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Microwave plasma pyrolysis for the valorization of VFA extracts from HTC process water

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Abstract Volatile fatty acids (VFAs) in HTC liquors are a promising but underutilized resource for energy production. This study examines the recovery of VFAs from HTC process water via liquid–liquid extraction and the co-pyrolysis of the recovered stream with methane in a microwave plasma reactor to produce syngas. Experimental analysis at the HYDROPYR pilot of the BioFairNet project, has provided the real VFA composition in the HTC liquor. The experimental results are used as input in a newly-developed thermodynamic model (implemented in MATLAB-Cantera) and simulation were performed for 1000–2500 K. The model results at 1500 K, simulate syngas production with >99.9 mol% of H2/ CO in the gaseous phase, and the simultaneous production of carbon black. Ongoing work will incorporate reaction kinetics and techno-economic analysis to inform scale-up for municipal wastewater-treatment applications.

Keywords: Waste-to-Energy; HTC; Plasma Pyrolysis;

1. Introduction

Pilot site 1 of the BioFairNet project, hosted on Lesvos (North Aegean), includes an 8 L Hydrothermal Carbonisation (HTC) reactor that will be coupled with a downstream pyrolyser and a 3 kW PV system to form the HYDROPYR unit, which aims to process olive-mill wastewater mixed with pruning residues and convert them into high-grade biocarbon and an aqueous co-product, i.e. HTC process water. While the solid hydrochar can potentially used as fuel, soil enhancement or a conductive additive for anaerobic digestion, the focus is also on the valorization of the liquid HTC effluent. Hydrothermal processes enhance the propagation of thermochemical pathways that produce C2–C6 volatile fatty acids (VFAs) such as acetic, propionic and butyric acid, by means of hydrolysis/ depolymerization and carboxylation. An established isopropanol-assisted extraction method along with a GC-BID measurement protocol has been applied in order to extract these VFAs from the process water, yielding a recoverable bio-based chemical feedstock while simultaneously cleaning the effluent for reuse or safe discharge.

2. Materials and Methods

GC-BID measurements show that volatile-fatty-acid (VFA) levels in hydrothermal-carbonisation (HTC) liquors fluctuate sharply with temperature. In sewage-sludge trials from 280 °C to 340 °C, the peak sample at 340 °C contained about 33.7 mg L^{-1} formic acid, 32.3 mg L^{-1} acetic acid and 22.9 mg L^{-1} propionic acid. HTC effluents can contain up to several hundred mg L^{-1} of VFAs, with the highest values occurring near the upper end of the standard HTC temperature range.

This study presents a novel idea for the valorization of VFAs. In this framework a new thermodynamic model simulates the co-pyrolysis of the extracted VFAs from the HTC liquor (that are dissolved into an organic solvent) together with the methane as an injected mixture into a microwave plasma pyrolysis reactor for the production of H_2/CO syngas and carbon black. The idea is presented in Fig. 1. A MATLAB-Cantera script has been developed as a zero-dimensional thermodynamic-equilibrium model. It uses the Graphite (solid phase) mechanism and the Curran mechanism (gas phase). The gas/ vapor phase contains 50–100 % methane mixed with experimentally measured solutions of organic solvents and VFAs. The simulated equilibrium temperatures are from 1 000 K up to 2 500 K.

3. Results

The preliminary modelling results for 1500 K are presented in Fig. 2. Because no reaction kinetics or transport resistances are yet included, the model delivers rapid upper-bound estimates of methane conversion and product distributions.

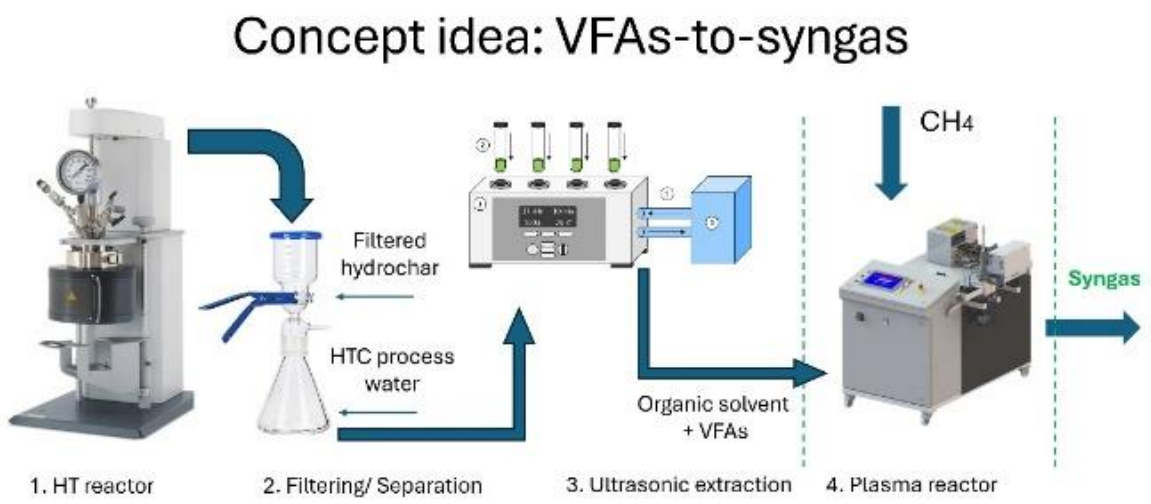

Figure 1. The concept of VFAs-to-syngas via plasma pyrolysis

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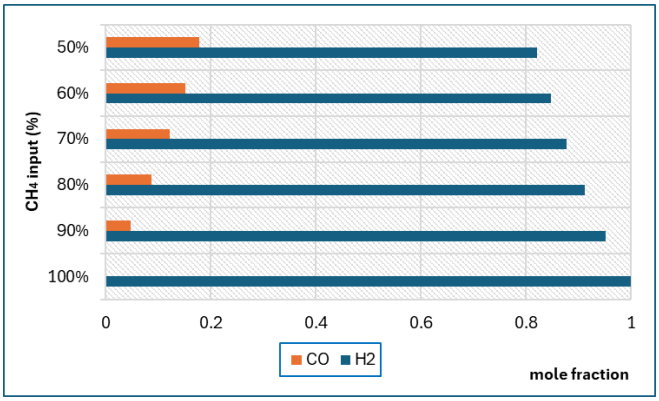

Figure 2. Syngas composition for plasma pyrolysis at 1500 K for VFAs in ethanol.

Future work will incorporate the model into Aspen Plus in order to provide a TEA of a scale-up system that can support municipality-level wastewater treatment plants. In respect of modeling, future work will extend the model to include kinetics, inter-phase mass transfer, and spatially resolved heat-transfer descriptions, enabling time-accurate prediction of reaction rates, advancing the tool from an equilibrium solver to a comprehensive reactor-design platform.

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