1 Publishable summary

1.1 A summary description of project context and objectives

Declining petroleum resources, increased demand for petroleum by emerging economies, and political and environmental concerns about fossil fuels are driving our society to search for new sources of liquid fuels and commodity chemicals. The only current sustainable source of organic carbon is plant biomass. Large amounts of biomass are present throughout the world and the European Biomass Industry Association (EUBIA) has estimated that Europe could produce 8.900 PJoule of biomass per year. Biofuels, produced in biorefineries, give out significantly less greenhouse gas (GHG) emissions than fossil fuels and can even be greenhouse gas neutral if efficient methods for production are developed.

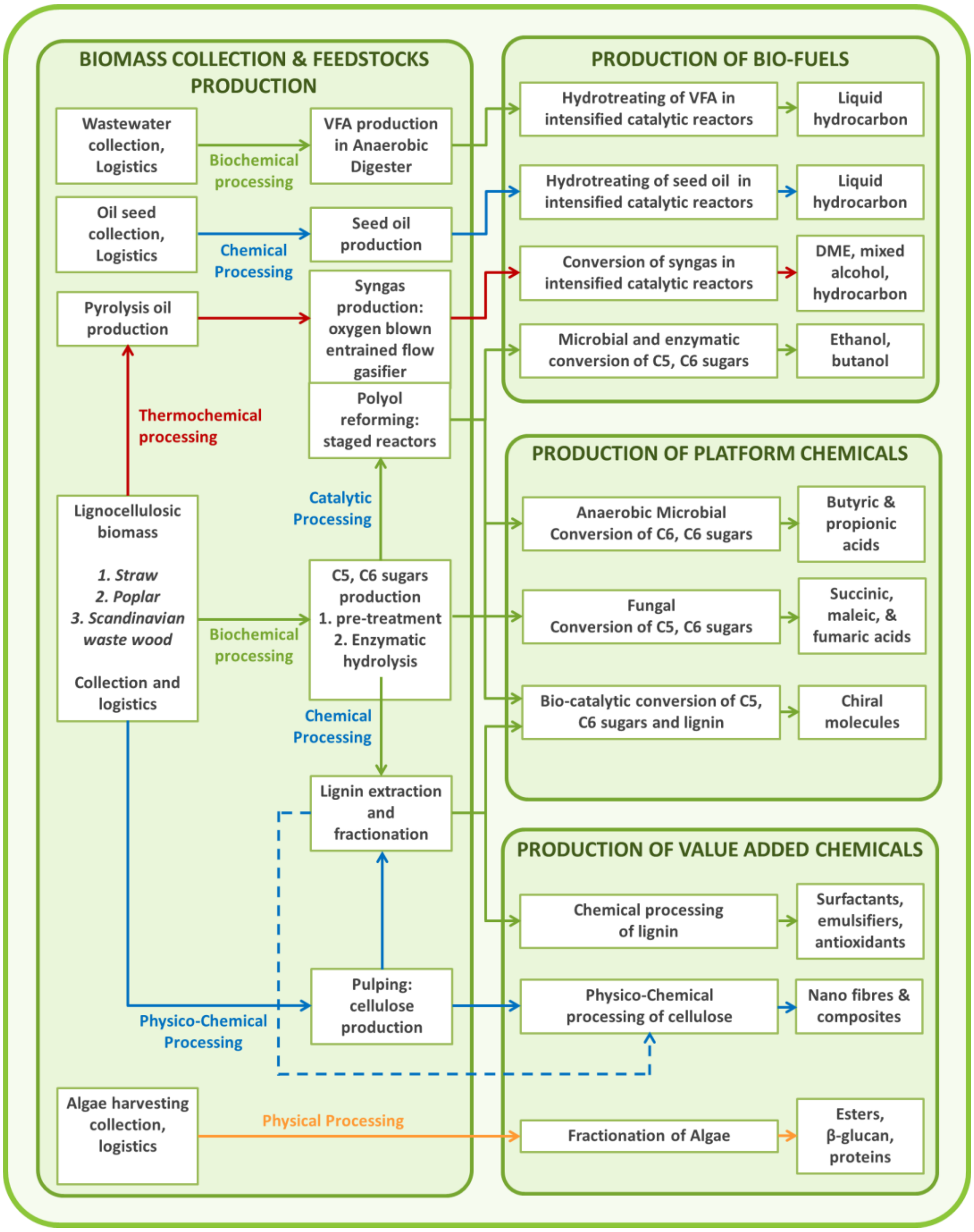

Figure 1: Organisation and scope of Suprabio

The biorefinery itself must address two strategic goals. A well-recognised driver is the substitution of imported petroleum with domestic raw materials, but realization of the energy goal requires a financial incentive to build or retrofit facilities capable of utilising renewable biomass as feedstocks, to justify industrial use of new raw materials and to incorporate technology for their conversion. Since fuel is a high volume, low value product, new, standalone fuel facilities are often burdened by a low return on investment, making their construction less desirable. A biorefinery based on chemical products alone can realize a much higher return on investment, but lacks the potential for a large energy displacement impact as chemical production accounts for only about 7 to 8% of our oil imports. Analysis reveals that producing both chemicals and fuels in an integrated biorefinery meets the energy and economic goals simultaneously. In integrated operations, such as those developed in SUPRABIO, high value products become an economic driver. This provides higher margins to support lower value fuels, leading to a profitable biorefinery operation that also exhibits an energy impact.

The SUPRABIO project researches, develops and demonstrates a toolkit of novel generic processes together with advanced intensification and integration methodologies that can be applied to a range of biorefinery scenarios based on sustainable biomass feedstocks. Supporting economic and lifecyle assessment of the resulting gains in energy efficiency and conversion of renewable carbon, together with an implementation strategy based on a product mix with optimal value, will inform step changes that contribute to achieving a more secure and sustainable economy in Europe. The organisation and scope of SUPRABIO is illustrated in figure 1.

1.2 A description of the work performed since the beginning of the project and the main results achieved so far

