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Energy from Bioresources

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The capacity of European biodiesel production is increasing rapidly, from approx. 3 million tons per year in 2005 up to an expected amount of 7 million t in 2007. Biodiesel is generally made when fats and oils are chemically reacted with an alcohol, typically with methanol, to produce an ester, or biodiesel. This reaction is generally known as trans-esterification and the most useful catalysts are sodium or potassium hydroxide. As every tonne biodiesel roughly consumes 100 kg methanol and produces the same amount of crude glycerine, consecutively the glycerine market becomes glutted. Due to the fact that European directives prescribe that 5.75 % of all transportation fuels should be made from renewable sources an interesting option is to produce methanol from the crude glycerine. Since 2005, BTG (Biomass Technology Group) explores the potential to substitute 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). 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.

1. Introduction

Biodiesel fuel is derived from triglycerides (vegetable oil and animal fats) by transesterification with methanol and present the promising alternative substitute to diesel fuels and have received the most attention now a day. Not only the vegetable oils and animal fats are sources of biodiesel, but algae are also, as well (Figure 1).

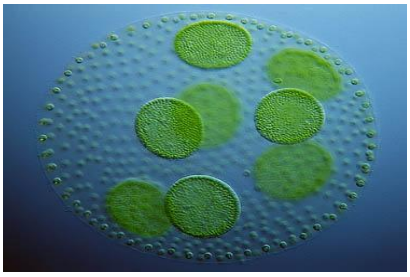

Figure 1: Algae as sources of biodiesel

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The main advantages of using biodiesel are its renewability and better biodegradability (Singh and Singh, 2010). Glycerine as a by-product of biodiesel production can be ideal feedstock for new technology which will reduce the cost of scale methanol synthesis. In the project glycerine will be reformed in supercritical water (RSW), followed by a high-pressure methanol synthesis process (producing ‘super methanol’). A wide range of experiments (BTG) show that with (crude) glycerine the reforming can be carried out without major problems. There is no need for (pure) oxygen or catalysts. The quality of the methanol is expected to be good enough for use in the biodiesel production and methanol price should be below 250 €/t. Expensive methanol purification may be limited or absent, but preliminary mass and energy balances need to be established for the GtM process (Figure 2).

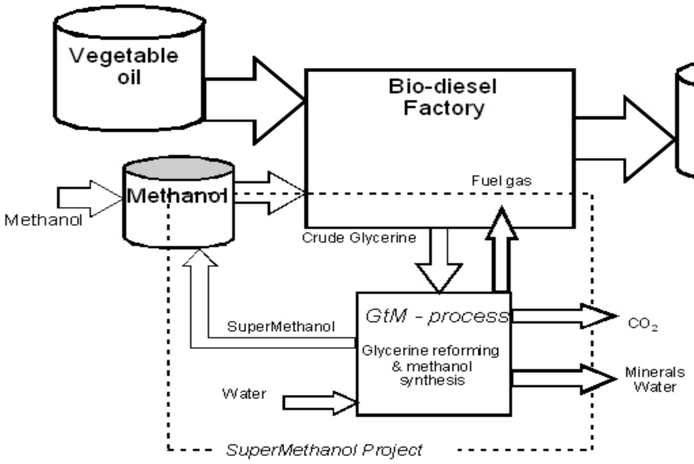

Figure 2: Simplified diagram of a biodiesel production unit coupled with the GtM process.

For each of the separate processes, selected research issues have been identified based on prior research that needs further investigation. Due to tremendous interest in developing sustainable energy systems there is the aim of harnessing the chemical energy in biomass, which is a renewable resource. Therefore, there is interest in processing methods suitable for biomass with high moisture content. 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 water at a temperature and pressure exceeding the thermodynamic critical point (Tc = 374 °C and Pc = 22.1 MPa) <www.supermethanol.eu>, DiLeo and Savage, 2006).

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. 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 rations. Approx. 50 catalysts will be screened and later tested using artificial gas. The best candidates were tested in the pilot plant on real RSW gas. Moreover, phase equilibrium data of water and CO_2, water- and mixtures of CO_2-CO- H_2 - CH_4 and CO_2 - H_2 were investigated.

