

SUPERCRITICAL WATER AS REACTION MEDIA FOR BIOFUELS PRODUCTION

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Abstract: European directives prescribe an increase in use of fuels from renewable sources. Biomass could be used as renewable source of energy.

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 gaseous or liquid fuels. Therefore, there is interest in processing methods suitable for converting biomass with high moisture content to the fuels. 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 ($T_c = 374^\circ C$ and $P_c = 221$ bar).

In Laboratory for Separation Processes and Product Design of University of Maribor an experimental SCWG unit operated up to $750^\circ C$ and 300 bar coupled with gas chromatograph were installed. Experiments on conversion of different wet substrates were performed and results are quite optimistic. Beside the results on supercritical water gasification with and without different catalysts, results on experimental determination of phase equilibrium in the systems water- /gas mixtures of CO_2 - CO - H_2 - CH_4 and water- CO_2 and - H_2 will be presented.

Key words: biofuel, biodiesel, glycerin, phase equilibrium, supercritical fluids

Introduction

Crude glycerin 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 tone biodiesel roughly consumes 100 kg methanol and produces the same amount of crude glycerin, the world's methanol demand increases while on the other hand the glycerin 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 [1]. 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. Glycerin 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) glycerin (**GtM – Glycerol-to-Methanol**) 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 CH₄ and C₂⁺) should be returned to the biodiesel production plant.

Reforming in supercritical water (RSW):

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. A large percentage of the mass of harvested biomass is 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. 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 (H₂, CO, CO₂, and CH₄) via reactions in and with water at a temperature and pressure exceeding the thermodynamic critical point ($T_c = 374^\circ\text{C}$ and $P_c = 221$ bar) [2-4]. By treatment at supercritical water conditions, but in the absence of added oxidants, organics can be converted into a hydrogen-rich gas [5-7].

In our research on RSW process, glycerin/water solutions were directly injected in the reactor operating at supercritical conditions. For the gas derived from the RSW unit further upgrade tests were performed to reduce the hydrocarbon concentrations (CH₄ and C₂⁺), and to obtain a syngas with higher CO/CO₂ ratios. Several catalysts were screened and later tested using artificial gas. For optimization of separation process of gas/gas mixture from water phase equilibrium data has to be known. For the systems under investigation no data could be found in the literature. Therefore experiments on phase equilibrium determination for the systems gas/water and gas mixtures/water were performed.

Phase equilibrium determination for the systems gas/water and gas mixture/water

Fundamental research on determination of phase equilibrium for the systems gas/water and gas mixtures/water, together with modeling is an important input for the construction and operation of the pilot plant and to design the full-scale industrial plant. The aim is to support analyses of supercritical gasification of glycerin, particularly in the reactivity of supercritical water and the further reforming of the methane and higher hydrocarbons in the syngas. Gas-Liquid equilibrium data for tail water/hydrogen, tail water/helium and tail water/carbon dioxide, as well for the mixtures of CO₂-CO- H₂ - CH₄/water and CO₂ - H₂/water has been experimentally determined.

Materials and methods:

Materials:

Glycerol was supplied by Kemika, Croatia with a purity $w \geq 99.5\%$.

CO₂ was from Messer (Ruše, Slovenia) and purity was 5.2.

Gas mixture H₂:CO:CO₂:CH₄ = 50:20:20:10, (vol.%) – was provided by Messer (Ruše, Slovenia).

The catalysts, as grains, were provided by BIC (Novosibirsk, Russia)

Methods:

Reforming in supercritical water (RSW):

Reforming of glycerol in supercritical water was performed in reaction system shown on Figure 1. Experiments were performed in temperature range from 300°C to 600 °C and in pressure range from 75 bar to 250 bar. The emphasis was on research of the influence of process parameters on gas yields, carbon conversion, reliability and on determination of optimal process parameters.



Figure 1: RSW unit

Phase equilibrium determination for the systems gas/water and gas mixture/water

Phase equilibrium determinations for the systems gas/water and gas mixtures/water were performed in high pressure view cell shown on Figure 2. The cell was filled with water, later the cell was stripped with gas (for which the measurements were performed) and later the cell was heated to desired temperature.