Within the biochemical route, dilute acid steam explosion pretreatment of wheat straw and poplar has been optimized based on multiple uses still fulfilling the project requirements. Wheat straw based biomass has been produced at a demonstration scale unit (now up to 1,000 kg biomass per hour) for further processing at various partners in Suprabio, e.g. fermentation at small demo scale. One of the main results obtained within the project was long term pretreatment. The objective was to obtain a steady state continuous pretreatment operation for more than 8 hours. This has been achieved several times during the project period.

Through several steps of testing and benchmarking, a high temperature separate hydrolysis and fermentation process was selected for demonstration based on highest overall productivity and yield. The process was tested at $2m^3$ fermentation volume and the promising results of the pre-demonstration work were successfully replicated. The demonstrated process shows significantly higher ethanol yield (4-9%) and ethanol productivity (30%) compared to state-of-the-art and, as it is still a young technology, the potential for further improvements is high. The experience gained by the work with different enzymes and organisms has eased the future work on setting up fermentations for biorefineries dealing with lignocellulosic biomass. The learnings of the project are important to improve the understanding the factors affecting biomass conversion.

As part of the work to develop bacterial strains for the production of 2,3-BDO, we have established a method and a toolkit for the mutation of key virulence genes to make *Klebsiella pneumoniae* safe which is applicable to all strains including those for products other than 2,3-BDO. Further work is following that will combine these with high-producer mutations. We are completing validation in our test strains to confirm continued production of 2,3-BDO.

Separation of BDO from fermentation broth has been successfully achieved, using a number of different methods, including salting and solvent extraction, and distillation. The cost of isolation of the BDO from the biological broth by distillation was generally thought not to be energy efficient, as large amounts of water have to be distilled off before the recovery of the BDO. However, process and economics analysis and show that the large difference between the boiling points of water (100 °C) and BDO (180-182 °C) makes the distillation process a more suitable and preferable alternative to other methods as the yield of recovery can be as high as 96 % and the only waste product is water. The distilled water can also be re-used or utilised for other purposes. Moreover, the cost of the distillation process reduces drastically when the BDO content in the broth is around 10%. The subsequent conversion of BDO to methyl ethyl ketone has been successfully carried out using both chemical dehydration and heterogeneous catalyst. The latter method is more cost efficient and environmentally benign.