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. University of Maribor (Laboratory for the separation process and product design) leads the modeling work on the RSW and the MeOH process The intention of this work 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. Modelling 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 (Wen D. et al. 2009).

2. Materials and Methods

2.1 Mass balances, production and conversion constraints

H_2, He, CO_2 (>99.9 % purity) were obtained from Messer (Ruše, Slovenia). Mixture of H_2:CO:CO_2:CH_4=50:20:20.10 was obtained from Messer (Germany).

2.2 Apparatus and methods

2.2.1 Apparatus and procedure for phase equilibrium determination

Phase behaviour data were measured by using a high pressure, variable –volume cell (Figure 3). The cell is made of the stainless steel (AISI 316) with tuneable internal volume between 30 and 60 cm^3 by means of a piston operated by a hydraulic pressurization system, and was designed to operate up to 750 bar and 200 °C. The piston position is determined by measuring the electric resistance through a cable sealed to the piston and connected to an ohmmeter (mod. 2210, MISCO-Systemax Europe Ltd, Wellingborough, UK).

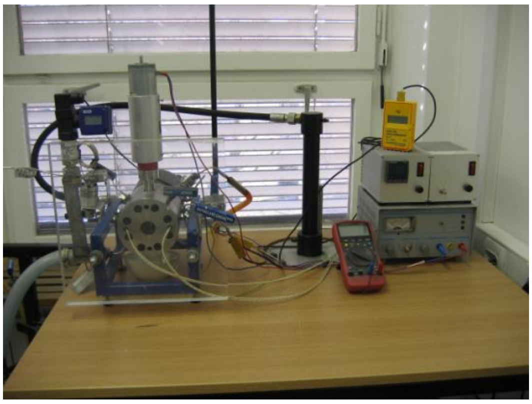

Figure 3: Variable-volume view cell apparatus

The cell is equipped with a two sapphire windows for observing the content of the cell and a blade–turbine stirrer to mix the phases. The cell is heated by using two stainless steel heaters with a length of 60 mm (mod. Firerod, WATLOW, Missouri, USA) lodged in cavities of the metallic body of the cell (Figures 3 and 4). The equilibrium cell was loaded with water and afterwards the gases (H_2, CO_2 and He) from a gas cylinder was cooled to a liquid state and compressed into the cell by a high pressure pump. The content of the cell was mixed with a blade-turbine stirrer under constant operating conditions (temperature and pressure) until equilibrium was reached. After 2h of phase separation the samples of the liquid phase were taken by the sampling valves, connected to the top and bottom of the cell, into a glass trap. The amount of released gas was measured by the disposal of water in graduated cylinder, while the amount of water was determined gravimetrically (accurate to ± 0.0001 g). During the sampling the observed pressure change was up to 13 bar, while the temperature was constant.

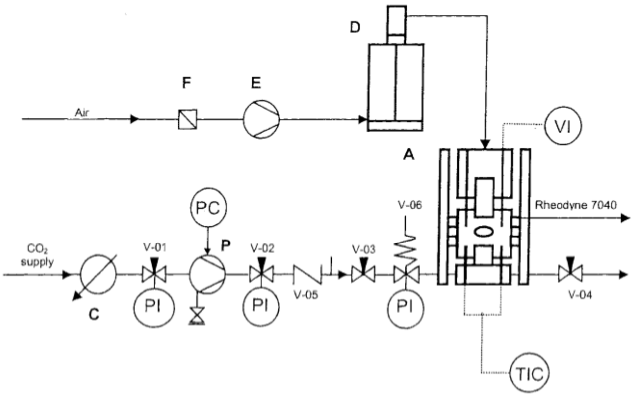

Figure 4: A – variable-volume view cell; C – cooler, D – hydraulic oil system; E – air compressor; F – filter, P – high-pressure membrane pump, V01-04 – high-pressure needle valves; V05 – one-way valve; V06 – safety valve; PI – pressure indicator; VI – voltage indicator; PC – pressure controller; TIC – temperature indicator controller.

