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Design of an aqueous phase reforming process demonstration unit for the production of green hydrogen from organics-laden residual waters

# **Highlights**

- First APR process demonstration unit
- Upscaling by a factor of 666
- Process up to 44 l/h of residual water
- Product gas contains up to 75 vol% H<sub>2</sub>

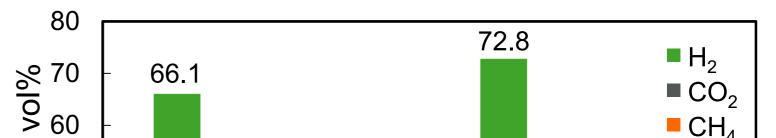
## Introduction

Aqueous phase reforming (APR) describes the conversion of oxygenated hydrocarbons dissolved in an aqueous phase to hydrogen and carbon dioxide [1].

 $C_n H_{2\nu} O_n + n H_2 O \rightleftharpoons n C O_2 + (y+n) H_2$ 

## **Results and Discussion**

The PDU was operated successfully with both a glycolic acid solution and a synthetic aqueous phase mixture. The experiment with the glycolic acid solution yielded a product gas flow rate of 156 NI/h while that with the synthetic aqueous phase mixture resulted in a gas flow rate of 154 NI/h. The product gas of both experiments (see Fig. 2) largely consists of  $H_2$  and  $CO_2$  with small amounts of CH<sub>4</sub> and CO. The increased CH<sub>4</sub> content for the synthetic mixture is due to the presence of more challenging to reform compounds in the feed [3].



When applied to residual waters from biorefineries, it offers the possibility to valorize the organic compounds present in these effluents. Since research to date has only focused on bench-scale investigations, a lab-scale unit was built to prove the feasibility of APR at a larger scale.

### **Materials and Methods**

The process demonstration unit (PDU) built for this endeavor (see Fig. 1) is fully automated and able to process up to 44 l/h of residual water in a continuous manner.

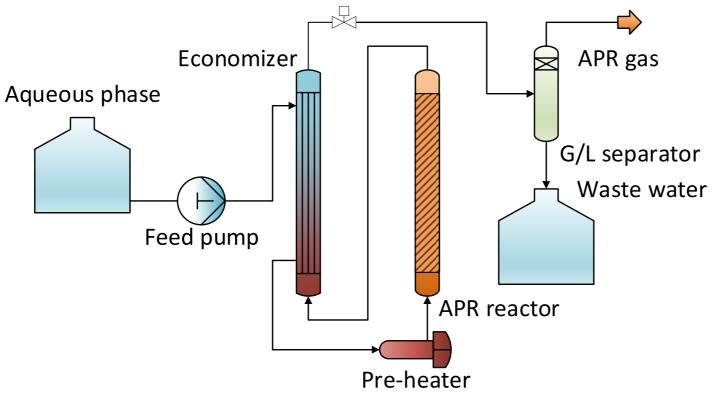


Fig. 1. Process flow diagram of the APR PDU

The plant is designed to process residual waters derived from lignin-rich hydrothermal liquefaction, which typically contain carboxylic acids, alcohols, ketones, polyalcohols, aromatics and aldehydes [2]. The first experiments, however, were conducted using a 0.5 wt% glycolic acid solution. Further experiments were conducted with a synthetic aqueous phase mixture composed of five model compounds selected residual resemble obtained water from to hydrothermal liquefaction [2]. The composition used was 0.16 wt% glycolic acid, 0.19 wt% lactic acid, 0.18 wt% acetic acid, 0.42 wt% methanol and 0.05 wt% glycerol. The reactor used for reforming the aqueous phase was a fixed bed reactor with an internal diameter of 70.1 mm. It was filled with 666 g of a 5 wt% Pt/C catalyst. A temperature of 250 °C, a pressure of 52 barg and a WHSV of 0.283 and  $0.575 g_{org}/(g_{cat} \cdot h)$ , respectively, were selected as the operating conditions.

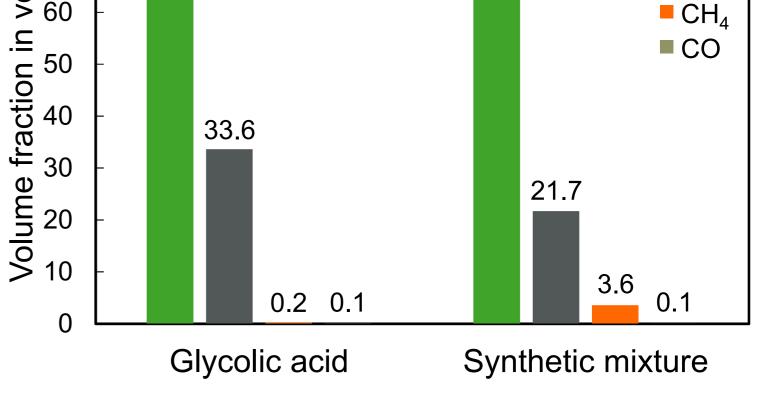


Fig. 2. Product gas composition

Successful operation of the APR PDU proves that an upscaling of the APR process from bench scale to larger scales is possible from a process technological standpoint. Furthermore, demonstrating that the process works flawlessly with a continuously-operated fixed bed reactor instead of a batch-operated stirredtank reactor is an important step to prove the industrial viability of APR.

## References

[1] Cortright et al., 2002: Nature, 418, 964–967, https://doi.org/10.1038/nature01009 [2] Pipitone et al., 2020: Catal. Today, 345, 267–279, https://doi.org/10.1016/j.cattod.2019.09.040 [3] Pipitone et al., 2019: Chem. Eng. J., 377, 120677 https://doi.org/10.1016/j.cej.2018.12.137

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