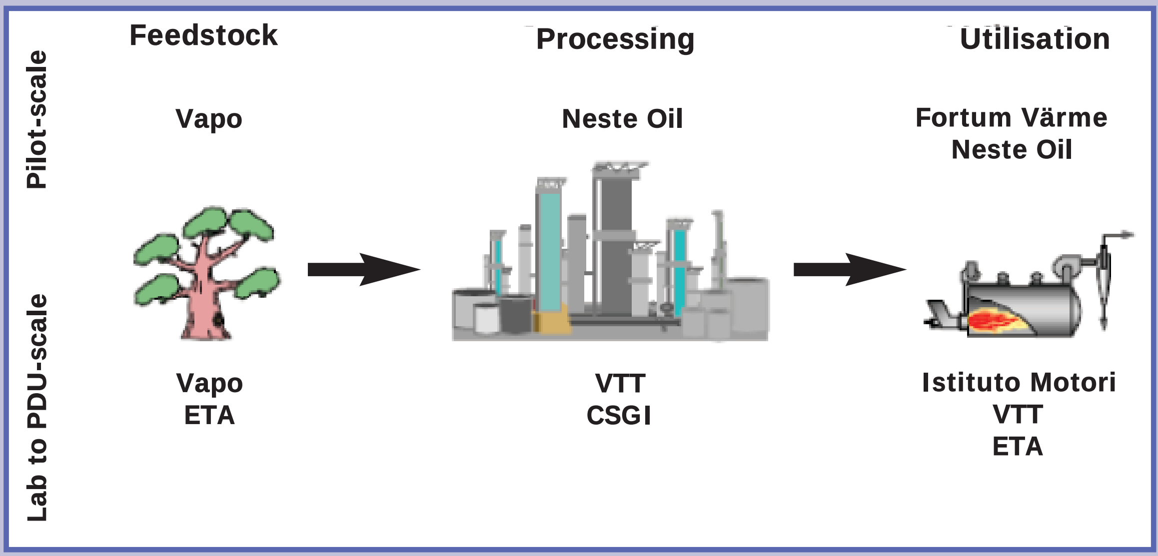
One of the main issues in PO production is char removal, as fine char is carried over from cyclones and can be removed by means of hot vapour filtration or by liquid filtration.
Hot vapour filtration is a technique under development and has been studied and tested in the project as a mean of PO upgrading.

The requirement for pyrolysis oil to be used is to have a solid content<0.05%wt, as even a small amount of inorganics in the liquid could lead to erosion in the nozzles and pump of the feeding system.

One of the most promising application for PO is in heat production. It can be used in conventional boilers with minor modifications.

However some problems should be taken into account, such as PO instability, high viscosity and polimerization, high ignition point and the need of acid resistant materials.

An interesting method for PO upgrading is given by emulsification with conventional diesel oil.
As PO and diesel are not miscible, a third component, called emulsifier or surfactant, has to be added to obtain a stable emulsion. The percentage of surfactant to be added is about 1% by weight.




## MAIN ACTIVITIES IN THE PROJECT

### Assessment of feedstock potential in Finland and Italy

An assessment of biomass potential for PO production in Finland and Italy has been carried out, taking into account availability, harvesting/collection, transport and competing markets.

### PO pilot plant performance

PO has been produced in a pilot plant. The process and the product are registered under the name Forestera™.
The Forestera™ fast cracking process uses circulating fluid bed pyrolyzer with the special feature of solid separation using multi-inlet cyclones for highly efficient solid removal.

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The main results of the pilot production have been:

- Reaction conditions very stable with small reaction temperature variations;
- Process could be run on a continuous basis for 4-5 days;
- An high quality product could be obtained by removing solids using commercial centrifuges;
- Nominal capacity of 500 kg/hr feed could not be reached due to high temperatures in the char combustor. Further development on cooling required;
- The liquid yield has been approximately 65±2%, lower than expected and most likely due to a feedstock average particle size larger than in other pyrolysis processes;
- The process requires further development work in order to allow for very long duration runs, to improve availability, especially in better tar removal, and methods to combust built-up coke in transfer pipes, to achieve maximum capacity and to process wet feedstock.