Also fermentations for acid production showed good yields. Moving toward continuous fermentation, the sugar conversion increased significantly. The used strain showed high sugar utilization when fed with 100 % substrate only adding few nutrients to the fermentation.

Regarding chiral molecules, the Suprabio project has brought exploration of the use of super critical CO_2 into the light. This technology has been tested with biocatalysis and now demonstrated proof of principle of production of sugar fatty acid esterases. Also, production of glucosamine has been explored by the use of biocatalysis.

The lignin derived from the biomass has been further analysed for usability within health care products, emulsifiers and surfactants. The lignin obtained from the dilute acid steam explosion does not have the right properties for health care products, emulsifiers or surfactants. The work within the project showed that alteration of the lignin is necessary for the lignin to be reused for non-energy purposes.

For pulping of biomass, the pretreated wheat straw has been tested along with woody biomass. Pulp with low lignin content has been obtained and used for production of adhesive nanocellulose composites. Dispersion trials were made and showed good results that are very interesting for the adhesive producers and the end users of the adhesives. Also, a demonstration plant for the production of nanofibres has been setup and optimized. This plant is now generating data important for future scale up of the nanofibre production.

During the final 18 months of the SUPRABIO project, the planned activities on the pyrolysis oil production, the testing of the pump skid and the optimisation of the gasification tests at ETC were all completed according to the schedule.

Laboratory developments of syngas conversion to Fischer-Tropsch liquids, mixed alcohols and dimethyl ether (DME) were all completed. The work on mixed alcohols was always planned as an exploratory activity; nevertheless some very interesting results were obtained using state of the art catalysts which showed promising levels of C2+ alcohols. Further work would be required to optimise the selectivity, particularly the yield of butanol and minimising methanol formation. The work on DME production demonstrated very high yields are possible in a single step process using a Cu/Zn catalyst incorporating an alumina acid function. The yields obtained are better than published data.

Laboratory development of FTS culminated in the fabrication of a miniplant reactor consisting of around 80 plates, built especially for the planned gasifier sidestream demonstration. Following recommendations by the Reviewers and the project officer, the demonstration was carried out on the large industrial gasifier in Pitea, Sweden, belonging to Lulea Technical University, and operating on black liquor feed at high pressure (>30bar).

The multi-plate catalytic miniplant reactor, which was coated with a nanocrystalline Co/Alumina catalyst, was coupled to the LTU gasifier for the demonstration. Prior to the demonstration run, the reactor was commissioned in a test run at IMM that lasted 80 hours. The demonstration run, which was interrupted by unexpected shutdown of the gasifier, lasted a total of almost 70 hours. The reactor performed well, with little or no deactivation after reduction with hydrogen, following the unplanned gasifier shutdown. Conversion of CO was around 85%, and there was high selectivity to C12+ diesel hydrocarbons with small amounts of lower hydrocarbons. Following completion of the gasifier run, the reactor was returned to Brunel University, where it was checked on a synthetic syngas mixture and shown to have the same activity as the Pitea test, highlighting the overall robustness of the catalyst and reactor system.

A techno-economic evaluation has been carried out on the results obtained in the demonstration as a comparison with the evaluation of the mature 2025 thermochemical biorefinery carried out previously.

Wastewater, algal biomass, and seed oil offer significant potential for biofuels and high value products in an integrated biorefinery scheme via other routes. For VFA production and recovery (a) It was possible to achieve up to 80% hydrolysis with caustic treatment under certain condition (b) In batch fermentation with a mixed culture, VFA accumulates over the first 5 days and then begins to distribute due to an onset of methanogenesis (c) Ethanoic, propionic and butyric are the major VFA products but the ratios depend of the wastewater source (d) Membrane technology could prove a viable means of VFA separation and concentration. (e) The maximum VFA concentration achieved, from pre-treated sludge was 13,000 mg/l, which is significantly lower than the 5% level typically achieved in commercial acetic fermentation. Trials performed using GBT (gravity belt thickened) filtrate as the VFA source showed a 300% increase in VFA concentration.

