SUPERMETHANOL
The GtM Concept

Project Summary (March 2012)

Grant agreement number:	212180
Project acronym:	SUPER METHANOL
Project name:	Reforming of Crude Glycerine in Supercritical Water to Produce Methanol for Re-Use in Biodiesel Plants
Call:	Call FP7-ENERGY-2007-1-RTD
Activity code:	ENERGY.2007.3.3.2: New Uses for Glycerine in Biorefineries
Keywords:	glycerine, valorisation, biodiesel production, biofuels, methanol
Duration:	January 2008 – December 2011 (48 months)
Total cost:	€ 2,997,449
Commission funding:	€ 2,093,414
Project website:	www.supermethanol.eu

Project partners

- BTG Biomass Technology Group BV (NL)
- Acciona Servicios Urbanos s.r.l. (Spain)
- Boreskov Institute of Catalysis, Siberian Branch of Russian Academy of Sciences (Russia)
- Rijksuniversiteit Groningen (The Netherlands)
- University of Maribor (Slovenia)
- UHDE High Pressure Technologies (Germany)
- SPARQLE International B.V. (The Netherlands)

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Justification

Biodiesel is produced by transesterification of vegetable oils with methanol. Glycerine is a major by-product of this process. Due to the rapid increase in biodiesel production capacity in Europe also the amount of (crude) glycerine has increased rapidly. Since 2004 the amount of glycerine produced exceeds the actual consumption, and the mismatch is increasing. By lack of viable market outlets for the extra glycerine supply its price has plummeted, and in late 2006 the price was not much higher than its value as fuel. With the flattening of the growth in biodiesel production, glycerine prices have increased significantly again. Nevertheless, leading stakeholders in the EU biodiesel sector confirm that there is an urgent need to identify new (crude) glycerine applications.

Project objectives

The *overall objective* of the project is to produce methanol from crude glycerine, and re-use the methanol in a biodiesel plant. This project aims to improve the energy balance, the carbon performance, the sustainability and the overall economics of biodiesel production, and to reduce the sensitivity of biodiesel plant economics to volatile methanol and glycerine prices.

The *specific project objectives* include:

- Demonstration of the complete glycerine-to-methanol process on laboratory and pilot plant scale. The specific targets are to achieve glycerine conversions >90%, and to produce a syngas with $H_2/CO > 1$, < 20 vol.% CO_2 and < 10 vol.% (CH_4+C_2^+). The overall target is a yield of 50 wt% methanol from glycerine (energy efficiency > 70%).
- Preparation of a detailed design for a full-scale methanol production facility integrated in a commercial biodiesel production plant, and to establish production costs for the glycerine-derived methanol. The target is to produce methanol at a price below 250 EUR per tonne.

Background

The work in this project expands on expertise of the project partners on the reforming of biomass in supercritical water[1], among others in research projects financially supported by Dutch, European and Japanese research programmes. E.g. in a previous EU funded project, SUPERHYDROGEN[2], a large number of biomass types were tested for their suitability as feedstock for the reforming process. Glycerine was identified as the ideal feedstock for this technology.

In a subsequent study project co-ordinator BTG explored the technical and economic potential to substitute fossil fuel based methanol with "renewable" methanol, produced through supercritical reforming of crude glycerine. The Dutch study, completed in December 2006, showed the glycerine-to-methanol (GtM) process to be promising. A simplified diagram of the proposed system integrated in a biodiesel plant is shown in Figure 1. Through GtM more than 50% of the required methanol can be produced, while some combustible gases are returned to the biodiesel production plant. Water is required as a feed, while the ash in the crude glycerine is the main by-product together with CO_2.