Through the sampling system the samples of upper and bottom phase were collected.

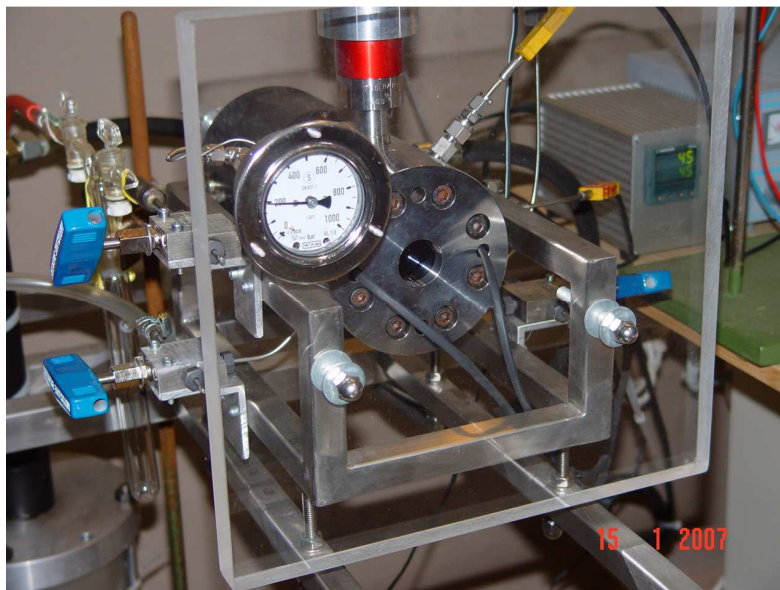


Figure 2: Phase equilibrium view cell

Results and discussion

Reforming in supercritical water (RSW):

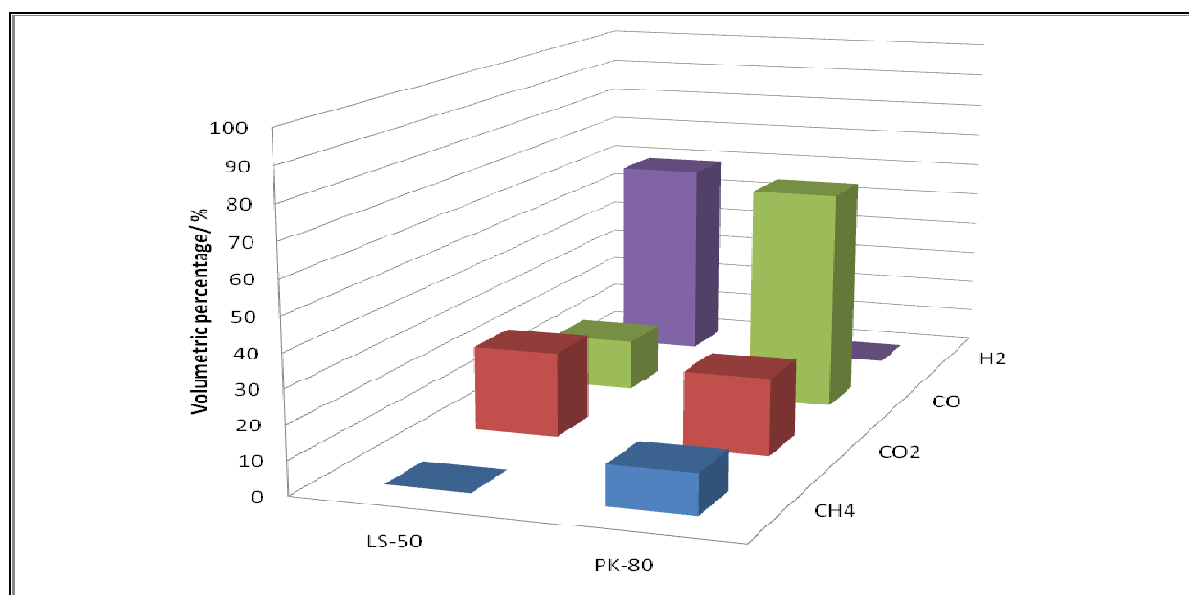


Figure 3: Catalytic gasification of glycerol in supercritical water ($T = 600^{\circ}\text{C}$, $P = 250$ bar, 2 mL/min)

Two catalysts were studied for the supercritical water reforming of glycerol: LS- 50 and PK-80. Reaction parameters were selected considering previous thermodynamic and literature studies.

