Developing advanced Biorefinery schemes for integration into existing oil production/transesterification plants

The SUSTOIL project has carried out a review of the state of knowledge relating to available options for adding value to the different stages of the biodiesel production. The review has collated results of previous and on-going projects in this area as well as published data from both governmental sources and scientific literature. It has consulted the technological expertise base of the industries involved in this project to provide a practical and commercial insight into the innovative technologies, which can be utilised to maximise the output of oil-rich crops into energy and bio-products. The key objective of SUSTOIL is to improve the economics of biodiesel production by adding value to its major by-products in addition to identifying other potential avenues for commercial exploitation of oil-rich biomass residues from biodiesel production as well as other by-products of the process.

This project has been a two-year collaboration between twenty three partners from ten countries representing academic groups and relevant industrial companies.

The scope of the work has covered every area from crop agronomy to advanced downstream processing and the development of new added value product streams.

The ability to develop very large scale industrial uses for oilseeds (such as biofuels) is limited by the amount of land area available for growing industrial crops and by the yield potential of individual crops. It has been estimated that using the best management practices, combined with the optimum characteristics of several current OSR varieties to produce new germplasm, the potential realistic yield that could be attained is in the region of 6.5 tonnes/ha, compared to typically 3-3.5 tonnes/ha achieved in most of Europe. If the yield in those countries already attaining the EU average yield and above could be raised to this potential, then a further 12.4 million tonnes of oilseed rape could be produced in the EU, an increase of 76%, without increasing demand on land. Where farm yields are currently failing to keep up with those of the best performing crops, a number of causal agronomic problems have been identified. Fungal pathogens that affect early growth, and later stems and pods, are identified as key causes of yield loss in many crops.

The potential seed yield of sunflower has increased greatly over the past 30 years due to improved harvest index; however actual seed yield has not increased so much because of limiting factors such as water stress and diseases. The main short term strategies are communication in order to inform farmers of the best cultural practices, based on both the post-emergence strategy to control weeds and the increased possibility to irrigate the crop. Longer term strategy should focus on the adaptation of crop management to the expected water availability and the drought tolerance of varieties should be better investigated.

The biorefinery concept should exploit the availability of all potential raw materials from the chosen feedstock and the opportunity to capture valuable by-products from straw prior to their conversion to biofuels cannot be ignored. The application of a green technology such as the use of supercritical CO_2 offers substantial benefits within the biorefinery concept as 100% of the required energy and extraction solvent can be obtained from other unit operations. It is envisaged that within this concept the raw materials (straws) can be pre-treated by extraction with supercritical CO_2 to recover a range of valuable molecules before being used as a biofuel feedstock. The main barrier to the adaption of this step within the biorefinery is the development of the markets for the extracted molecules rather than the technology. Alternative uses for the straw include the production of levulinic acid and methane via anaerobic digestion. Opportunities also exist for the physical separation of straw components to produce composite materials, the fibrous outer husk can be used in the production of particle boards or paper and the light-weight pith from the sunflower stalk could be used for insulation products or in absorption of metals from waste water.

The primary processing of olives, rapeseed and sunflower has been examined and alternative novel processing technologies, improved residual oil recovery and the valorisation of residues/wastes have all been proposed. Traditionally, for oilseeds a combination of pressing and solvent extraction is used. Alternative processes or process adaptations include e.g. dehulling, enzymatic (watery) pretreatments, extrusion, supercritical fluid extraction, or microwave application were all considered and the advantages of each identified. Significant changes of the process will influence the composition, properties and quality of the meals. For example, low temperature extraction will probably result in proteins with better functional properties and therefore these potential process changes were also evaluated in respect of their impact on the recovery and quality of by-products.

Conversion of the seed oils to biodiesel is a key step and one in which process improvements and reduction of waste products can significantly improve profitability. One of the main by-products is glycerol and although a number of potential applications for glycerol have been identified, the generally low purity of crude glycerol (crude glycerol from a biodiesel process currently contains only 35% to 50% glycerol) limits its potential applications. The high cost of glycerol purification and increasing overcapacity force's small and medium biodiesel producers to pay for the disposal rather than utilise the crude glycerol. Hence, biodiesel's future stability and viability is likely to be dependent on innovative and economical technologies for the utilisation of the low-grade crude glycerol in order to offset the cost of biodiesel production. Novel routes to biodiesel including using immobilised lipases that can yield high purity glycerol and novel enzymatic glycerol-free routes to biodiesel production were considered. One example involves partial transesterification using lipases to obtain two fatty acid methyl esters (FAMEs) and one molecule of 2-monoglyceride instead of three molecules of FAME. Another potentially attractive route is the transesterification of triglycerides (TG) with methyl acetate, which yields three mols of FAMEs and one molecule of glycerol triacetate, which can also be used as a fuel. Both routes are potentially attractive due to a current surplus of glycerol in the market which seriously hinders the biofuel sector.