Both rape seed oil and Jatropha oil have been successfully hydrogenated and isomerised in Statoil’s pilot hydrogenation equipment. These results have been taken on board for intensified reactor/catalyst development (and testing) using so-called staged reactors at Brunel University. Achievements here to date are (a) Staged-reactors incorporating a membrane system have been constructed (b) The new reactor concept has been proven with the development and trials of a 3^{rd} intensified reactor system. (c) Isothermic behaviour was observed together with a selectivity shift to the desired products. Algal process development, performed at IGV GmbH so far has succeeded in the identification of new microalgae strains suitable for large-scale production and more efficient lighting in an improved photo-bioreactor design. Progress has been made on the extraction of ß-glucans and fractionating of the fatty acids, EPA and DHA (laboratory scale). Finally, The University of Manchester is working on novel enzyme development and modification for high value products such as pharmaceuticals, cosmetics and paints.

The integrated assessment of sustainability developed a new methodology to further streamline and integrate assessments of environment, process economy, markets, social and political aspects, biomass competition as well as a SWOT analysis. The methodology adopted works very well and is applicable to identify all main quantitative and qualitative sustainability implications of a biorefinery system including strengths and weaknesses. Furthermore, it is very useful to depict all measures and options to improve the biorefinery pathway to become best possible sustainable, supplemented by respective conclusions and recommendations.

A highly successful joint final international conference with close to 250 participants was organised in Brussels in February 2014, by the three sister biorefinery RTD projects SUPRABIO, EUROBIOREF and BIOCORE). The two-day conference "Tomorrow's biorefineries in Europe" integrated oral presentations, poster presentations, exhibition, roundtable debate, networking cocktail, and 1-to-1 partnering event. Technology highlights as well as policy implications resulting from the biorefinery research were presented.

1.3 The expected final results and their potential impact and use

The production of pretreated biomass will be tested with a long run pretreatment at demonstration scale. The pretreated biomass already produced should show positive results on alcohol fermentations and sugar conversions, showing a viable process which is applicable for more than one substrate and for more than one desired product. The pretreatment equipment, Carbofrac® has therefore shown to be both biomass and product flexible, which is relevant for future biorefineries.

Suprabio ethanol can achieve considerable environmental advantages such as greenhouse gas savings but also causes considerable additional burdens in other aspects such as acidification. If on-site energy generation is economically optimised, Suprabio ethanol can be profitable.

In the field of lignin, the results from Suprabio show that chemical alteration is needed for the residual lignin to become an intermediate for antioxidant production or for use as emulsifiers or surfactants. The chemical alteration was not a part of the Suprabio project, thus the final result from this end is only a note on potential use in various industries.

The work on adhesive nanocellulose composites gave insight in a new utilization of the cellulosic biomass other than for fermentation of sugars. With this insight, the biochemical route may give whole new opportunities for utilization of lignocellulosic biomass. With the results obtained from the dispersion trials, the nanofibre production shows to be interesting for the adhesive market. The market analysis gave positive feedback to support this fact.

For both the main biorefinery concepts (biochemical and thermochemical) only waste treatment integration was implemented. No other relevant integration between the proposed processes in the biochemical refinery concept was found viable.

Analysis of the thermochemical pathways has shown that none of the investigated scenarios is economically profitable. This is mainly due to the rather low net efficiency, which together with a large investment cost result in strongly negative Met Present Value (NPV). The largest contributors to the low efficiency are the pyrolysis and gasification stages, so further improvements are required in these areas.

The "Forest residues to FT fuels (2025)" scenario is less sensitive to product price and biomass cost but most sensitive to the investment cost: NPV values would still be negative even with a theoretical 50 % CAPEX cut. It becomes clear that the Suprabio systems need further technological improvement to be sustainable options for biofuel production.

