CONVERSION OF GLYCEROL TO “GREEN METHANOL” IN SUPERCRITICAL WATER

Maša Knez Hrnčič, Mojca Škerget, Ljiljana Ilić, Željko Knez*,
University of Maribor, Faculty of Chemistry and Chemical Engineering,
Laboratory for separation processes and product design,
Smetanova ulica 17, 2000 Maribor, Slovenia
zeljko.knez@uni-mb.si

Crude glycerine is a by-product of biodiesel production. European directives prescribe that 5.75% of all transportation fuels should be made from renewable sources in 2010. The capacity of European biodiesel production is therefore increasing rapidly, from approx. 3 million tons per year in 2005 up to an expected amount of 7 million tons in 2007. Biodiesel is generally made when fats and oils are chemically reacted with an alcohol, typically methanol, and a catalyst to produce an ester, or biodiesel (generally known as trans-esterification). As every tonne biodiesel roughly consumes 100 kg methanol and produces the same amount of crude glycerine, the world’s methanol demand increases while on the other hand the glycerine market becomes glutted. In the process glycerin should be reformed in supercritical water (RSW), followed by a high-pressure methanol synthesis process (producing ‘super methanol’).
An interesting option addressing the surplus of glycerin and the request for methanol is to produce methanol from the crude glycerin by the biodiesel producer itself. They will then be less dependent on the methanol spot price. When improved technologies should be developed, the costs for small-scale methanol synthesis can be reduced considerably. Glycerine is an ideal feedstock for this technology. Extensive research on substitution of fossil fuel based methanol with “green” methanol, produced through a process referred to as supercritical reforming of (crude) glycerine (**GtM** – **G**lycerine-**t**o-**M**ethanol) is performed. Preliminary results showed that GtM is a very promising route. Through GtM more than 50% of the required methanol can be produced, while some combustible gases (mainly CH_4 and C_2^+) should be returned to the biodiesel production plant.

Key words: biofuel, biodiesel, glycerine, methanol, supercritical fluids

INTRODUCTION

Biodiesel is generally made when fats and oils are chemically reacted with an alcohol, typically methanol, and a catalyst, typically sodium or potassium hydroxide, to produce an ester, or biodiesel (generally known as trans-esterification).
Because of tremendous interest in developing sustainable energy systems there is the aim of harnessing the chemical energy in biomass, which is a renewable resource.

Figure 1: Bio diesel production plant

A large percentage of the mass of harvested biomass is in water. Removing this water from biomass prior to processing increases the energy requirements and costs needed to convert biomass to gas or liquid fuels. Therefore, there is interest in processing methods suitable for biomass with high moisture content.

