1. Publishable Summary

The GLYFINERY project is an initiative aimed at the sustainable and integrated production of biofuels, energy and green chemicals from glycerol in newly implemented biorefineries. The GLYFINERY concept represents a sustainable solution for management of the glycerol by-product from biodiesel refineries improving the economics and environmental impact of existing processes.

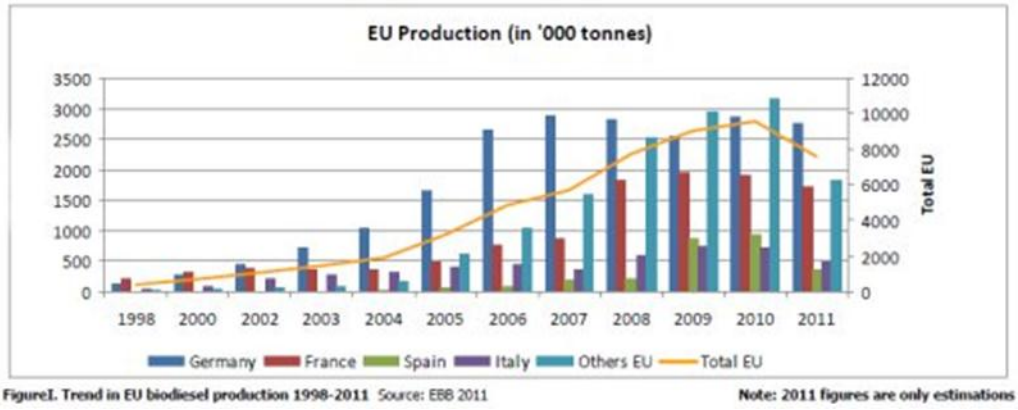

Figure 1.1: European biodiesel production from 1998 to 2011.

The EU target to increase the use of renewable energy in the transportation sector in the near future has already started to boost the production of biodiesel from rapeseed and other vegetable oils. Over 9.5 million tonnes of biodiesel were produced in the European Union in 2010 (Figure 1.1), a considerable increase over the 4 million tonnes produced in 2005. This has led to an immense increase in the production of glycerol (an unavoidable by-product from the transesterification process) in volumes which already exceed the current market demand for direct material use.

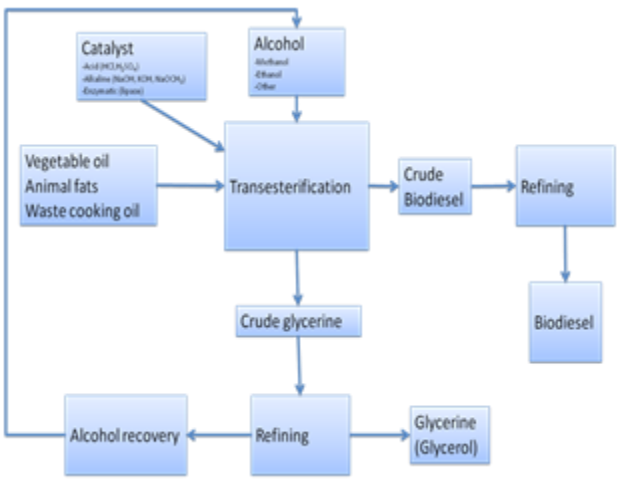

Figure 1.2: Flow chart of a typical biodiesel process showing raw materials and products.

In a typical biodiesel process (as shown in Figure 1.2), approximately 10% of the reaction volume ends up as crude glycerol. Glycerol production levels are increasing in line with biodiesel production (more than 900,000 tonnes in 2010). Although over 2000 pharmaceutical, food and other uses are known for glycerol, a large (and increasing) fraction is incinerated or stored as excess in an already saturated market. There is an urgent need, therefore, for research and technological development of processes for conversion of glycerol to valuable products, not only to solve waste disposal problems but also to improve the economy of biodiesel production.

The GLYFINERY project is targeted to developm conversion of glycerol by micro-organisms, into known and new advanced liquid biofuels,

bioenergy and biochemicals. Strains suitable for growth on glycerol and production of the desired products will be designed, tested and improved using metabolic engineering strategies. Bioprocesses will be designed and optimised for each of the selected desired products in turn at lab-scale, and the most promising process scheme will be tested at pilot-scale as an integrated concept. Efficient recovery processes will be developed for the products of interest. The ultimate goal of the project is to demonstrate the suitability and sustainability of the GLYFINERY concept for implementation into large-scale biorefineries.

The project is co-ordinated by the **Technical University of Denmark**. A team of 6 research staff are associated with the project at DTU, involved primarily in the tasks of strain discovery and improvement, biological conversion of glycerol and optimisation of the bioprocesses. The target products are biofuels and bioenergy. **BioGasol**, a Danish engineering and technology company, and **A&A Biotechnology**, a Polish biotechnology company, also work in parallel on strain development and optimisation of fermentation processes towards a number of different target products. BioGasol are primarily interested discovery of strains and development of processes for higher alcohols, with A&A Biotechnology directing efforts towards green chemicals. The glycerol for the project is supplied by the Slovakian biodiesel company **MEROCO**, who also provide technical data and chemical analysis on the glycerol feedstocks. **ProChimia Surfacees**, a Polish start-up company with expertise in purification, is responsible for development of lab-scale purification processes for the recovery of liquid biofuels and green chemicals in the post-fermentation broths. An integrated assessment on sustainability of the process as a whole will be conducted by **The Institute for Energy and Environmental Research** in Germany. The aim is to define the systems which represent an optimum between lowest costs and biggest environmental benefits. Throughout the project, each part of the process will be assessed in terms of technological, environmental and economic aspects as well as use and disposal scenarios for products. The proposed GLYFINERY concept will be compared to existing possibilities for biofuels and conventional energy sources.

