Supermethanol: Reforming of crude glycerine in supercritical water to produce methanol for re-use in biodiesel plants

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Introduction

The European Union is promoting the use of biofuels and other types of renewable energy in transportation. By respectively 2010 and 2020, 5.75 % and 10 % of the total transportation fuel should be derived from renewable sources. Therefore the biodiesel production is increasing rapidly.

The production of a ton biodiesel roughly consumes 100 kg methanol and produces the same amount of crude glycerine. As a result, the world's methanol demand increases while the glycerine market becomes oversupplied. An interesting option addressing the surplus of glycerine and the demand of methanol is to produce methanol from the crude glycerine by the biodiesel producer itself. This process of converting glycerine to methanol is known as the glycerine-to-methanol process (GtM process). The proposed concept is schematically depicted in Fig. 1 [1].

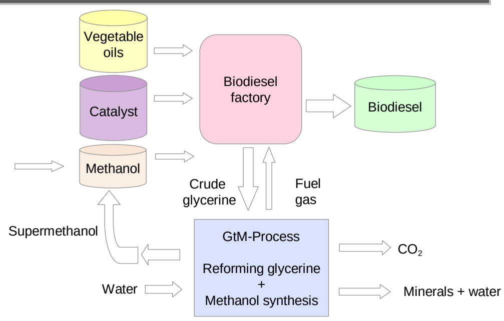

Fig. 1 Schematic representation of a biodiesel factory with a GtM unit

Experimental set-up

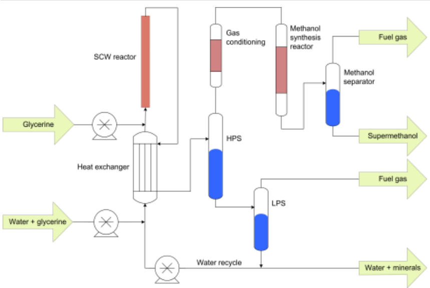

Fig. 2 Pilot plant for the reforming of glycerine coupled with methanol synthesis

The conversion of glycerine to methanol consists of two different stages which are integrated in one process. In the first stage (SCW reactor) crude glycerine is gasified in water at supercritical conditions (reforming in supercritical water) to syngas [2]. The syngas consists predominantly of H_2, CO, CO_2, CH_4 and smaller quantities of higher alkanes.

The composition of the syngas can be tuned to a certain extent by varying process parameters such as temperature, residence time, concentration of the feedstock and composition of the feedstock. After separating the syngas from the water phase in a high pressure separator (HPS), the syngas is fed to the second stage of the process: the methanol synthesis reactor. In this reactor the syngas is catalytically converted to methanol [3].

Project justification

Advantages of reforming in supercritical water:

- Energy efficient process due to counter current heat exchange
- Wet biomass streams can be converted
- High conversion of glycerine
- The syngas comes available at high pressure

Advantages of high pressure methanol synthesis:

- High conversion towards methanol
- Once through process (no recycles)
- Good methanol quality (experiments)

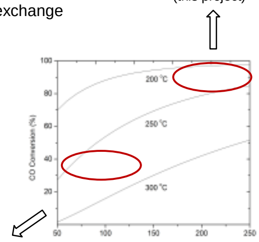

Fig. 3 Methanol synthesis equilibrium

Results glycerine reforming

Gas composition depends on several parameters:

- Concentration of the feedstock
- Composition of the feedstock
- Residence time
- Process temperature

Process conditions

- P = 230 – 300 bar
- T = 550 – 700 ºC
- t = 5 – 35 s
- [feed] = 5 – 20 wt%

Gas composition (glycerine gasification):

H_2 (vol%)	CO (vol%)	CO_2 (vol%)	CH_4 (vol%)	C_2H_6 (vol%)
40-60	0-25	10-35	2-15	0-4

- Glycerine conversion up to 100 % can be obtained

Results methanol synthesis

Reactions involved in methanol synthesis:

- $CO + 2H_2 \Leftrightarrow CH_3OH$
- $CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O$
- $CO + H_2O \Leftrightarrow CO_2 + H_2$

Process conditions

- P = 200 – 300 bar
- T = 200 – 250 ºC
- f_V = 0.5 – 5 l/min
- [feed] = 5 – 20 wt%

Proof of principle:

Gas composition[1] (glycerine reforming):

H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
43.8	29.1	9.0	12.8	1.4	2.8	1.1	0.0

*All concentrations are in vol%

Compostion[2] of the liquid obtained in the experiment:

Methanol	Ethanol	Propanol	Butanol	Other alcohols	Acids
96.3	0.6	0.7	0.6	0.3	1.5

*All concentrations are in wt%

Conclusions

- High glycerine conversion to syngas was obtained by reforming in supercritical water.
- The composition of the syngas can be tuned by changing the process parameters. Therefore an attractive gas composition for methanol synthesis can be obtained.
- Methanol yields at equilibrium are high at the chosen process conditions.
- Methanol was successfully synthesized from glycerine derived syngas.
- The impurity content of the methanol is low.

1. www.supermethanol.eu
2. M.J.Antal, S.G. Allen, D. Schulman, X. Xu, Biomass gasification in supercritical water, Ind. Eng. Chem. Res. 39, 2000, pp 4040-4053
3. G. Patart, Procédé de production d'alcools, d'aldéhydes et d'acides à partir de mélanges gazeux maintenus sous pression et soumis à l'action d'agents catalytiques ou de l'électricité, 1922, FR patent 540543

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btg biomass technology group

SUPERMETHANOL The GtM Concept

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