The industrial partners in this project identified short term measures that could enhance the efficiency and competitiveness of existing processes and biorefineries. These measures include modifications to the primary oil extraction process, developing new product streams and reducing waste streams. Improvements to the primary oil extraction process is mostly applicable to seed oils and a number of possible changes that could be made to an existing oil mill to improve the recovery of valuables components of oilseeds while conserving the main unitary operations of the processing were suggested. Dehulling of the seed and the use of alternative solvents including alcohols, water and supercritical CO_2 were all considered to be viable options. An alternative approach would be to skip the extraction step by immerging flaked oilseeds in ethanol and catalyst and then using ethanol for extraction of ethyl esters of fatty acids. Ethyl esters would be more environmentally friendly as ethanol is produced by fermentation of biomass as opposed to methanol from fossil fuels. Moreover, this method is hexane free.

The supply of olive oil is in surplus so improvements to the processing of olives needs to be focused on quality improvement and the reduction of aqueous waste streams so alternative methods of extraction and the treatment of waste water have been considered. Supercritical CO_2 extraction has been presented as a more efficient extraction method alternative to solvent extraction in seed oil refineries and these conditions are very suitable for olive oil extraction. These extraction conditions (28-30^{o}C and 300bar) are very similar to the old traditional cold pressing and this was good enough reason to examine the possibilities. Supercritical CO_2 has produced much higher extraction yields of oil from most mediums, the oil was of much higher quality due to low temperature and no solvent residues remain in the extracted oils.

Examination of the wet waste effluents of the olive mill confirmed that high value by-products could be derived from this waste stream, potentially generating sufficient income to eliminate the environmental impact of the effluent. These by-products include polyphenols, recovery of 3- 5% residue olive oil by filtration or skimming, soluble, fermentable sugars for ethanol and

CO_2 generation and a possible source of Squalene. The technology for reduction and/or utilization of olive mill wastes exists but it must be tailored to the size and economic means of the olive mill in order for these technologies to be applicable at the point of production and thus offer the maximum benefit.

There are existing, and potential value added applications for renewable oils and these are predominantly related to specialised consumer use such as, in order of end value, industrial, food and personal care. As the value chain grows the degree of purification and natural/green nature of the extracted oils becomes more important. For example, there is a move away from solvent extracted oils to crushed seed oils as traditional solvents are viewed as non-green and potentially harmful. ‘Greener’ solvents could be considered but ideally oils recovered without solvent use are now required. Value and diversification can be added by producing more functional oil derivatives or extracting additional materials. Proteins, polysaccharides, liposomes and squalene were all identified as having both high value and market potential

As well as short–term, practical considerations, modelling and optimization studies were conducted on a range of oil biorefinery-related processes. The processes ranged from upstream schemes such as oil extraction (cold-pressing and hexane-based extraction), protein extraction and supercritical CO_2 extraction from wheat straws to actual biodiesel production and downstream processing of biodiesel by-products and their subsequent conversion to added-value chemicals such as succinic acid. Levulinic acid production was identified from the modelling as a high value product that could be produced cost effectively from the biorefinery. Overall 11 different schemes were studied. The economic viability and the environmental impact of each scheme was investigated through economic studies and integrated Life Cycle Analysis (LCA) taking into account production rates for main products, by-products/wastes, prices of materials, emissions’ rates/energy requirements, capital and other operating costs. Direct comparisons between different biodiesel production processes including various upstream and downstream routes were made using results from the optimization and Life Cycle Analysis studies performed.

The expansion of oil crop production or of an increased number of oil biorefineries will have social and economic impacts. Various policy scenarios to understand any potential environmental, economic and policy constraints which the bioenergy and biorefinery sector could face within a sustainable development framework have been developed. Within a selected region potential stakeholders were identified and the social network within which firms and institutions (potentially involved in the production of biodiesel) operate was identified. Data related to the niche creation mechanism and the knowledge base of the stakeholders was also identified and from this the optimal balance of economic drivers and knowledge transfer was determined. Such a policy-mix would guarantee the emergence of a clear and stable converging trend towards the full innovation niche within the considered ten-year timeframe and would ensure an efficient allocation of public resources.

This project has drawn together academic and industrial knowledge in the field of oil crop biorefineries and has delivered a wide range of reports that have proposed both short-term and longer term changes that can enhance the competitiveness of this sector. It has developed practical solutions and models for future growth and has disseminated this information widely. Further information can be found on the SUSTOIL website at www.sustoil.org