



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 has 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 hydrodeoxygenation and to scale it up to Process Development Unit (PDU)-scale;
- To study co-processing opportunities of these upgraded bio-oils in archetypal refinery units such as Fluidized Catalytic Cracking (FCC) and Hydrotreating units on a laboratory scale;
- To produce discrete oxygenated target chemicals;
- To evaluate the most promising biomass-refinery chain(s) 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

VTT
BTG
University of Twente
Shell Global Solutions International
CNRS
Arkema
Metabolic Explorer
INNVENTIA
University of Groningen
Technical University of Helsinki/ TKK
Institute of Wood Chemistry – Hamburg/ vTI
National Institute of Chemistry, Slovenia
Boreskov Institute of Catalysis
ALMA Consulting group
Albemarle
CHIMAR
Technical University Eindhoven

Work performed

Research 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 shows the interaction between the sub-projects.

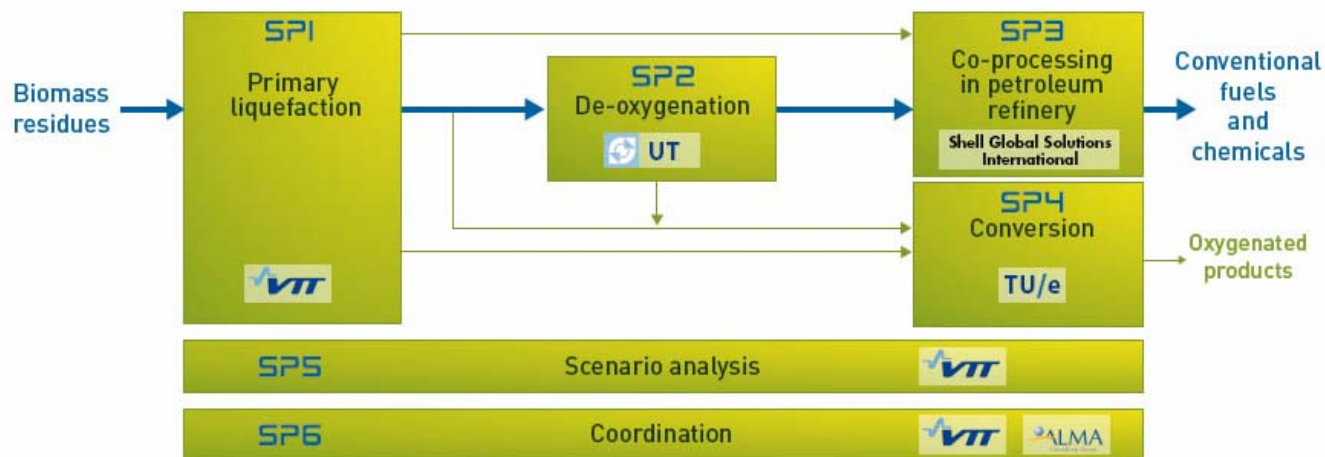


Figure. Project structure

During the first 3 years of the project, several important findings have emerged.

- In SP1, a fractionation strategy has been identified to determine feeds to SP2 in BIOCOUP
- In SP2, HDO offers potential for improvement as an upgrading technology, and this route is emphasised in the future BIOCOUP work. In SP3, it has been found that the upgraded bio-oils from SP2 can be converted to lignocellulosic based hydrocarbons by co-processing under either a FCC or hydrotreating conditions
- In SP4 isolation and fractionation of selected key chemicals has been verified and their practical application demonstrated
- In SP5 the first BIOCOUP biorefinery chain is under evaluation and will be compared to the reference chain already studied. In SP6, as well as essential project management and coordination activities, a coordinated effort in characterising bio oils and intermediates is been carried out. Partners are continuously sharing their experiences related to bio oil characterisation.

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

Compared to the more traditional stand-alone fast pyrolysis approach, the integrated concept has some innovative features. In the integrated concept either recycle gas or boiler flue gas may be used instead of inert recycle gas. If boiler flue gas is used, oxygen will be present in the pyrolysis reactor. It is known that oxygen in pyrolysis causes reduced organic yield and increased water yield. When oxygen corresponding to a typical content in a fluidized bed boiler flue gas was added to the fluidizing gas the organic yield decreased by about 10 wt % and the product liquid was markedly 'aged'. This ageing resulted in a decrease in carbonyl compounds (aldehydes, ketones), an increase in water and of heavy material insoluble in water. The consequences of this ageing is not yet known concerning the upgrading of this material.