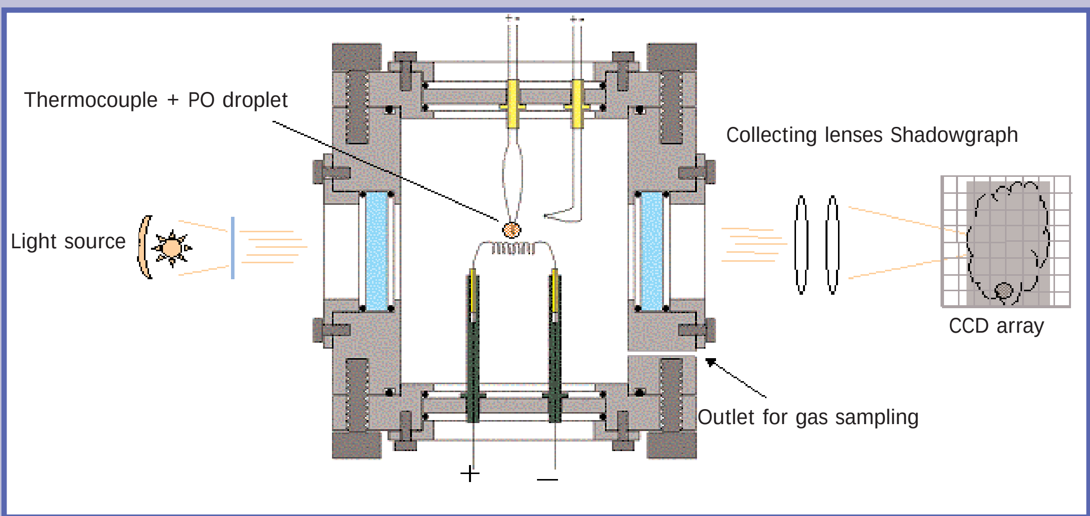
### Specifications for PO

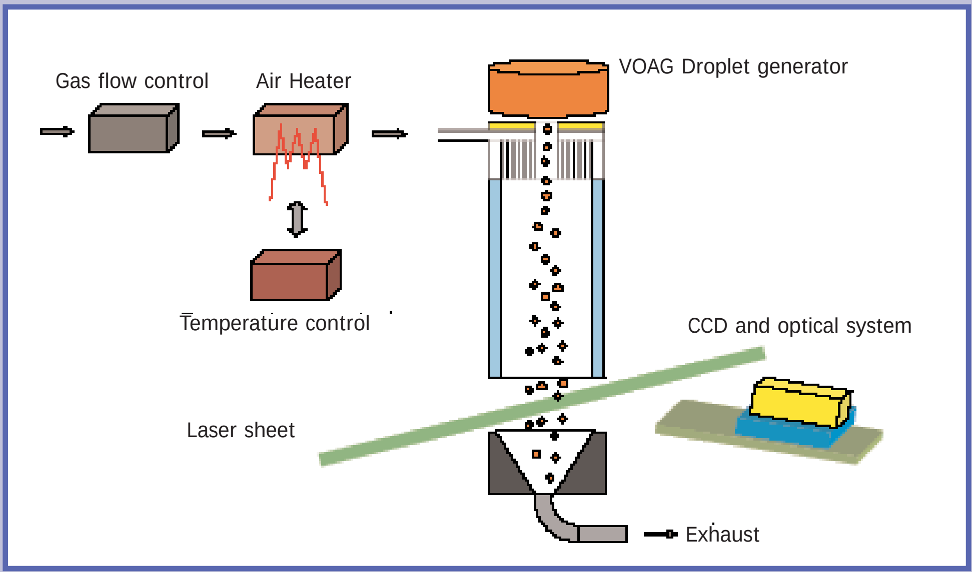
A survey has been performed on the existing and ongoing standardization of biomass derived fast pyrolysis liquids and recommendations and priorities have been indicated for future work on standards and specifications, as the commercialization depends on successfully providing a fuel of an acceptable quality to the end-user.

### Combustion fundamentals of PO and PO based fuels in laboratory scale equipment

Fifteen PO based fuels (pure POs and emulsions) have been studied in order to characterize their combustion behaviour with specific attention to ignition, emissions and influence of ageing on combustion.

Tests have been carried out using a drop tube furnace (DTF) and a single droplet combustion chamber (SDCC). Experiments in DTF are used to study the overall combustion quality and the emissions for different fuels. Single droplet combustion chamber is used to define ignition quality and residual formation tendency of fuels.






A database relative to spraying, heating, swelling, vaporization, ignition, liquid burning, cenosphere formation and combustion processes, gaseous emissions, ageing, has been formed and all the relevant parameters have been recognized and correlated with the fuels properties.