Tests were conducted at pressure $P = 250$ bar and temperatures $T = 400$ °C, 500 °C and 600 °C. Input flow was held constant at 2.0 mL/min with a HPLC pump. The concentration of the input solution was 10 wt. % glycerol in water. The products were separated in a gas – liquid separator. The gases were analysed by gas chromatograph Shimadzu 2010 connected online with the reactor.

The best results for both catalysts were obtained at 600 °C (Figure 3). At temperatures 400 and 500 °C a large amount of CO_2 is obtained. At temperature of 600 °C the volume fraction of CO_2 decreases in comparison to lower temperatures and the volume of the obtained gas increases more than 6 times in comparison to gas formed at lower temperatures.

From the obtained results we conclude that gasification is the preferred reaction at 600 °C, based on increasing volume of obtained gas at higher temperature. LS-50 catalyst promotes formation of H_2 and prevents formation of methane; however the amount of CO_2 is larger than that of CO . Although the formation of CO is favored by the PK-80 catalyst, no hydrogen was obtained in this case, while the amount of methane is important.

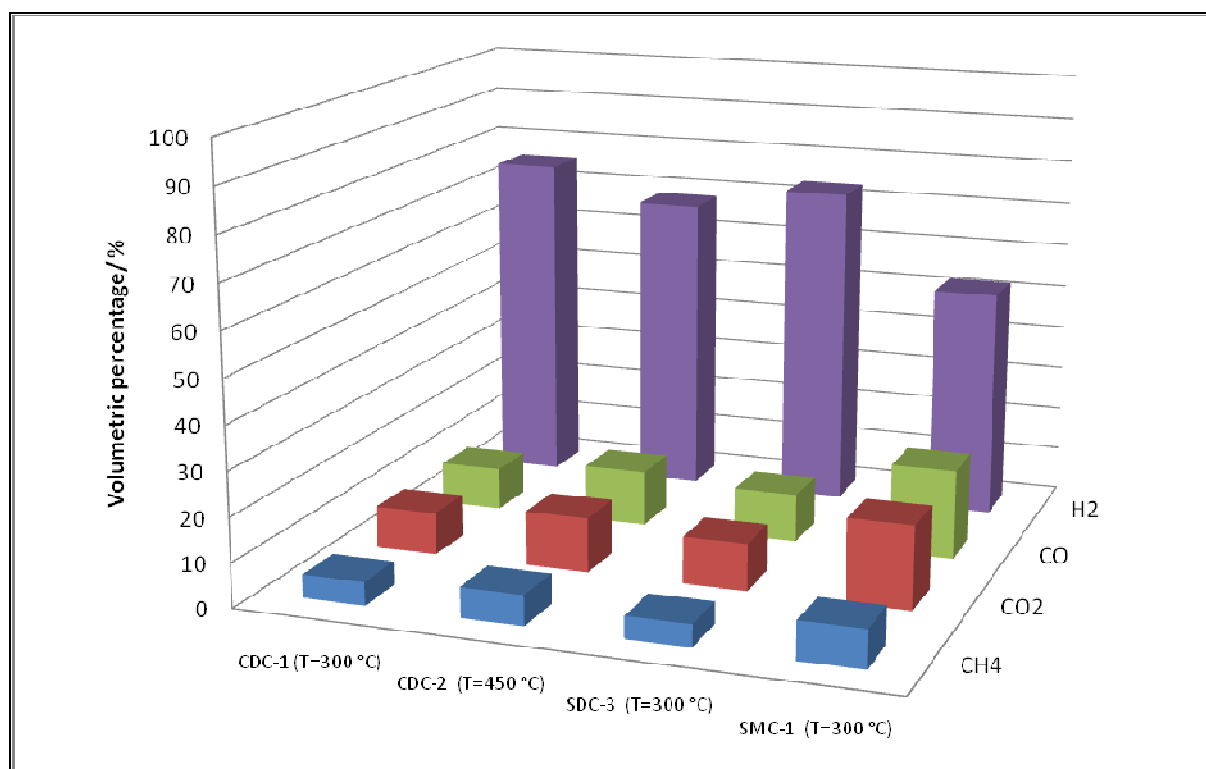


Figure 4: Catalytic dry reforming of methane ($P = 75$ bar)

