

## LABORATORY EQUIPMENT FOR AUTOTHERMAL REFORMING OF ORGANIC MATTER IN SUPERCRITICAL WATER

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**ABSTRACT.** The ability of water to dissolve organic substances is very limited. However, its ability to dissolve them changes if pressure and temperature values reach the so-called critical point ( $p = 22.06$  MPa,  $T = 373.95$  °C). Fluid water in this state is called supercritical water (SCW), and values of its physical properties are included among the values of such properties for liquid phase and gaseous phase. Various types of organic matter can be treated in SCW, and it is especially useful for materials that cannot be treated cost-effectively with conventional technologies (incineration, etc.). Suitable input materials are mainly industrial waste or biomass with high water content. Conventional processing of these materials requires energy-intensive drying or densification. Processing the inputs in SCW completely removes these problems, since sufficient water content is a prerequisite for creating a suitable environment for efficient operation of the system. In this paper, glycerol as a by-product of alternative fuel production was chosen for evaluation in the SCW autothermal reforming cycle. The paper analyses the influence of several processing parameters on the operation of model laboratory equipment.

**KEYWORDS:** Supercritical water; autothermal reforming; organic matter; glycerol.

### 1. INTRODUCTION

Supercritical water treatment of organic matter is a novel but as yet unproven way to process large amounts of biomass or organic content in municipal waste. Two known approaches are supercritical water oxidation (SCWO) and supercritical water gasification (SCWG) [1]. The proposed autothermal reforming in SCW combines the advantages of both approaches [2].

The design of the cycle in ASPEN PLUS software is shown in Figure 1. In this case, the conversion is carried out in equipment operating with continuous water pumping (WAT-PUMP) and organic matter pumping (GLY-PUMP). Glycerol was chosen as a model organic input substance.

The water is pre-heated (HEAT-EX1) and is fed with glycerol and compressed oxidant (by COMPRESS) into the REACTOR, where the chemical reactions take place. A mixture of 93% oxygen and 7% nitrogen was introduced as the oxidant, since a similar composition can be found in commercial oxygen generators. Due to the exothermic character of the reactions, the temperature increases and the product stream can be used for pre-heating the “cold” input stream. The product stream is depressurized (VALVE1) and cooled down (HEAT-EX2). The gas is separated from the water (SEPARAT); the water is depressurized (VALVE2), and can be used as an input stream.

The target product of the cycle is hydrogen, which is currently produced mainly from fossil fuels, in particular by thermochemical conversion (up to 96% of world production). The remaining 4% of the produc-

tion comes from electrolysis of water [3]. Hydrogen obtained by electrolysis utilizing a renewable (sun, wind, or geothermal energy) can be considered as a renewable energy source. An advantage of the proposed cycle is that hydrogen can also be produced also from biomass or from municipal waste, instead of from fossil fuels.

### 2. SENSITIVITY ANALYSIS

An analysis of various processing parameters of the cycle was performed in the ASPEN PLUS code with the Predictive Soave-Redlich-Kwong estimation method for calculating the phase equilibrium of the reacting components. The product composition was calculated using the Gibbs free energy rule. The composition has a “synthesis gas — syngas” character, with the following main components: water (H<sub>2</sub>O) hydrogen (H<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and carbon monoxide (CO).

#### 2.1. PRE-HEATING IN THE HEAT EXCHANGER

In order to ensure the autothermal character of the process, it is necessary to recuperate the thermal energy in the heat exchanger. The water pre-heating value (the temperature at which the water (W) stream enters the reactor — Stream 3) affects the reactor temperature and thereby affects the composition of the product stream. This dependency can be found in Figure 2, which shows that increasing the pre-heating temperature increases the temperature in the reactor up to the critical temperature value (647 K). Due to the elevated temperature, the proportion of H<sub>2</sub> and

