

Publishable executive summary – Year 2

Objectives

The aim of BIOCoup is to co-process upgraded bio-liquids in conventional refinery units and to selectively separate value-added chemicals. To achieve this, the Consortium will integrate their competencies to achieve the following scientific and technical objectives:

- To develop processes of primary fractionation and biomass liquefaction to produce quality-controlled bio-oils;
- To develop bio-liquid upgrading technology such as deoxygenation including development of specific catalysts and to scale it up to Process Development Unit (PDU)-scale;
- To study co-processing opportunities of biomass derived components in archetypal refinery units;
- To produce discrete oxygenated target chemicals;
- To evaluate the most promising optimised biomass-refinery chain(s) (biomass feedstock → final products) through scenario analysis based on estimates of the technical, economical and LCA (life-cycle analysis) performances of the chains.

Coordinator

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Contractors involved

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University of Twente
Shell Global Solutions International
CNRS
ARKEMA
UHPT
Metabolic Explorer
STFI-PACKFORSK
University of Groningen
Technical University of Helsinki/ TKK
Institute of Wood Chemistry – Hamburg/ vTI
National Institute of Chemistry
Borskov Institute of Catalysis
ALMA Consulting group
Albemarle
CHIMAR
TUE

Work performed

Work is carried out within six sub-projects (SP). The overall structure of the project is shown below with a rough outline of material flows from biomass to end products. This also approximates the interaction between the sub-projects.

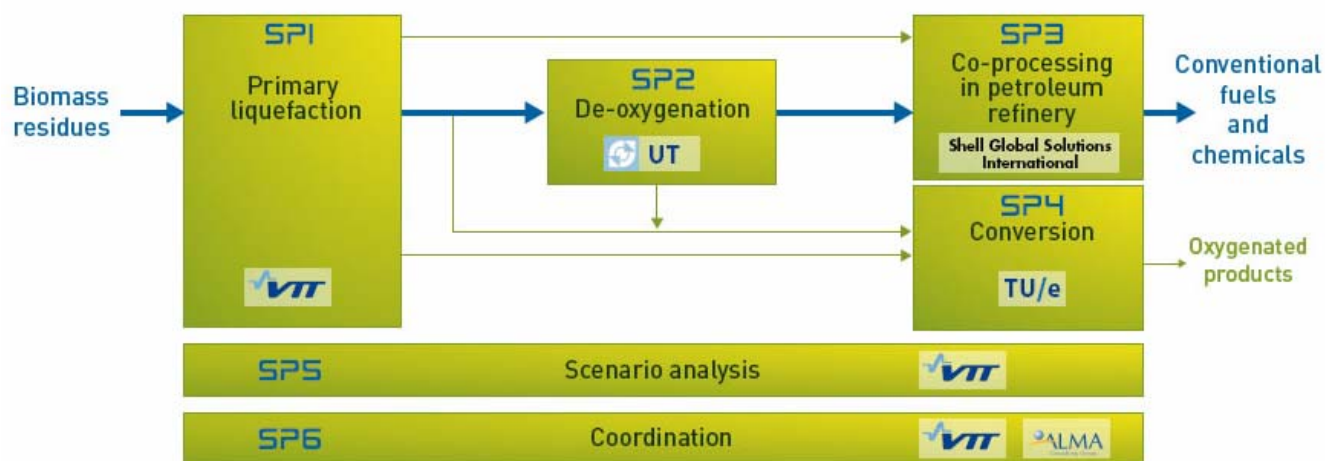


Figure. Project structure

Conversion of lignocellulosic biomass to pyrolysis oil is known to proceed with ca. 70 % yield (as well as making char and gases). A smart, integrated approach to upgrading and/or selective separation is required. Back-of-the-envelope calculations show that the upgrading cost should be minimised (hydrogen is expensive !) and that the selective separation of even small quantities of value-added chemicals (oxygenates) is key for the overall economics. Ideally bad actors in the form of coke precursors will also be selectively removed.

SP1: Integration of bio-oil production to existing biomass users

In SP1 the work is carried out in three tasks:

- Further development of an integrated fast pyrolysis concept
- Pyrolysis liquid samples are provided for partners in SP2 and SP4, and
- Means of providing biomass feed for the concept from a pulping process are studied.