An on-line Karl-Fischer analysis technique has been developed as an alternative for the on-line measurement of water in pyrolysis oils. The water content is one of the few means of evaluation the performance of pyrolysis in real time.

Six successful runs have been carried out in a bench scale continuous pilot plant with both an immersed filter and cyclone line incorporated. The filtered oil has a lower solids, char, ash,

alkali/alkaline and water content compared to the oil produced via the cyclone line. The elemental composition of both oils was nearly the same but the average molecular weight of the filtered oil was slightly lower. Although extremely low in ash/char content, both oils were not stable in an accelerated aging test, resulting in a substantial increase in molecular weight. Experiments with the solids-free vapors produced via the filter line showed that the vapors are still highly reactive resulting in char formation.

The influence of the temperature of the sieve plate column of the pyrolyser on the pyrolysis oil quality was investigated.. At higher temperatures more water was removed from the sieve plate column and electrostatic precipitator to the glycol cooler and side stream sampler. More organics were also removed from the sieve plate column to the electrostatic precipitator. Most of these compounds are water-soluble such as aldehydes, ketones, organic acids and sugars.

Three runs have been carried out producing a total of about 1 000 kg bio oil. These bio oils are stored cold to prevent further reactions. Samples for other Sub Projects have sent to partners on request. This procedure ensures that partners are working with the same feed materials all the time.

The experimental part of WP1.3 has nearly been completed. A techno-economic assessment of the process which produces lignin from kraft pulping liquor has been developed experimentally, is reported in SP5. Previous publications on the direct catalytic hydrogenation of lignin have been evaluated and the possible need for complementary experiments within BIOCOUP has been analysed. It was concluded that experimental kraft lignin liquefaction work within BIOCOUP will not be started as of now. It is believed that converting fractionated lignin in Task 1.1.4 to be further upgraded in SP2 will be more critical.

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

Three strategies have been studied for the upgrading of pyrolysis oils. These are hydrodeoxygenation (HDO), High Pressure Thermal Treatment (HPTT) and decarboxylation (DCO).

In the work package on HDO there has been good progress. BTG, RuG and UT have produced upgraded oils using incremental changes in operating conditions (T, P). FCC testing with these oils within SP3 has continued. For HDO oils with high remaining oxygen levels (low HDO severity), hydrogen consumption is relatively low, which is beneficial with respect to economics. Further reduction of hydrogen consumption might be accomplished by using certain pyrolysis oil fractions. BIC is continuing their work on catalyst development using model components. Albemarle, BIC and RUG have initiated a study towards the stability and leaching of new BIC catalysts. TTK has further worked on the reaction pathways of guaiacol and unraveled this complex mechanism and showed it to depend on temperature and type of catalyst selected, which means that extrapolation of the results to pyrolysis oil must be done cautiously.

It has been established that HPTT oil is not well suited for either further upgrading by HDO or direct processing in lab scale refinery units (plugging, miscibility problems with typical refinery feed). The coking tendency of fractions/model components of HPTT oil have been studied . It has been shown that glucose is a component prone to coke formation. Water dilution did have a mitigating effect in decreasing the coking tendency. Acids (formic acid, acetic acid as present in pyrolysis oil) increased coke formation.

Commercial catalysts have, so far, not given (substantially) higher degrees of decarboxylation (DCO) than seen in HPTT alone. New catalysts have been prepared and tested by BIC using pentanoic acid as a model component. The performance of these new catalysts when applied to pentanoic acid seems reasonable, although reaction times are in the range of hours (BIC) and thus much longer than the typical polymerization phenomena seen in pyrolysis (minutes). UT has tested the available BIC catalysts with pyrolysis oil. The decarboxylation of these new BIC catalysts on pyrolysis oil was approximately the same as that of the commercially available catalysts and again not much better than in HPTT alone. New catalysts are now (M36) awaiting testing after which DCO will be halted.