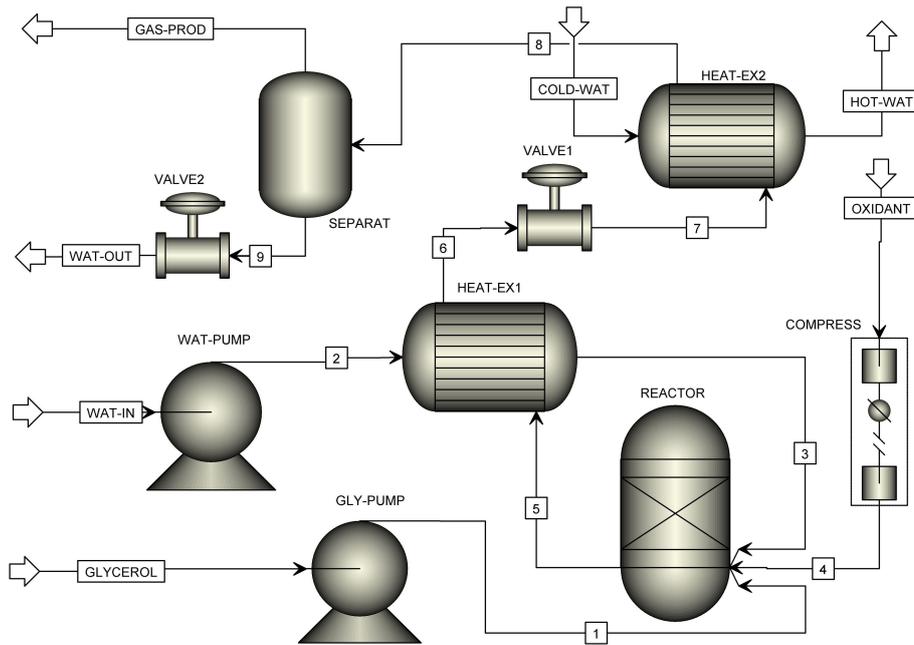


FIGURE 1. Design of the autothermal reforming cycle in ASPEN PLUS software.

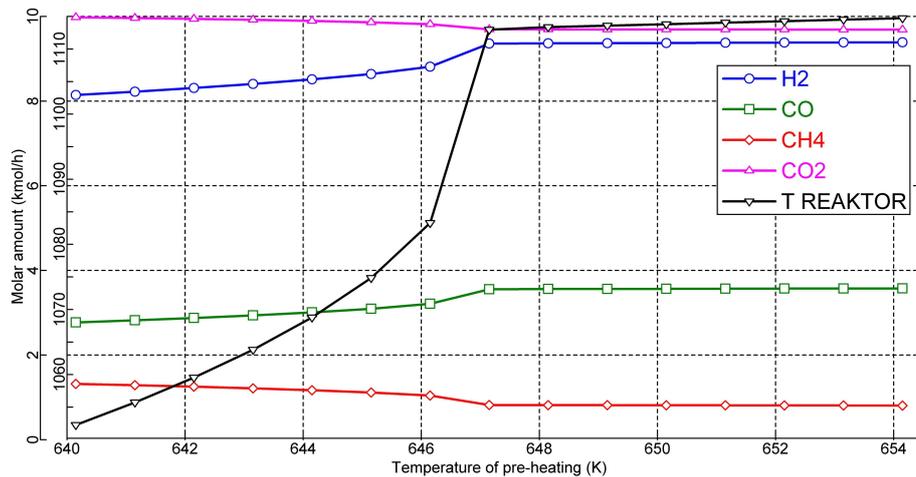


FIGURE 2. Dependence of the temperature in the reactor and the molar amount of syngas components on the pre-heating temperature ( $M_W = 60$  kmol/h,  $M_G = 4.7$  kmol/h,  $M_O = 8.9$  kmol/h).

CH<sub>4</sub> is increased, which is in accordance with the findings of Gutiérrez, F.J. et al. [4]. To maximize the H<sub>2</sub> content, it is recommended to reach the critical temperature before entering the reactor.

## 2.2. PRESSURE IN THE REACTOR

Increased pressure in the cycle causes increased power consumption of pumps and compressors as well as increased safety requirements. It is therefore necessary to consider the value of the operating pressure in the cycle. Figure 3 shows that a change of pressure in the reactor (from 240 to 280 bars) has a minor influence on the composition of the syngas. An increase in the pressure value slightly increases the proportion of CH<sub>4</sub> and reduces the H<sub>2</sub> content. This finding is in agreement with the experimental and numerical results presented in Gutiérrez, F.J. et al. [5]

## 2.3. RATIO OF INPUT STREAMS

The composition of the syngas depends on the temperature and the pressure in the reactor, and also on the ratio of the inputs ( $W$ ,  $G$ , and  $O$ ). Figure 4 shows the dependence of the syngas composition on the  $G/W$  ratio, when the oxidant input is constant. The increasing  $G/W$  ratio has a positive influence on the overall amount of all gaseous substances (the curves of the same colour). The increase in the proportion of H<sub>2</sub> and CO for a particular value of the  $G/W$  ratio is reduced, while the share of CH<sub>4</sub> and CO<sub>2</sub> still grows (almost constantly).