Performance data on the integrated concept has been generated during the reporting period. The Process Development Unit (PDU) was specifically modified for this purpose, and tests were carried out. The expected loss of organic liquid was lower, and the increased water yield was less than predicted based on bench scale work. On-line Karl-Fischer analyzer for in-situ water determination has been under development integrated to the PDU. The main remaining problem is the tendency of particles blocking in the sampling line and sample valve. A modified sampling valve will be tested. A bench-scale pyrolyzer was modified for filtering of pyrolysis vapours. Six successful runs have been carried out related to in-situ filtering. The amount of filtered oil produced so far is about 1300 g. During the reporting period a bench scale recovery unit has been build-up and tested. A bench-scale pyrolyzer was modified to study the bio-oil fractionation during the liquid recovery stage. Several experiments have now been carried out with acceptable mass balances (about 95 % mass yield of products). The physical (solids, water) and chemical properties (solvent fractionation method) of pyrolysis liquid fractions have been analysed. A total of 212 kg of reference pine pyrolysis oil and 150 kg of pyrolysis oil from forest thinnings has been sent to partners. Data concerning the new pulping process is partly confidential as of time of reporting. Detailed results on black liquor fractionation have been reported.

SP2: Develop smart upgrading strategies of pyrolysis oils to enable co-processing

The overall objective of SP2 is to develop knowledge and technology for de-oxygenation of bio-oils. Three de-oxygenation processes have been selected for this project:

- High-pressure thermal treatment (HPTT)
- Catalytic decarboxylation (DCO), and
- Catalytic hydrodeoxygenation (HDO).

First test results of using upgraded pyrolysis oils in lab scale refinery units (FCC) are available. The results will guide further work in the determination of the goals of upgrading and optimization of these deoxygenation processes. In HDO work, high deoxygenation levels of pyrolysis oil have been achieved with remaining oxygen levels around 10%. This requires high hydrogen partial pressures and high temperatures. Hydrogen consumption and reaction times (hours) are still too high/long, respectively, for industrial implementation, but the FCC tests within SP3 indicate that deoxygenation down to 10% oxygen content is sufficient. New developed catalysts within the project have also been used in small scale HDO setups with promising results. In conjunction with SP3, optimisation of the smart upgrading of the bio-oils will be addressed.

Substantial deoxygenation has been achieved by HPTT. However, one problem is the increase in molecular weight during HPTT (accompanied by coking tendency). This made the HPTT product not well suited for either further upgrading by HDO or direct processing in lab scale refinery units (SP3). Progress in DCO work has been delayed because of three reasons:

- Commercially available catalysts do not seem to work
- The supply of the new catalyst was delayed
- Just like HPTT, coke formation is prevalent in DCO.

Understanding the mechanisms leading to this polymerization/coke formation is needed in the selection and development of the catalyst. However, recently new, promising catalysts were made available.

SP3: Co-processing of upgraded bio-oils in archetypal refinery units

Suitable refinery processes inventorisation has been carried out in order to discuss the possibility of bio-liquid refinery co-processing, primarily in Fluid Catalytic Cracking (FCC) and hydrodesulphurisation (HDS) processes.

The upgraded bio-oils from SP2 have been extensively evaluated. First results are promising: compared to the use of 100% VGO (vacuum gas oil), mixtures of VGO/HDO (80/20) show similar gasoline yields, with only slightly higher yields on coke and dry gas, indicating that the co-processing of upgraded bio-oils with FCC feeds using standard FCC conditions and catalysts can give high hydrocarbon yields from a lignocellulosic feed source.

This SP also focuses on gaining fundamental understanding from the study of model molecules. We have identified possible degradation compounds involved in a loss of efficiency of the HDS process. The study of the co-processing of bio oil with SRGO (straight run gas oil) confirms the presence of phenolic degradation product related with a decrease of the desulphurization rate. Co-processing of hydrocarbons and oxygenated model compounds were performed. The products can be effectively monitored by both on-line and off-line analytical systems. The system is being optimized. Additionally, different types of liquid feed delivery systems for an adequate bio-oil injection were studied. Evaluation of bio-liquid and catalyst quality for co-processing, bio-liquid specification for the different co-processing scenario, and economic approach of the co-processing are also studied.