2 2 1 RSW-unit

Figure 5 shows a ‘RSW’ unit which was constructed to operate at pressures up to 300 bar and at temperatures up to 650 °C.

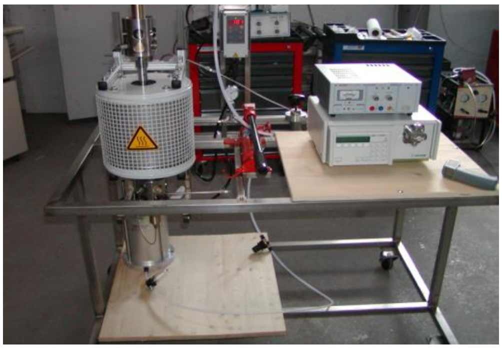

Figure 5: RSW unit

3. Results and discussion

In RSW process, (crude) glycerine will be directly injected in the reactor where water is present at supercritical conditions. Upgrading steps and other aspects of RSW will be observed: the consequences of recycling tail water on the process characteristics and the possibilities for the (liquid) CO_2 recycle will be investigated. 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. Selected catalysts, prepared by BIC (Boreskov Institute of Catalysts), were tested. Phase equilibrium data for the systems water (pure and tail water) / various gas mixtures were determined. High pressure solubility data were performed for He-H_2O system at 40 °C at pressures between 50 and 350 bar. Moreover, phase equilibrium data were obtained for CO_2-H_2O and H_2-H_2O systems at the same pressure range but at temperatures of 40 °C, 60 °C and 80 °C. 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 BTG 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 modelling 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 (Figure 6). Thermodynamic behaviour 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) -Tang H. and Kitagawa K., 2005.

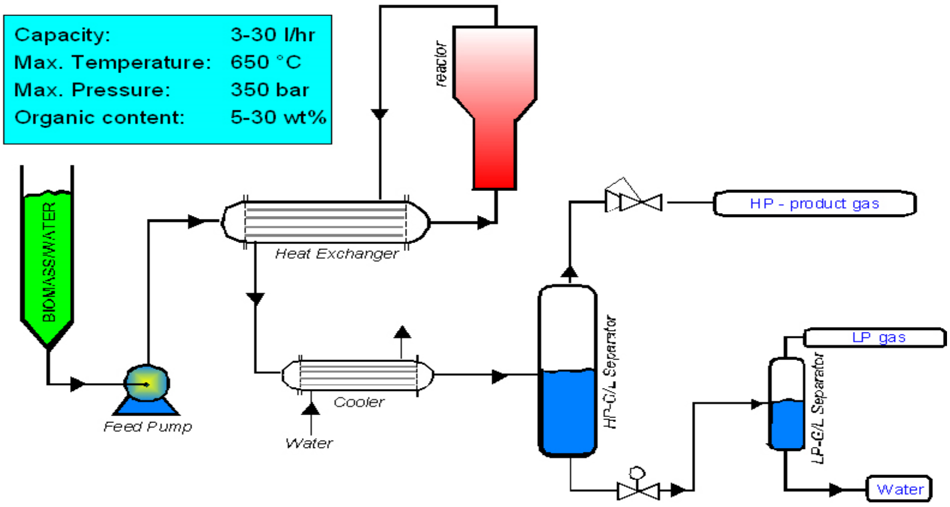

Figure 6: Basic flow diagram of supercritical gasification process.

4. Conclusions

The solubility of gases were obtained at 40 °C, 60 and 80 °C for CO_2-H_2O and H_2-H_2O systems and at 40 °C for He-H_2O system in the pressure range between 50 and 350 bar. Moreover, the influence of temperature and pressure on solubility was studied. It was found that the solubility of gases increases with increasing pressure at constant temperature. Additionally, the stability of catalysts at high temperatures (750 °C) has been studied and it was found that the catalysts show neither optical change in colour nor the structure. The possibility of tail water and/or CO_2 recycle has been studied by mathematical modelling (Aspen Plus). Various conditions (P, T) and compositions were proposed.

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