Similarly, an analysis was also made of the impact of the  $G/O$  molar ratio for a constant input of water. Figure 5 shows that increasing the  $G/O$  ratio causes an increase in the amount of all gaseous products until they reach a certain value (for this case, the value is

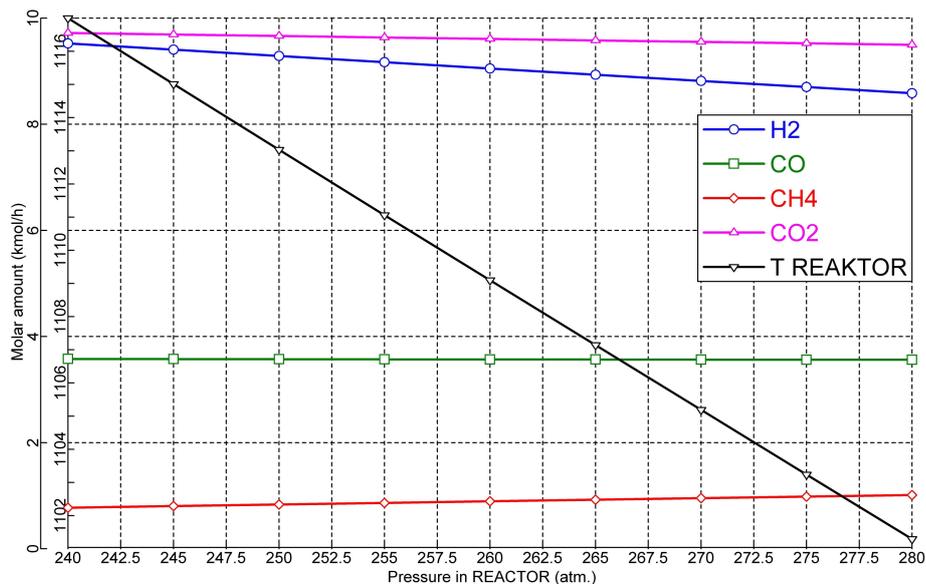


FIGURE 3. Dependence of the temperature in the reactor (in K) and molar amounts of syngas components on the pressure in the reactor ( $M_W = 60$  kmol/h,  $M_G = 4.7$  kmol/h,  $M_O = 8.9$  kmol/h).

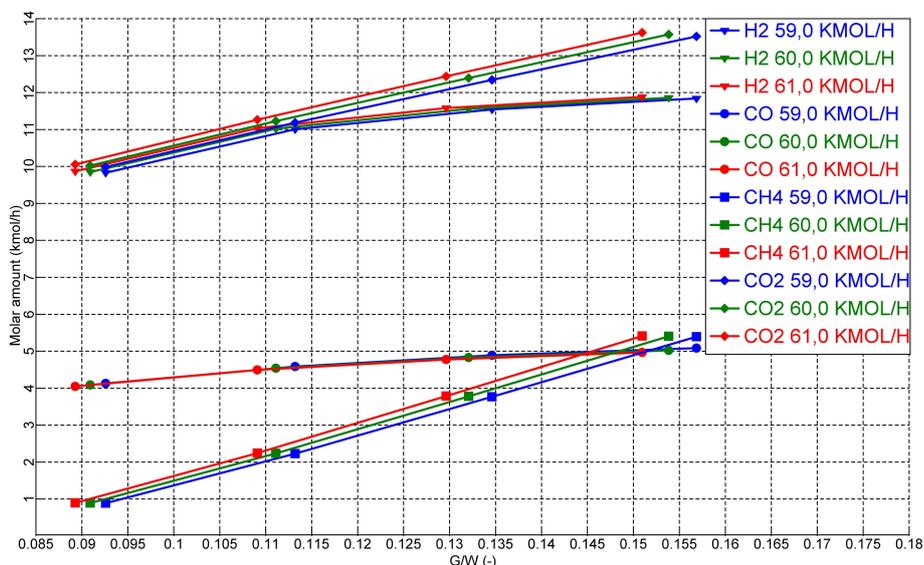


FIGURE 4. Molar amounts of syngas substances dependent on the G/W molar ratio for various input levels of glycerol and water ( $M_W + M_G = 59.0 - 61.0$  kmol/h;  $M_o = 8.9$  kmol/h).

in the range of  $G/O = 0.5 - 0.7$ ). A further increase in the  $G/O$  ratio causes a reduction in the amount of  $H_2$  and  $CO$ , while the  $CO_2$  and  $CH_4$  proportions continue to grow.