## Utilization in medium size boilers

A total of more than 12000 liters of Forestera™ have been combusted, of which 4000 litres for the COMBIO project, in over than 1500 on-off cycles giving valuable feedback to further process improvements and quality requirements. The main modifications to the existing equipment have been in the area of the burner retention head, in the control system and in the pump.
Early tests have pointed out that hard solids, such as micro sand, can cause erosion in the pump and nozzles which lead to higher emissions.
The emissions in the flue gas have been very low, approaching those of a light fuel oil boiler.
Technically the combustion system has been a success and could be used for long term heat production. The cost of the combustion system has been however higher than conventional systems due mainly to the cost for the industrial pump required, but also to the increased automation.

## Tests with a PO emulsion in a small boiler

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

The main results from the pump tests have been:

- Under high speed motion PO, even in emulsion and regardless the percentage, starts to corrode standard materials, to stuck to the surfaces and act as a glue;
- AISI 316 and 304 materials stand PO;
- Graphite stands PO, but even small percentages of PO in diesel oil makes this material loose its self-lubricating properties;
- Adding small quantities of ethanol to PO reduces PO viscosity and deposit formation.

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Possible solutions could be: investigating the best additive for pump protection or building the pump gears in a corrosion resistant material, increasing considerably the cost.

The adoption of stainless steel material for the more sensitive components, which could be a possibility, nevertheless has to be proven over long term operation.

In order to investigate the spray properties an experimental spray test rig has been designed and set-up, aimed at investigating the droplet size and distribution when using PO/LFO emulsion as fuel for small scale heating boiler. The spray phenomenology has been described, literature reviewed and main parameters investigated. A correlation model has been defined and compared with data available on literature.

### Tests with PO in a large boiler

The combustion test has been carried out in a 9 MW boiler at the Årsta District Heating Plant in Stockholm.

The main results have been:

- Handling of the PO has been easy and the test has worked out well;
- Emissions measurements have indicated a dust content higher than expected while the $NO_x$ level has been more or less the same than with pure fatty acid;
- Further tests are needed.

In order to have an industrial use of PO his heating value has to be increased or the combustion conditions have to be modified. This could be done by adding some refractory bricks at the bottom of the boiler and close to the burner to create a radiating shield. Another option could be air preheating or pre-combustion chamber.

### Emulsion production from PO

Different POs have been studied, as composition and physical-chemical properties of oils are extremely important to obtain a stable emulsion.

In order to formulate a stable emulsion, several trial and error tests have been performed. Approximately one hundred different surfactants, cationic, anionic, zwitterionic, polymeric and non-ionic were tested.

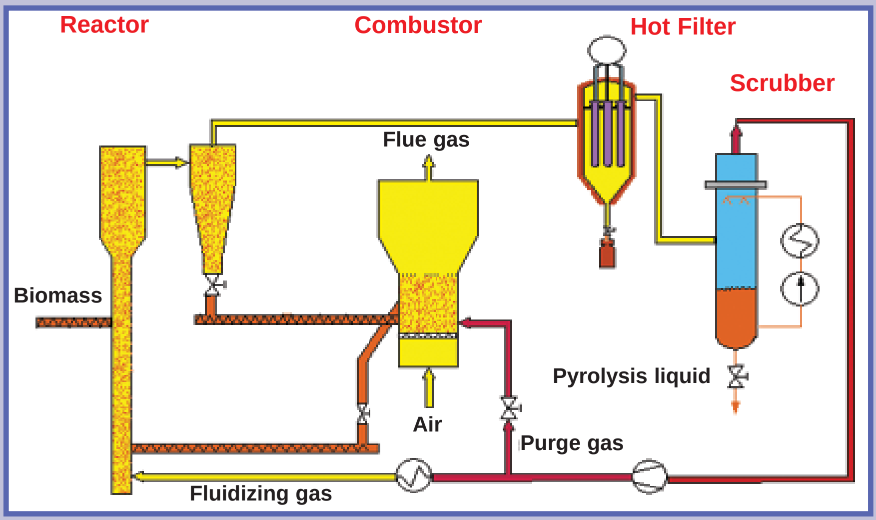
The stability of emulsions was checked both leaving the emulsion at room temperature and in oven at 65°C in order to accelerate the aging process.

The main results have been:

- Emulsions containing forestry residue oil are less stable than the ones prepared with spruce oil, due to a higher tendency of forestry residue oil to separate in different phases;
- Emulsions in time undergo a sedimentation phenomenon due to the highest density of PO with respect to diesel, with no variation in droplet dimensions;
- The minimum surfactant amount needed to obtain a stable emulsion was found 1%wt calculated on PO.