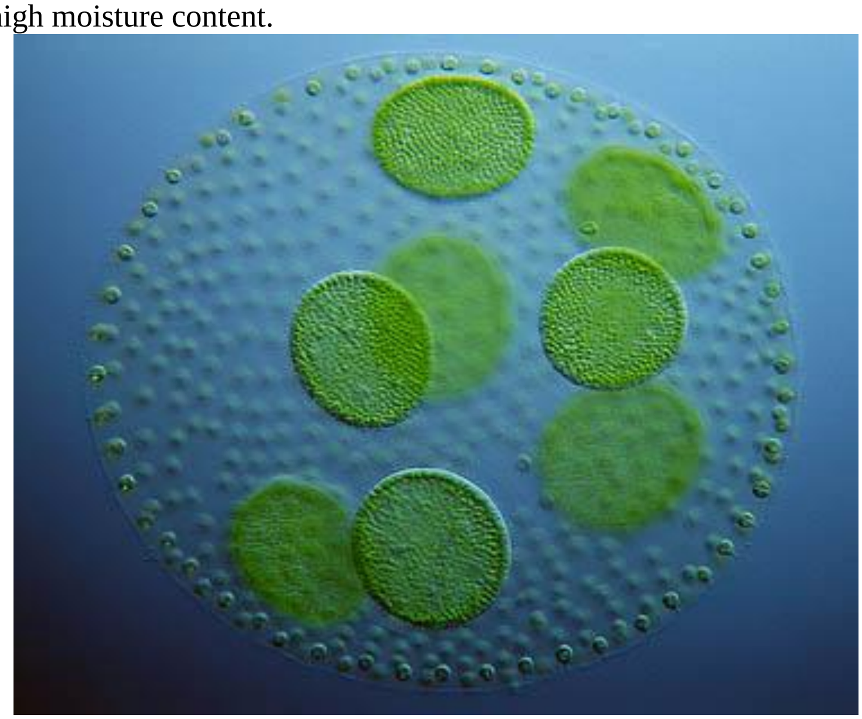

Figure 2: Algae as a source of bio fuel

One general approach is to process the biomass in an aqueous phase. The specific implementation of this approach of interest is supercritical water gasification (SCWG), which involves the conversion of organic compounds to gaseous products (H_2, CO, CO_2, and CH_4) via reactions in and with water at a temperature and pressure exceeding the thermodynamic critical point (Tc = 374 ◦C and Pc = 22.1MPa) [1,2].
Laboratory for separation processes and product design of University of Maribor suports the analysis with (fundamental) experimental work by determination of phase equilibria in the systems (Gas-Liquid equilibrium) of water and CO_2, water- and mixtures of CO_2-CO- H_2 - CH_4 and water- CO_2 - H_2.
Additionally, the water used in the process will extract the main, if not all, contaminants from the gas. Additional gas cleaning is not required. Some gas conditioning (like adjusting the gas composition) may be required. The syngas becomes available at 300 bar. This has the advantage that due to the high pressure a once-through option for the methanol synthesis is possible. There is no need for any recycling of gas, thus avoiding high gas compression costs.
The quality of the methanol is expected to be good enough for use in the biodiesel production. Expensive methanol purification may be limited or absent.

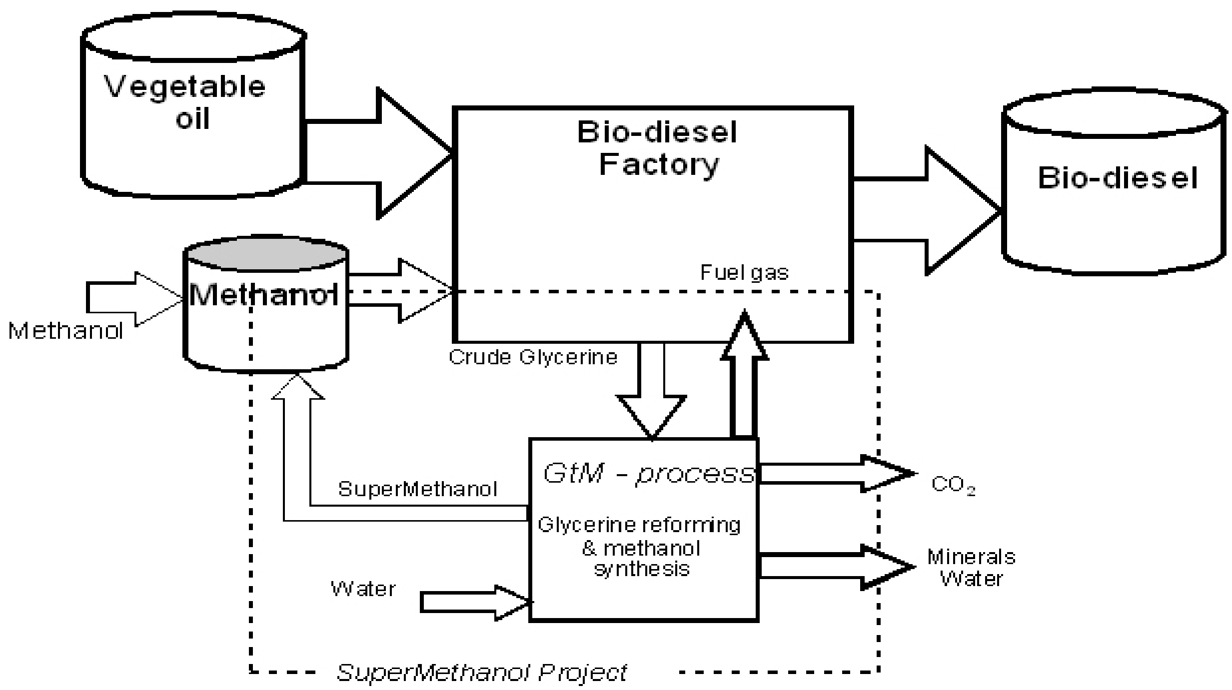

Figure 3: Simplified diagram of a biodiesel production unit coupled with the GtM process