The aim of the research was to reduce the hydrocarbon (methane) concentration from a synthetic mixture of gases (H_2 , CO , CO_2 and CH_4) and to increase the content of H_2 and CO (synthesis gas) by catalytic reactions at high pressure and temperature. Reactions were performed under a continuous regime at temperatures of $100 - 700$ °C and pressure of 75 bar. The flow rate of the

output gases was of 0.5 mL/s. Four catalysts were tested and the best results for each are presented in Figure 4.

When catalysts CDC- 1 and SDC-3 were used, the highest concentration of hydrogen was obtained during reactions performed at 300°C. At the same conditions the concentration of methane fell to the lowest measured level of 5.00 vol. %.

Catalyst CDC-2 seems to influence the gas conversion at 450°C. Hydrogen concentration increases but concentration of other gases decreases.

Under the employed conditions catalyst SMC-1 favors the reverse reaction, with formation of methane and carbon dioxide, and also of large amounts of water and carbon.

Phase equilibrium determination for the systems gas/water and gas mixture/water

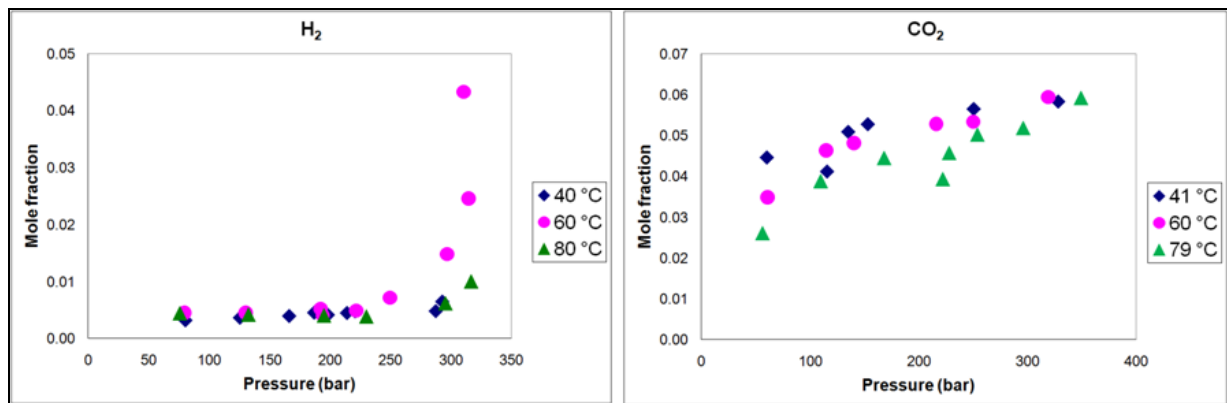


Figure 5: Solubility of pure gases in water

Phase equilibrium determinations for the H₂/water and CO₂/water systems were performed in high pressure view cell for temperatures between 40 and 80 °C and pressures 80 – 350 bar. Samples of liquid phase were collected, phase separation was performed under atmospheric conditions and the solubility of gas in water was then calculated. The results are presented in Figure 5. It was observed that for both gases solubility increases with increasing pressure. The solubility of CO₂ in water decreases with increasing temperature, while no significant differences were observed between the solubility values of H₂ in water for the studied temperatures.

Similar to pure gases, the solubility of the gas mixture in water was measured using a high pressure view cell at temperatures 50°C, 75°C and 100°C and pressures between 100 bar and 400 bar. After sampling and separation of the phases, the obtained gas was analyzed by gas chromatography. The results for the solubility in water of individual gases from the mixture are presented in Figure 6. It was observed that CO₂ and CO have the highest solubility in water, followed by H₂ and CH₄. All solubility values increase by increasing the pressure in the system. By increasing temperature, the solubility of CO₂, CO and CH₄ decreases, while the solubility of H₂ increases.

