

## 4REFINERY public summary M18

4REFINERY will develop and demonstrate the production of next generation biofuels from more efficient primary liquefaction routes integrated with upgraded downstream (hydro)refining processes to achieve overall carbon yields of >45%. The consortium will aim for successful deployment into existing refineries, including delivering a comprehensive toolbox for interfacing with existing refinery models.

The main objectives of 4REFINERY are:

- To develop new biofuels production technology while at the same time increase understanding and control of the entire value chain
- To scale up testing procedures and define scenarios for the best further implementation in existing refineries
- To develop solutions to answer key societal & environmental challenges

The project will focus on the transformation of bio-liquids from fast pyrolysis and hydrothermal liquefaction into advanced biofuels, through intermediate process steps combined with downstream co-processing technologies. The goal will be to bring these technologies from TRL3-4 to TRL4-5. The project will establish relations between product's properties, the quality of renewable feedstocks and all relevant process parameters along the value chain. The study of these combinations will allow a full understanding of the influence of feedstock and treatment processes on product characteristics.

4REFINERY will (i) use inexpensive biomass, (ii) require low capital cost processes at small scale, (iii) reduce costs for further treatment due to scaling up and reduction in OPEX and (iv) leverage existing infrastructure, ensuring the new developments can be rapidly implemented at a commercial scale for production of biofuel with competitive prices compared to its alternatives.

Overall Process Integration:

Specification and limits for target fuels, testing protocols, benchmark and key performance indicators have been established. Early in the project a database for collection and recording of project results was made to establish a good overview and facilitate communication of collected data within the 4REFINERY project. Twelve value chains have been selected for techno-economic assessment (TEA) in which eight will undergo detailed TEA. Mass, energy and elemental balances for the pre-processing steps in fast pyrolysis and hydrothermal liquefaction (HTL) have been retrieved. For the HTL process, Life Cycle Analysis (LCA) with 60% heat recovery has been developed and analysed.

Public perception of Danish debate on liquid biofuels reveals limited knowledge in media coverage of the topic. While there exists an overall positive perception in academia towards second generation biofuels for transportation, the mass media apply an overall negative discourse against biofuels. Only about 25% of the press mentions differentiate between different generations of biofuel.

Furthermore, only 40% of these simply states that there are two different generations of liquid biofuels, without giving any further explanation.

Primary conversion:

A total of 100 litres of an initial reference stabilized pyrolysis oil (SPO) has so far been produced and delivered to partners. 60 kg of a reference HTL bio-liquids and 310 kg of pyrolysis oil (PO) have also been produced. The two alternative reference bio-oils are being investigated in alternative co-refining steps in order to establish the basis for selecting the optimal co-refining routes, as determined by the feedstock and end use application.

With respect to the primary conversion of the biomass to intermediate bio-oils, a number of approaches have been evaluated to optimise the efficiency and cost of the process:

Removal of ash from feedstock is carried out prior to the pyrolysis process to increase the overall carbon efficiency of the biofuel chain. All three industrially relevant feedstocks (forest residue, eucalyptus, straw), selected as relevant for a broad range of European biogenic resources, have been washed in laboratory scale to reduce the ash (especially alkali and alkali earth metals) content. A wide range of parameters (temperature, washing time, acidity of washing liquid and the amount of liquid) were investigated to establish the influence on the efficiency of alkali metal removal. Of the above mentioned parameters, acidity of the washing liquid was found to be the most important parameter.

Use of cheap industrial residues as alternative catalytic materials. These have a composition which gives them catalytic activity in the conversion of biomass and can thus be a cost-efficient alternative as potential catalyst materials. Five different slag materials produced as by-products from steelmaking industry have been compared in bench-scale experiments for fast pyrolysis. Currently, only one of the slags were found to show promising catalytic activity. This candidate slag material was therefore selected for further testing to produce larger volumes of fast pyrolysis bio-liquid. However, the selected slag material proved to not have the necessary physical-mechanical properties needed to survive the rough treatment in a scaled-up pilot fluidized-bed reactor. The conclusion is therefore that the tested slag materials, in their current form, are not suitable as a cheap catalyst alternative in fast pyrolysis.

Fractionation of the Bio-oil. Due to the complex composition of bio-liquids, fractionation is carried out prior to upgrading in order to increase the carbon efficiency of the overall process value chain. Several methods for fractionation of pyrolysis oils and HTL bio-liquids have been explored in 4REFINERY.

For pyrolysis bio-liquids, solvent extraction experiments and other phase separation experiments have been explored to separate the water-soluble sugar-like compounds from lignin derived materials. While solvent extraction using organic solvents did not show any good results, phase separation using water combined with efficient mixing is promising. For higher bio-oil moisture content most of the water-soluble compounds were distributed into the aqueous phase.

The baseline HTL bio-liquid biocrude was fractionated using fractional distillation. To avoid thermal degradation of the bio-liquid, the distillation procedure was divided into several steps. The results show that there is a decreasing H/C and O/C molar ratios as the boiling point increases.

## Refining Processes:

In order to establish the basis for selection of the optimal routes for integration of the intermediates from primary conversion of biogenic feedstocks into the refinery all the major co-FCC and co-HDT refinery processes will be explored. This involves co-refining of both pyrolysis and HTL bio-liquids produced from all three types of biomass feedstocks (forest residue, eucalyptus, straw).

For the co-FCC route, a baseline has been established by performing a test run in an FCC pilot unit using an FCC equilibrium catalyst together with typical FCC feedstocks.

For tests involving bio-liquids from the pyrolysis route, current results foresee that only a mildly treated pyrolysis oil will be sufficient for integration via the co-FCC route. However, for the alternative co-hydrotreating route, a more severely deoxygenated treatment of the pyrolysis bio-liquid is currently required.

Our miscibility studies have shown that HTL bioliquids are incompatible with straight run gas oil (SRGO). Commercial surfactants have proven to be inefficient. Nevertheless, substantial amount of HTL bioliquids can be solubilized in SRGO by using co-solvents. Interestingly, the heavy distillate fractions derived from the fractional distillation of HTL biocrude showed complete miscibility in SRGO at any proportions. These studies show that fractional distillation is an efficient concept for dividing biocrude oil in to different chemical groups to produce transportation fuels.

The final results from the project will provide an understanding of the influence of the main parameters on the fuel quality and is expected to optimize the overall primary conversion steps and co-refinery processes for the production of biofuels. Moreover, the results will move technology from lab-scale to pilot scale, allowing for further investment in technology scale-up relevant to industrial implementation. The data generated (energy/mass balance, process efficiency, links between process parameters) will be further exploited for accurate modelling, and feedback from this modelling will be considered for further process developments. Techno-economic assessment (TEA) of the above mentioned value chains for co-feeding bio-liquids into existing refinery assets will give a good indication of which value chains could be interesting, both in terms of technical and economic feasibility for mineral refinery co-feeding. Three to four of the most promising value chains identified in the TEA will be used as a starting point for developing business cases. TEA and life cycle analysis (LCA) will deliver scenarios allowing refiners to make the best choice for integration into refineries.

Supply chain and market assessment will give an estimation of feedstock costs and sensitivities, define supply chain logistics, market characterization (including potential barriers) and defined pricing strategy.

Results from the project are assumed to increase the share of bio-based carbon in conventional fossil fuel refinery products and thus reduce the greenhouse gas emission impact and environmental footprint. Feasible value chains could potentially create jobs, especially in pre-processing (biomass handling, harvest, transport, etc.), but also in the stabilization process of fast pyrolysis bio-liquid which will be an additional process at the refinery site.