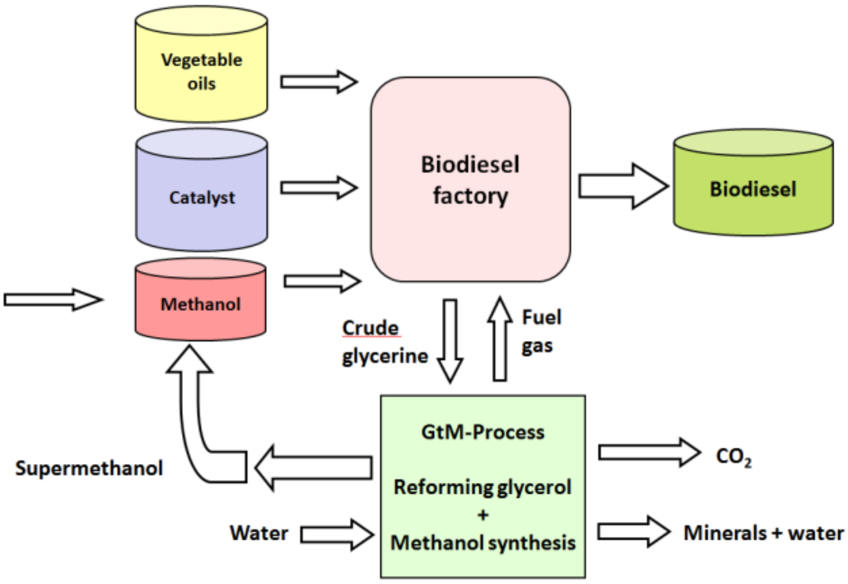

Figure 1. Simplified diagram of the biodiesel production unit coupled with the GtM process

Research issues

To demonstrate the complete glycerine-to-methanol process the three core processes of this chain were first analysed, developed and demonstrated at lab scale. The three core issues are (a) the reforming of glycerine in supercritical water – "RSW", (b) the conditioning of the raw synthesis gas and (c) the methanol synthesis process. Main research issues included e.g.:

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[1] Water becomes supercritical at T=374 °C and P=22 MPa.

[2] Full tile: Biomass and Waste Conversion in Supercritical Water for the Production of Renewable Hydrogen. Contract ENK6-CT-2001-00555. The project ran from December 2001 until November 2005 (48 months).

- The raw synthesis gas composition depends on a number of parameters: A dedicated study on the reforming of crude glycerine was carried out, focussing on longer term effects (especially build up of contaminants), and recycling of tail water;
- The raw synthesis gas is rich in CO_2: experiments, supported by thermodynamic calculations, were carried out to reduce the CO_2 concentration, within the RSW process itself or in subsequent conditioning steps. Further experiments however indicated that also CO2 can be selectively hydrogenated to methanol. Focus thus also included towards syngas with high CO_2 content. Experiments were directed to reduce hydrocarbons in raw synthesis gas, possibly by use of catalysts.

In the second phase of the project the core processes were integrated into a small pilot plant (near 1 litre/hr unit, fully integrated with syngas upgrading, and methanol synthesis). An experimental programme was carried out in this set-up to generate data for a blueprint for a 1 t/hr full-scale demonstration unit that would be integrated with an existing ACCIONA biodiesel plant. The detailed design is based on the results from experiments and modelling, and includes the integration with the biodiesel plant, legislation and safety aspects, etc. A cost estimate (investment, operation and maintenance costs) and a calculation of the production costs for glycerine-derived methanol will be part of the design. The construction of the demo unit is outside the scope of this project.

Results
The main outputs of the project include:
- Tested lab rigs for three unit operations, respectively (a) supercritical biomass reforming, (b) raw synthesis gas improvement and (c) methanol synthesis
- An integrated glycerine-to-methanol pilot plant (100-1000 g/hr glycerine input)
- Process models for the three unit operations and the integrated glycerine-to-methanol chain validated with the results of pilot-scale and real-scale experiments
- Knowledge of the economic viability of decentralised glycerine-to-methanol (GtM) production vs. large-scale centralised fossil fuel based methanol production
- A detailed design of a full-scale GtM demo plant to be installed at an existing biodiesel plant
- Contribution to future bio-based economies
- An international workshop on new applications and uses of glycerine

Impact
Strategic impacts of the project include:
- Development of an innovative technology for the conversion of glycerine into a raw material for renewable transport fuel production
- Optimal integration of this innovative technology with current and future medium-scale biodiesel plants
- Maximisation of the renewable energy output from biodiesel production plants
- Fundamental and experimental know how on methanol synthesis, process- and quality related.