For the GtM process preliminary mass and energy balances need to be established. For each of the separate processes, selected research issues have been identified based on prior research that needs further investigation. Methanol price should be below 250 EUR per tone. Laboratory for separation processes and product design of University of Maribor leads the modeling work on the RSW and the MeOH process. The intention of this research is to generate additional know-how on the pilot plant design (heat transfer, CO_2 liquefaction, reactor design), assist in the design of the demonstration unit, and to generate a learning model. Besides, overall mass and energy

balances for the GtM concept need to be generated. Modeling work should enable to justify process configurations and reactor choices (both for RSW and methanol synthesis), establish possibilities for water and CO_2 recycle streams [3].
Reforming in supercritical water is in its infancy. By treatment at supercritical water conditions of 600°C and 300 bar, but in the absence of added oxidants, organics can be converted into a hydrogen-rich gas. Main advantages of the RSW technology are suitable to convert very wet biomass and liquid streams; the produced gas is very clean, and free of tars and other contaminants; the raw gas is very rich in hydrogen (50 - 60 vol%), the gas becomes available at high pressure, avoiding the need for expensive compression. Water can be part of the feedstock or added to the system. Besides being a reagent, water is also the "heat carrier" in the system. The emphasis are on gas yields, carbon conversion, reliability and optimal operating window. A specific task here is to determine the effect of heating rate, biomass to water feed ratio, operating conditions on the gas composition. In RSW process, (crude) glycerine is directly injected in the reactor where water is present at supercritical conditions. Upgrading steps and other aspects of RSW is observed: the consequences of recycling tail water on the process characteristics and the possibilities for the (liquid) CO_2 recycle are investigated. Likely the gas derived from the RSW unit should to be further upgraded to reduce the hydrocarbon concentrations (CH_4 and C_2^+), and to obtain a syngas with higher CO/CO_2 ratios. Approx. 50 catalysts will be screened and later tested using artificial gas. The best candidates will be tested in the pilot plant on real RSW gas.

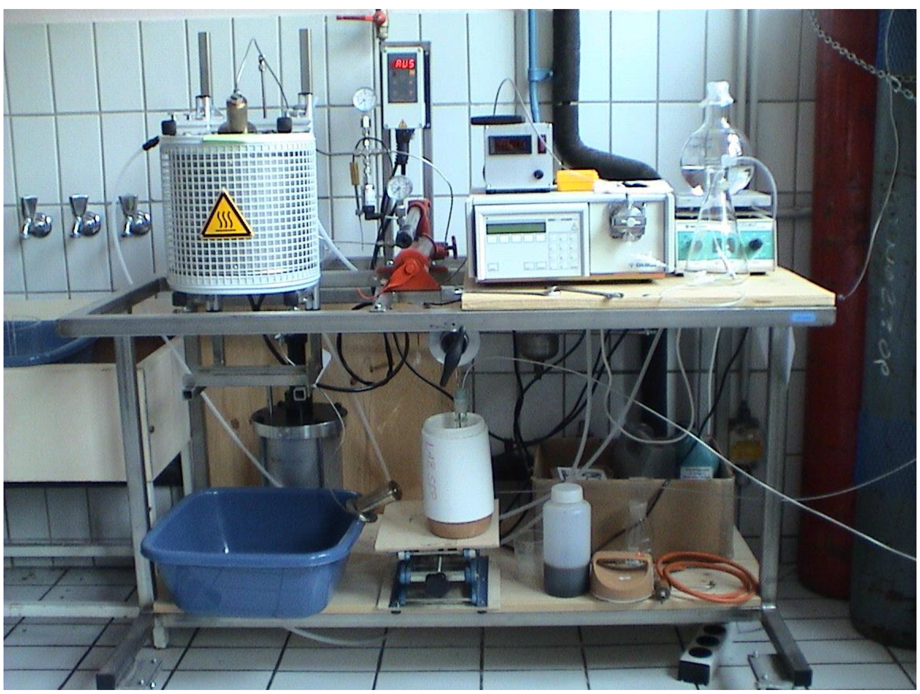

Figure 4: RSW unit, located at Laboratory for separation processes and product design (UM, FKKT)

Through GtM more than 50% of the required methanol can be produced, while some combustible gases (mainly CH_4 and C2+) 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.

Together with modeling it is an input for the construction and operation of the pilot plant and to design the full-scale demo. The aim is to support analyses of supercritical gasification of glycerine, particularly in the reactivity of supercritical water and the further reforming of the methane and higher hydrocarbons in the syngas.