GLYFINERY is a 4 year project, with a pilot-scale GLYFINERY for integration into large-scale biorefineries as the final goal. Towards this goal, the work is divided into 6 key research areas which are overlapping and interdependent (Table 1.1).

Table 1.1: Timeline for the GLYFINERY project, showing key research activity areas.

Research activity	**Year 1**		**Year 2**		**Year 3**		**Year 4**	
Characterisation of glycerol feedstocks								
Discovery of microorganisms								
Biological conversion of glycerol								
Product recovery								
Process integration in pilot scale								
Integrated assessment								

The first and second years of the project focussed on characterisation of the glycerol is the substrate in the Glyfinery, the discovery of micro-organisms which can utilise this substrate, and the development of fermentation processes for the biological conversion. In parallel to bioprocess design, recovery processes for the target products have also been investigated and optimised.

The glycerol feed stock for the project was supplied by the biofuels company Meroco. A number of batches of glycerol were analysed over the first year of the project in order to obtain information on batch-to-batch variability, with no significant differences being found. Following the chemical analysis, preliminary research was performed on assessing the biodegradability of the glycerol feedstocks. Our results have shown that glycerol can be effectively consumed and converted to biogas under both mesophilic and thermophilic conditions. The glycerol consumption rates achieved in the systems indicated that glycerol was highly biodegradable under the conditions employed, with an acceptable level of methane in the biogas derived.

The target products for the GLYFINERY project are biofuels (ethanol and butanol) and the green chemical 1,3-propanediol (1,3-PDO). Work has, therefore, developed along parallel lines towards the production of tailored biocatalysts for these products. Anaerobic bacteria of the genus Clostridium have been developed as hosts for the conversion of glycerol to 1,3 – PDO and butanol. A non-conventional yeast, *Pachysolen tannophilus*, which is well known for conversion of xylose to ethanol was optimised for production of ethanol from glycerol. Laboratory scale fermentation processes were performed to provide initial data on sustainability and viability. The post-fermentation broth samples of alcohol and 1,3-PDO processes were subjected to the variety of recovery techniques, including specifically steam distillation, solid phase extraction and liquid-liquid extraction. Recommendation of the most suitable product recovery method for pilot-scale process will be in line with the final processes selected for scale-up.

In the third and fourth year of the project product spectrum of the GLYFINERY was expanded to five potential products: 1,3-PDO, butanol, ethanol, biodiesel and biomethane. Each of these processes was optimized to define the scale-up procedure, and initial pilot scale tests were conducted. The residuals from the fermentation processes were fed into an anaerobic digester for the production of biomethane. There was close collaboration between production and recovery in order to develop methods and processes which are economically viable and environmentally responsible. To support this concept, the consortium has collaborated closely on the Integrated Assessment of all processes, studying further the technical, environmental and economic parameters and goals for the integrated GLYFINERY concept. The first LCA calculations based on preliminary data and the current status of definitions and specifications were performed. There was also particular focus on the economic assessment, including costing of equipment, utilities, and non-process parameters, as well as a market analysis and development of a country specific plant index.

The consortium has worked further on scale-up and optimisation of the processes and recovery at larger scale. This has involved incorporation of novel technologies and in particular optimisation directed towards economically viable operation. There has been focus on integration of results and application of the data in the assessment reports which determine the technical, environmental and economic viability of the processes.

Overall the GLYFINERY project has demonstrated that biological conversion of glycerol to value added products is a relevant and necessary route to a sustainable society with effective waste management. As with all industrial processes, the benefits can be further increased continuous improvement of process efficiency towards higher product titres.

The GLYFINERY project has focussed on alternative uses for glycerol in an effort to establish technologies to convert waste streams to value added products. As fossil oils continue to be depleted, the demands of modern society for alternative sources of biochemical, energy and fuels

will be increasingly dependent on biotechnological solutions. Biodiesel production has been increasing in capacity considerably over the last 10 years and thus has provided a glycerol glut. Direct material use of the glycerol is possible, but in a limited market. Direct material use of glycerol will be likely to lose importance, depending on the expansion of the biodiesel market and thus the increase in the production of glycerol – at least if no completely new material use options will be identified. To the extent to which a direct material use cannot be realised anymore because of limited capacities, innovative use options and the use for energy production including biogas can play a bigger role in future. The conversion of glycerol to ethanol, butanol or PDO by means of innovative biotechnological processes is technically demanding and energy consuming, which causes high economic and environmental expenditures. However, alternative energy and fuel sources are needed, and thus society, politicians and industries will be required to support biotechnological solutions in a future biobased economy.

The glycerol pathways assessed in this study represent only a part of the future use options of glycerol resulting from biodiesel production (although an important one), if a considerable increase of the glycerol supply should really take place in the next years. Thus, it will be the subject of future research to identify further use options for glycerol and to assess their environmental impact, economic effects and technological performance – analogous to the evaluation criteria used in this study. Furthermore, a politically relevant and comprehensive rating of glycerol use options also has to take other aspects into account like the security of the energy and food supply, social aspects or the progress of knowledge, gained through development of high-tech processes, which is especially important for industrialised countries in Europe. This also must be left for further studies to investigate. Nevertheless, this study already shows a substantial potential for future alternative use options of glycerol resulting from biodiesel production if its supply considerably increases in the future.

The results of the project can be followed at our website - www.glyfinery.net. Further information can be received by using the contact form on our website or by contacting the manager of the project at the Technical University of Denmark. Email: Mhairi Workman, mwo@bio.dtu.dk, telephone +45 4525 2700.