SP4: Selective separation of discrete target oxygenates

In SP4, the main objectives were the evaluation of the technical feasibility of the identified isolation, fractionation and chemical synthesis and bio-chemical synthesis technologies. A second important objective was the production of the first generation isolated fractions (aldehydes), first generation fractionated oxygenates (phenolics), synthesis of first generation oxygenated products and application performance evaluation of bio-liquid derived phenol-formaldehyde resins in particle-board applications.

The main objectives for WP 4.2 (Work Package 4.2) were to experimentally validate the identified isolation technologies for the isolation of target compound fractions and select the most promising isolation technologies for further development. Furthermore the objective was to isolate the first generation isolated fractions for delivery to the three other Work packages. The main objectives for WP 4.3 were to experimentally validate the identified fractionation technologies for the separation of discrete target compounds from the isolated compound fractions and select the most promising fractionation technologies for further development. Furthermore the objective was to produce the first generation fractionated oxygenates for delivery to two other work-packages. The main objectives for WP 4.4 were the technical feasibility evaluation chemical and biochemical synthesis of discrete target oxygenate products (oxygenated solvents, diols, acrylics and surfactants) and optimisation of the bio-liquid oxygenates specifications for successful (bio)chemical synthesis chemicals. In the M1-M12 period only some initial work on adhesive resin synthesis has been done. The main objective for WP 4.5 was the synthesis of thermosetting phenol-formaldehyde adhesive resins from phenolic biomass derivatives and their product application evaluation in particleboard. A second important objective was the selection of ARKEMA product applications for performance evaluation.

SP5: Evaluation of the technical, economic and LCA (life-cycle analysis) performances

The main objective of SP5 during the reporting period was to complete the techno-economic assessment of the state-of-art reference BIOCoup production chain. Another objective was to carry out a preliminary evaluation of the new pulping and recovery process being investigated in SP1. Both these activities have been realised. According to the results of the techno-economic analysis, the BIOCoup reference production chain has the potential to produce transportation fuels at a cost that compares favourably with costs estimated for other second-generation biofuels. In particular, the present evaluation indicated that the final products of the BIOCoup reference chain would cost about the same as transportation fuels produced from the same feedstock via gasification and Fischer-Tropsch (FT) synthesis. Another activity of this task was a preliminary evaluation of the new pulping-recovery process being investigated in SP1. This process is being evaluated in two stages. The aim of this first preliminary evaluation was (1) to obtain a general idea of the competitiveness of the new process concept in the light of the experimental results so far and (2) to identify any gaps in the knowledge base that is needed for a detailed techno-economic analysis of the process. Complementary experiments with the aim of filling these gaps will be instigated in SP1 in the period M25 - M36.

SP6: Transversal activities

All the activities in SP6 (with the exception of work related to training) run for the whole project duration and aim to facilitate the achievement of the project objectives, as well as to maximise their impacts. Four phases have been defined for the dissemination, the first WP. The public website has also been updated, www.biocoup.eu. In the second WP, partners planned to identify outputs of the project that are susceptible to contribute to ongoing

standardisation activities or to foster new standardisation initiatives in biorefinery-related topics. Training was started at M11 with the organisation of a biofuels course by TKK. A training session of the young scientists working within BIOCOUP also took place in the Netherlands, organised by UT and RUG. Analytical support to the other subprojects and to improve existing methods for feedstock and bio-oil analysis is also provided in SP6. Analysis and characterization of the feedstock materials (biomass feedstocks and primary bio-liquids), products (deoxygenated bio-liquids), by-products (water phase) and possibly intermediates is a major task undertaking within BIOCOUP. Project management is also carried out as part of SP6.

In conclusion, after 2 years BIOCOUP has generated some promising leads which we shall continue to build on, although it should be appreciated that the research is in an exploratory stage and the upgrading of pyrolysis oil to hydrocarbons performed on a small (gram) scale.