SUPERMETHANOL
The GtM Concept

Project Summary (February 2011)

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)

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+$C2^+$). 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, and with global mass balances, 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.

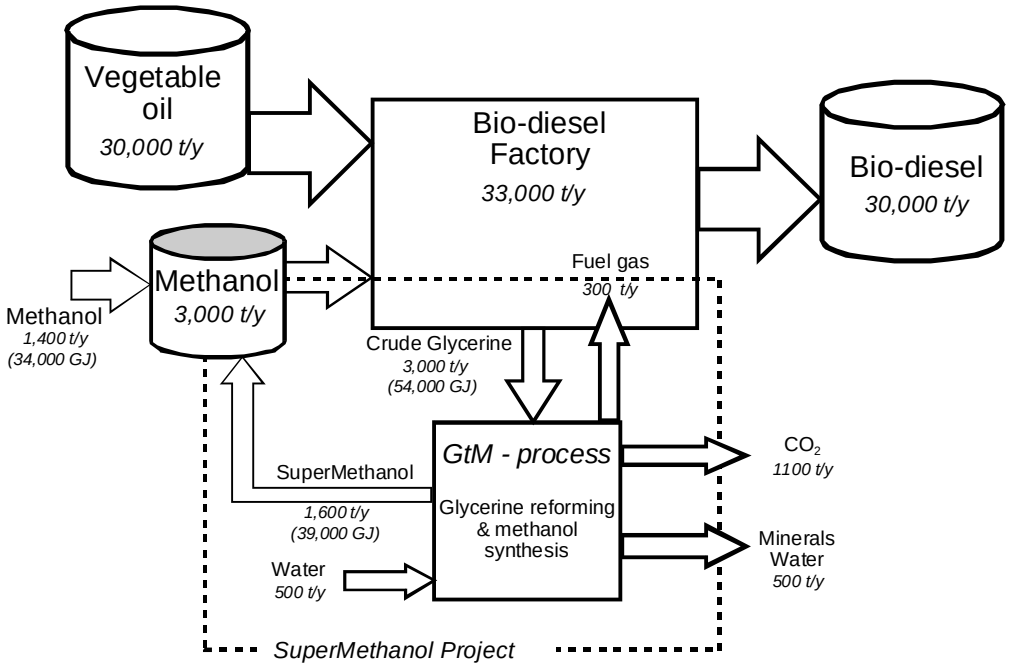

Figure 1. Simplified diagram of the biodiesel production unit coupled with the GtM process

Research issues

To demonstrate the complete glycerine-to-methanol process the three core processes of this chain will first be 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 include e.g.:

- The raw synthesis gas composition depends on a number of parameters: A dedicated study on the reforming of crude glycerine will be carried out, focussing on longer term effects (especially build up of contaminants), and recycling of tail water;

[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 is rich in CO_2: experiments, supported by thermodynamic calculations, will be carried out to reduce the CO_2 concentration, within the RSW process itself or in subsequent conditioning steps.

Experiments will be directed to reduce the hydrocarbons in the raw synthesis gas, possibly by use of catalysts.

The second project phase has gone underway and the core processes have been integrated into a small pilot plant (near 1 litre/hr unit, fully integrated with syngas upgrading, and methanol synthesis). An experimental programme is underway in this set-up to generate data for a blueprint for a 1t/hr full-scale demonstration unit that would be integrated with an existing ACCIONA biodiesel plant. The detailed design will be based on the results from experiments and modelling, and will include 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.

Expected results

The main outputs of the project include:

- Tested lab rigs for three unit operations, respectively (a) supercritical biomass reforming, (b) raw synthesis gas upgrading, 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 GtM production vs. large-scale centralised fossil fuel based methanol production
- A detailed design of a full-scale glycerine-to-methanol 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

Expected 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

Work performed since the beginning of the project

In WP1 a lab-scale test rig was constructed at BTG to study the reforming of glycerine. The rig has been integrated with a methanol synthesis set-up. Together with RUG, a testing plan has been finalised, and sufficient data are generated to help understand the main mechanisms behind reforming in supercritical water. Such data are used for further developing the demo plant design. ACCIONA supplied batches of crude glycerine for testing. A test rig was constructed and initially tested at MARIBOR for the further reforming of methane. BIC produced and tested a range of steam reforming catalysts as well as catalysts for the upgrading of the RSW gas. 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. In addition, a set-up was built to investigate and optimise the in-situ removal of the ash in glycerine in a dedicated desalination unit (BTG, BIC, MARIBOR).

In WP2, BIC developed, prepared, tested and delivered catalysts for methane steam reforming, methane dry reforming and reverse water gas shift reaction. MARIBOR, RUG and BTG constructed

test rigs for experimental testing of commercial and BIC catalysts. Methanol synthesis experiments are carried out successfully.. A patent application will be filed in due course.

In WP3 MARIBOR, BTG and RUG jointly develop process models. Different types of models were explored, ranging from models validating the RSW (MARIBOR), analysis / modelling of methanol synthesis (RUG) and an integral model of the complete GtM approach (BTG). RUG developed an adiabatic reactor model to describe methanol synthesis in a packed bed reactor. The model will be used to optimise reactor performance.

WP4 covers pilot plant design, setting up and experimental testing. BTG constructed a lab-scale pilot plant combined RSW - methanol synthesis reactor and reconstructed a larger pilot plant for this purpose. First initial mass and energy balances were made, based on the use of RME glycerine. UHPT summarised the known and unknown design conditions for the overall GtM concept.

For WP5 exploratory research was conducted. ACCIONA provided technical specs of its biodiesel plant in Caparroso (Navarra region, Spain). BTG and ACCIONA drafted a market study covering current glycerine uses, R&D on glycerine valorisation, and relevant market actors. The market study will be expanded and updated throughout the project.

WP6 covers project management, dissemination and exploitation. To date six meetings were held; two each in 2008, 2009 and 2010. ACCIONA prepared a Dissemination & Awareness Plan and an Exploitation Plan for use by the project consortium. Both documents will be updated throughout the project.

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