Two Process Development Units (PDUs) will be built by BTG and UT. In order to provide sufficient quantities of upgraded bio-oil for pilot plant testing and study the operability of the process, the first PDU, based on a current BTG design, will have a capacity of approximately 1 kg/h. To investigate the influence of process conditions on product quality, a smaller, more flexible, set-up will be constructed with a capacity of 100 g/h.

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

The upgraded bio-oils from SP2 have been extensively evaluated in both Fluidised Catalytic Cracking and hydrotreating on a lab scale. In co-processing these upgraded bio-oils with standard FCC feeds such as a VGO - (vacuum gas oil) or a Long Residue, similar gasoline yields, with only slightly higher yields on coke and dry gas, are obtained, compared to the FCC feed alone. This suggests that the co-processing of upgraded bio-oils with FCC feeds using standard FCC conditions and catalysts can afford hydrocarbons from a lignocellulosic feed source.

This SP also focuses on gaining fundamental understanding from the study of model molecules. The SRGO contains ca. 1 wt % sulphur – this needs to be considerably reduced, ideally to ca. 10 ppm, for transport fuel applications. The impact of the addition of these bio-oils and of reaction temperature on the hydrodesulphurisation performance has been studied. We have identified possible degradation compounds involved in a loss of efficiency of the HDS process. The hydrotreating of a mixture of upgraded bio oils with a SRGO (straight run gas oil) confirms the presence of phenolic degradation products related with a decrease of the desulphurization rate. The products can be effectively monitored by both on-line and off-line analytical systems.

SP4: Selective separation of discrete target oxygenates

At M21 the technical feasibility of extraction-based isolation techniques for aldehydes, phenolics and acids has been demonstrated by TUE, NIC and RUG. Using these techniques, first generation isolated aldehyde (TUE) and phenolics (NIC) were produced and delivered to ARKEMA, METEX and CHIMAR. The objectives for the M25-M36 period were their optimization and the production of improved fractions for delivery to and evaluation in the other Work packages.

Using the optimized isolation procedure for aldehydes through the bisulphite route TUE has produced a furfural containing fraction from VTT Pyrolysis oil (SP1). This fraction was contained in the toluene used for the recovery from the aqueous phase and delivered to WP4.3 for further fractionation.

TUE has used the new Fischer Spaltrohr setup for the production of 0.5 kg of a low toluene residue furfural fraction which was delivered to ARKEMA (WP4.4) for solvent synthesis and CHIMAR for evaluation as an additive in resin formulation in WP4.5. Analysis by vTI has shown that compared to the first generation aldehyde fraction the toluene content has been reduced from 75% to 6.2%. Furthermore a small amount will be delivered to CNRS for model studies in SP3. Due to the high toxicity towards bacteria it was decided that METEX will not evaluate these multiple aldehyde fractions and focus on purified single aldehydes, in particular glycoaldehyde.

At the start of the M25-M36 period the chemical and biochemical synthesis routes to convert aldehydes into alcohols as target oxygenate products were established. These have been optimised and used to synthesize the first generation and improved oxygenate products.

CHIMAR has replaced 15% of phenol in particle board resins by VTT bio oil and synthesized small quantities of resin based on the first generation fractions delivered by NIC. ARKEMA has selected the first product applications of the bio-liquid derived oxygenated target chemicals: solvents and adhesives.

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

The main activity for the current period is the compilation of, and the subsequent techno-economic evaluation of, improved BIOCOUP production chain(s) based on the new data and new process ideas so far generated in the BIOCOUP project. As is self evident, new data from other SubProjects will be used as a basis of the evaluations. Plans how to incorporate new data in these evaluations were considered at the beginning of the project.

SP6: Transversal activities

These activities, with the exception of WP6.3 related to training, run for the entire project duration and aim to facilitate achieving the project objectives. Dissemination is ongoing with an increasing number of conference presentations and publications being submitted to peer-reviewed journals. These can be found on the BIOCOUP Website www.biocoup.eu.

Two 1-week long courses were held at M11 and M35 and were organised by, and held at TKK. These were very successful with lectures and attendees from both industry and universities.

The project management activities have been essential for managing this large Integrated Project with 16 partners.

Much of SubProject 6 is associated with providing analytical support to the other subprojects and to improve existing methods for biomass and bio-oil analysis.