Project progress
In WP1 tests were carried out at **BTG** in the lab-scale test rig that integrates glycerine reforming and methanol synthesis. Together with **RUG**, the testing programme, started in Year 3, was completed. It generated abundant data to help understand the main reaction mechanisms. **MARIBOR** completed methane reforming tests in its lab rig. **BIC** produced a range of catalysts for upgrading of RSW gas. The catalysts supplied by BIC were extensively tested at **RUG,** and led to the production of 2 (including 1 joint) scientific articles on reforming experiments. **SPARQLE** formulated possible concepts for reforming technical grade glycerol, for separating salt from this feedstock, and for the recycle of tail water and CO_2. **BTG** led work on the conditioning of glycerine i.e. salt separation (ash recovery) and glycerol modification. A dedicated desalination unit to investigate and optimise the *in-*

situ removal of the ash in glycerine was set-up and tested. Glycerine desalination however appeared complicated as severe polymerisation of glycerine was noted.

In WP2 **MARIBOR, RUG** and **BTG** operated test rigs for experimental testing of commercial and BIC catalysts for methane steam reforming, methane dry reforming and reverse water gas shift reaction. **RUG/BTG** performed high pressure methanol synthesis experiments in a view cell reactor, and managed to demonstrate the formation of a *liquid phase*. **RUG/BTG** developed and validated a model to predict the equilibria in high pressure methanol synthesis when the formation of a liquid phase occurs. **RUG/BTG** also conducted an extensive research programme to high pressure methanol synthesis for different gas composition, temperatures and pressures. The high conversions the model predicted were confirmed experimentally. **RUG** arrived at conclusions for methanol quality, and specifically the water and higher alcohol concentration, versus operating conditions. **RUG** also analysed the synthesised methanol for biodiesel production.

In WP3 **MARIBOR, BTG & RUG** jointly develop process models and simulations, covering (a) the entire process and (b) the methanol synthesis reactor, to analyse effects of operating conditions on overall performance. Different models were explored, ranging from models validating the glycerine reforming (**MARIBOR**), analysis/modelling of methanol synthesis (**RUG**) and an integral model of the complete GtM approach (**BTG**). **RUG** extended the adiabatic model that describes methanol synthesis with heat withdrawal by a cooling medium.

WP4 covers design, setting up and testing of the process demonstration unit (PDU, or pilot plant). The set-up constructed at **BTG** integrates RSW and methanol synthesis. **RUG/BTG** implemented an extensive experimental programme, and identified a more cost-effective approach to demonstrate higher carbon conversion from glycerol to methanol. This led to the modification of the GtM-PDU and a change of reforming reaction conditions. Additional experiments were conducted focussing on the conversion of glycerol to mainly H_2 and CO_2, followed by methanol synthesis in the modified GtM-PDU. A methanol yield of over 63 % was reached, well above the initial 50% target yield.

In **WP5** BTG -supported by **ACCIONA-** prepared an update of the 2009 glycerine market study, covering current glycerine uses, R&D on glycerine valorisation, and relevant market actors. UHPT – supported by BTG and RUG- prepared an engineering package (blueprint) for the full-scale GtM demonstration unit. And ACCIONA, supported by various consortium partners, carried out a technical and economic feasibility study for a GtM demonstration unit to be built adjacent to ACCIONA's biodiesel plant in Navarra (Spain). As at the present time construction of such GtM appears not economic ACCIONA will not proceed (yet) to the actual building of the GtM demo unit.

Finally, within **WP6** project results were regularly presented at conferences, and several peer-reviewed articles were planned and/or prepared. Special achievements were the organisation by **ACCIONA/BTG** of the International Workshop on "*Innovative uses of glycerine from the biodiesel process*", and the production of a short promotional video on the GtM process. The dissemination workshop was organised in collaboration with the sister RTD projects GLYFINERY and PROPANERGY.

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SEVENTH FRAMEWORK PROGRAMME