RESULTS AND DISCUSSION

A 'RSW' unit was constructed (maximum 650^{o}C and 300 bar), in which specifically the conversion of methane, produced in RSW of glycerine, is to be reformed further. Selected catalysts, prepared by BIC (Borskov institute of catalysts), are tested. Initial gas phase composition H_2:CO:CO_2:CH_4 = 50:20:20:10 has been supplied. Target is to reduce hydrocarbon concentration at (relatively) low temperatures. Phase equilibrium data for the systems water (pure and tail water) / various gas mixtures are in progress to be determined. It has been found out that the solubility of gas (hydrogen, helium) in water is very low but it increases with increasing pressure at constant temperature. Solubility data for some binary systems were found in literature and were compared with measured data.

On basis of data generated by partners on the RSW and synthesis of methanol respectively, will be analyzed and interpreted in terms of overall mass and energy balances. Flow sheeting will be carried out ('Aspen'), and specific modeling tools in the area of heat integration ('Supertarget') for the overall GtM concept, and where relevant and possible, integration with biodiesel manufacturing will take place. Among all the methods for gasifying biomass, supercritical water gasification (SCWG) has its advantages of high efficiency and adaptation to a broad range of biomass feedstock. Thermodynamic behavior of SCWG has not been systematically studied yet. In supercritical state, according to the equation of state for the mixture, the fugacity of each species is an extremely complicated function of pressure, temperature and mixture composition (e.g. molar fraction)[4].

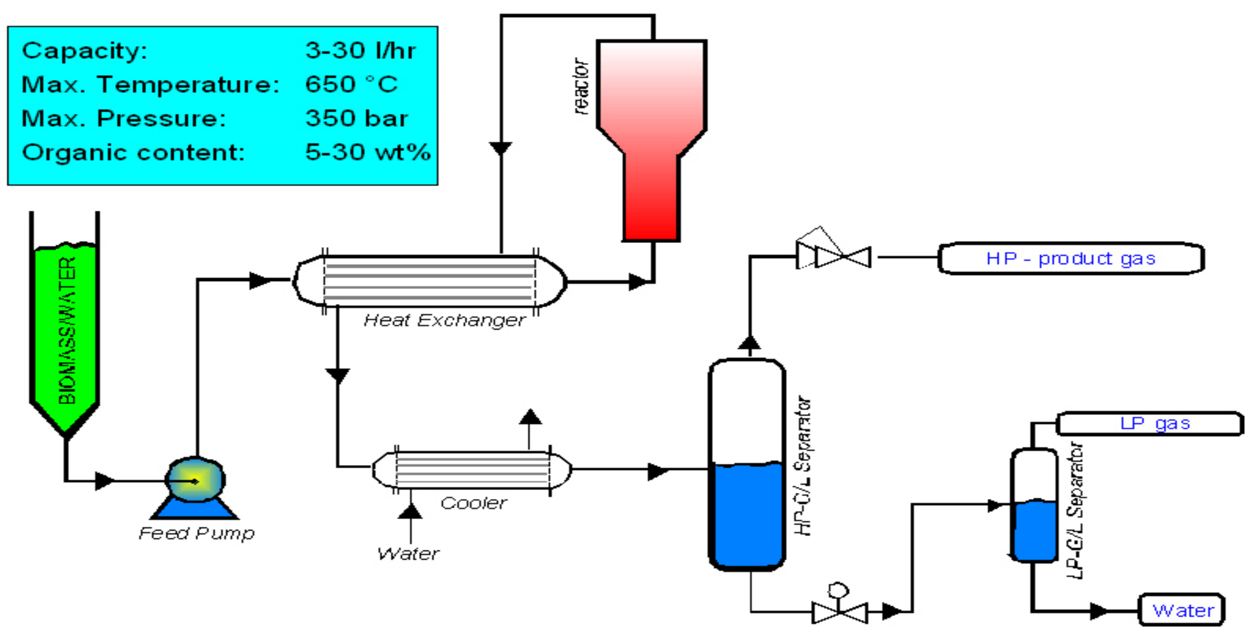

Figure 4: Basic flow diagram of supercritical gasification process

REFERENCES

[1] http://www.supermethanol.eu/

[2] DiLeo, G. J., Savage, P. E., Journal of Supercritical Fluids,Vol. 39, **2006**, p. 228

[3] Wen, D., Jiang, H., Zhang, K., Supercritical fluids technology for clean biofuel production, Progress in Natural Science, Vol.19, **2009**, p. 273

[4] Tang, H., Kitagawa, K., *Chem. Eng. Journal.*, Vol. 106, **2005**, p.261