This behaviour is caused by contradictory requirements on the oxidant. On the one hand, a high proportion of the oxidant causes a high degree of oxidation of glycerol to  $H_2O$  and  $CO_2$ , reducing the proportion of  $H_2$ . On the other hand, reducing the amount of oxidant lowers the temperature in the reactor and thereby increases the proportion of  $CH_4$  instead of  $H_2$ .

#### 2.4. SEPARATION OF GASEOUS PRODUCTS

One of the advantages of the cycle is in-situ separation of gaseous products and water. By increasing the pressure and reducing the temperature, it is possible

also to separate a small amount of  $CO_2$ . For higher efficiency of the separation process, a higher proportion of water is needed [6]. We should therefore include additional separation of  $CO_2$  by conventional methods. Separation of  $CO_2$  is mainly dealt with in research work on Clean Coal Technologies. One of the main problems encountered in this kind of application is the large volume of flue gas, which has to be cleaned. For example, for a 100 MW block of a coal power plant it is necessary to capture and process about  $23 \text{ t h}^{-1}$   $CO_2$  in order to achieve a 20% reduction in  $CO_2$  emissions [7].

However, in our case higher efficiency of the process can be achieved, since significantly lower quantities of the products are to be separated. The most widely used method for separating  $CO_2$  is by absorption in

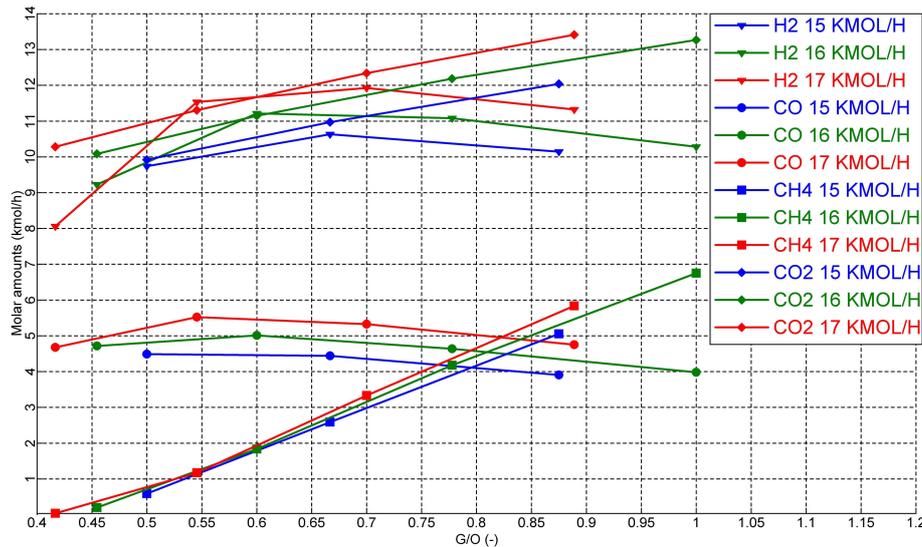


FIGURE 5. Molar amounts of syngas components dependent on the  $G/O$  molar ratio for various input levels of glycerol and oxidant ( $M_o + M_G = 15.0 - 17.0$  kmol/h;  $M_W = 50$  kmol/h).

aqueous solutions of ethanolamine. However, the processing stream should not contain nitrogen oxides and sulphur. In our case, this is ensured by the temperature in the reactor and by the exclusion of organic material with higher sulphur content.  $CO_2$  can also be separated by cryogenic or membrane separation [8].

### 3. CONCLUSIONS

This paper has presented autothermal reforming of glycerol in a supercritical water cycle, and assesses the influence of various processing parameters on the composition of the syngas that is produced with the use of simple laboratory equipment. Higher pre-heating temperatures and reactor temperatures are necessary to obtain a higher proportion of  $H_2$  in the syngas. A lower temperature increases the proportion of  $CH_4$ . The influence of the pressure in the reactor is negligible. However, higher pressure increases the power consumption of the feeding machines, and raises the safety requirements. In addition, the optimal input stream composition and separation parameters have been studied and fixed. The findings are in accordance with the cited bibliographic sources.

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