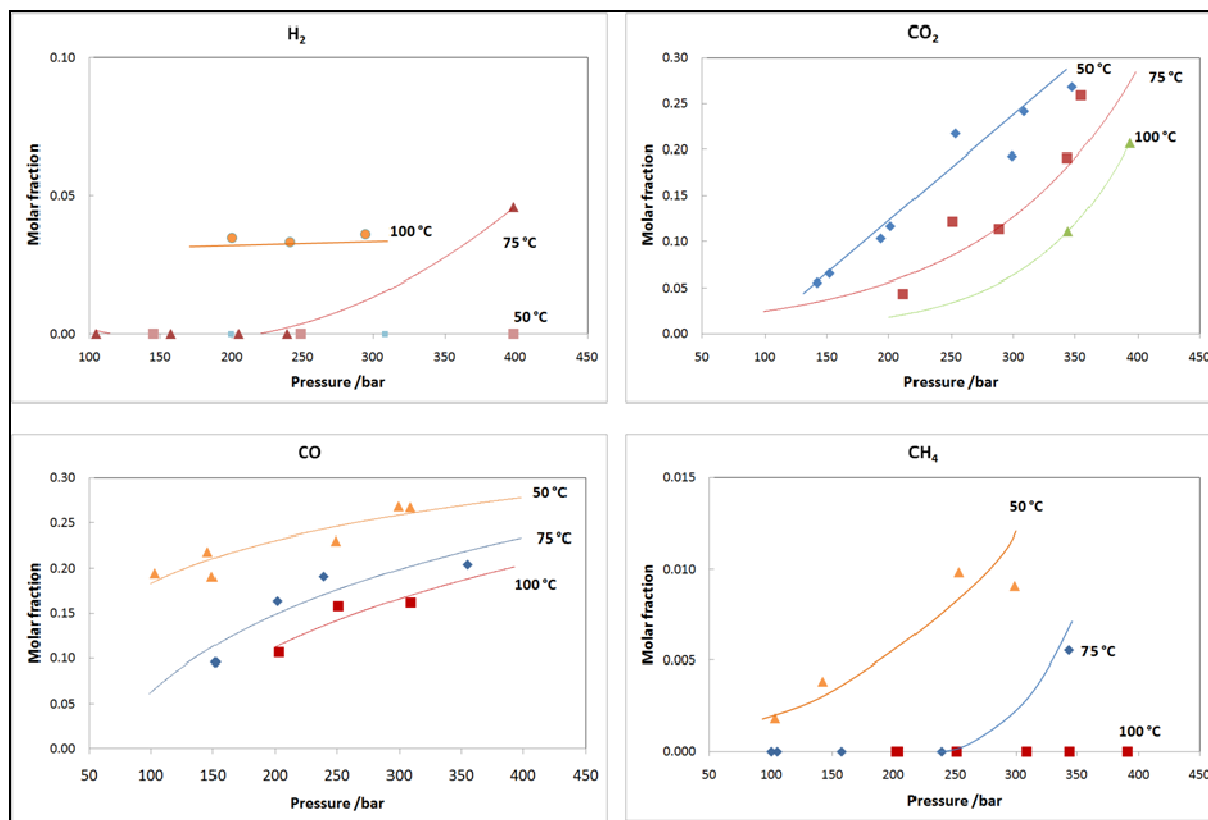


Figure 6: Solubility in water of gases from gas mixture H₂:CO:CO₂:CH₄

Conclusions:

Experiments verify main advantages of the RSW technology. RSW technology is 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.

In addition some new fundamental data on phase equilibrium for the systems gas/water and gas mixtures/water important for the design and operation of the pilot plant and for the design of industrial scale plant were determined.

We should point out that based on the preliminary research and very basic evaluation of process economy; we conclude that the major limitation of further propagation is the energy efficiency for the production of gaseous fuels from wet biomass.

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