Analysis of the biochemical (ethanol) case anticipated for year 2025 showed high energy efficiency about 55% and 70% LHV efficiency and net efficiency, respectively. This scenario can be economically profitable if using staged gasification/gas engine or boiler/steam turbine for the energy conversion from wastes. All other biochemical process need improvements to become economically profitable.

The market analysis showed that the market for bio-based products is increasing in specific areas and that the markets for bio-based chemicals and fuels will most likely grow in the future.

The environmental assessment shows considerable benefits for Fischer-Tropsch (FT) fuels and DME production in terms of global warming and other indicators. Unlike for most other biofuels, SUPRABIO's FT fuels and DME cause only minor disadvantages in other environmental aspects. However, CO_2 avoidance costs are generally higher than for 2nd generation ethanol.

The availability of lignocellulosic biomass from forestry, residues and cultures such as short rotation coppice is a main limitation for lignocellulosic biofuel production. Comparing alternative uses of the same biomass from an environmental perspective, direct combustion of lignocellulosic biomass for combined heat and power generation in most cases outperforms its biofuel use by far as long as significant shares of power are otherwise still produced from coal. The integrated sustainability assessment provides many concrete optimisation options and recommendations how the sustainability of 2nd generation biofuels can be improved in the future.

Trials performed using GBT filtrate as the VFA source showed a 300% increase in VFA concentration, whilst the increase obtained from fermented liquor was just 21%. These results indicate that with further development, membrane technology could prove a viable means of VFA separation and concentration.

Generally speaking, significant progress has been made with substrate hydrolysis, however product inhibition limits maximum VFA concentration to just 10,000-12,000 mg/l, which presents a serious issue for product recovery. At such a low concentration the VFA would be best exploited as a substrate in a Microbial Fuel Cell for optimum power yield.

Catalytic conversion by hydrogenation/isomerisation of both rapeseed oil and Jatropha oil has already been successfully carried out on a pilot plant at Statoil. These feedstocks have been converted to high valuable diesel (1.5G biodiesel) by a two-step process namely hydrotreating and hydroisomerisation. The diesel product density and cetane index values are outstanding when compared to EN 590 product specifications. Typical values are densities of 0.78 g/cm^3 and a cetane index in the range of 80 to 90. However, to achieve cold flow properties e.g. a CFPP (Cold filter plugging point) of -26°C, a conversion in the hydroisomerization step resulting in a naphtha loss of 20% (80% full range diesel product) is required.

This work has directed the development of novel integrated reactor/catalyst concepts which have shown improvements in fuel production via the hydrogenation of seed oil. Final tests are ongoing to assess the fuel properties of the hydrogenated products.

Hydrotreated plant oils show a similar environmental performance as 1st generation biodiesel: only small benefits in some aspects and additional burdens in other aspects. Fuels based on imported plant oils such as palm oil and Jatropha oil come along with substantial risks regarding social aspects and clearing of e.g. rainforests, which can have severe effects on biodiversity and greenhouse gas emissions.

The implementation of the algae *Porphyridium cruentum ("*P.*cruentum"* which is also referred to as *Porphyridium purpureum* within the biological taxonomy) strain into Suprabio has changed, the aimed for original product portfolio and the suggested downstream processing has had to be adjusted. The resulting products are the natural dye Phycoerythrin, sulphated polysaccharides and a biomass that is rich in EPA (eicosapentaenoic acid) and AA (arachidonic acid).

The change of the product portfolio gives a higher stability in terms of financial risks because more and different markets with higher prices are addressed. The production of EPA has now been optimized in terms of economics. The cultivation of *Porphyridium cruentum* was stable for 15 months in outdoor photobioreactors. The trials have been successful and more than 90 kg of biomass and 2 kg of polysaccharides from the supernatant were produced during the period. However, due to some physical limitations from the downstream processing the concentration of polysaccharides must not exceed 10 g/L.

1.4 Project public website

http://www.suprabio.eu/