## Hot Vapour Filter (HVF) design and operation in PDU-scale

The HVF has been installed by an existing Process Development Unit (PDU).
Several runs have been carried out in the fast pyrolysis PDU to demonstrate the performance in removing solids from the vapours and, as a consequence, from the PO. The objective has been to operate HVF continuously with pyrolysis vapours. Auxiliary material is fed to the line before the filter to improve filter dust removal. The primary criteria employed assessing the HVF performance operation is the pressure drop across the filter.
The longest continuous operation has been about 10 hours, then a continuous pressure-drop increase.
The conclusion is that with the present experimental arrangement HVF of pyrolysis vapours does not appear feasible.




## Techno-economic assessment

A techno-economic assessment from biomass collection to heat production has been carried out in order to provide concrete information about the possible exploitation and market application of the proposed technology and to promote PO use for potential customers in Europe. The investigation has been based also on the results obtained during the project development.
Two case studies have been assessed:

- Production of PO and use in medium scale boiler in Finland;
- Production of PO and diesel oil emulsion and utilization in small scale boiler in Italy.

The whole biomass to energy chain (bioenergy chain) has been studied, from biomass collection to PO or PO emulsion utilization. It is widely assessed that if each step of the bioenergy chain is not optimized, the final cost of the produced energy may result not competitive with the one from traditional fossil fuels.

## CONCLUSIONS

The pyrolysis process has been shown to be able to produce high yields of liquid products which can be shipped, stored and utilised more economically than solid fuels in the small to medium size boilers (20 kWth to 1 MWth). However, to date there have been no long term experiences with PO use in this size class due to lack of sufficient quantities of suitable quality fuel.

Therefore it is envisaged that to be able to enter into heating fuel markets, the new liquid biofuel chain has the following general objectives: to be competitive economically and to fulfil specifications required by users.

In Finland a strong demand for wood fuels continues and wood fuel prices have continued to increase during the years. Logging residues have been selected as the raw material for the pyrolysis liquid production.
In Italy agricultural residues have been considered as primary potential feedstocks for PO production. In Tuscany, used as case study for the Techno-economic assessment, wood industry residues could provide also significant amounts of biomass.

In pilot plant tests stable process conditions have been achieved. A high quality product could be obtained by removing solids using commercial centrifuges. The liquid yield, 65%wt, has been less than expected and most likely due to an higher feedstock particle size than in smaller systems. Further development work is needed on product cooling, on tar removal from non-condensable gases, on combustion of coke in transfer pipes, and on online phase separation in forestry residue pyrolysis.

In laboratory scale combustion a database relative to heating, spraying, swelling, vaporization, ignition, liquid burning, cenosphere formation and burning processes, gaseous emissions, ageing, has been formed and all the relevant parameters have been recognised and correlated with the fuels properties. Hard solids such as micro sand, even at levels of 0.03-0.05%wt, can cause problems in pumps, nozzles and higher emissions. The levels of emissions have been small except for the dust or particulate matter. Tar and PAHs have been reduced to very low levels.

Technically the medium scale (200 kW-1 MW) combustion system has been a success and could be used for long term heat production. The cost of the combustion system has been however higher than the goal due mainly to the cost for the pump required but also to the increased automation.

In large scale combustion (5-10 MW) PO should be single phase. Either the heating value has to be increased or the combustion conditions have to be modified. The latter could be done by modifying the boiler and place some refractory bricks at the bottom and to the side of burner to create a radiating shield. Another option could be having an air pre-heater or a pre-combustion chamber.

Based on the results from hot vapour filtration (HVF) it was concluded that with the present experimental arrangement HVF of pyrolysis vapours does not appear feasible.

Plants below 2-3 t/h feed rate are unlikely to be viable. However the profitability could be enhanced by fully recovering the heat associated to the char and flue gas produced in the pyrolysis reaction, or by selling waste heat and by-product char. Extra heat is available from pyrolysis, when a relatively dry feedstock is used, as assumed in the Italian case study.
Although a reasonable internal rate of return of 10% was calculated in the Finnish case study in replacing light fuel oil in boilers, increase of feedstock price in Finland made economics not so attractive during the time of assessment.

In summary pyrolysis oil utilization has great potential to generate a profit in the long term, but a process development and optimization is needed and it has to be proven over long term operation.