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CATALYTIC OXIDATION OF HTC-WASTE WATER IN SUPER CRITICAL H_2O

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INTRODUCTION

A problem of the HTC-process is that there is an enrichment of toxic organic compounds in the waste water (e. g. acetic acid, furanic compounds). 15 % – 37 % of the organic carbon is transferred to the liquid phase. So it has to be purified before disposal.[1],[2],[3]

In this contribution the toxic organic compounds are removed by a catalytic oxidation in super critical water (scH_2O) to CO_2 and water. Instead of HTC-waste water alternatively waste water of an organosolv process and a higher concentrated tailored waste water were used. Tests were done with H_2O_2 and O_2 as oxidants, with and without catalysts.

EXPERIMENTAL

9.54 ml/min of the waste water was fed together with 30 percent H_2O_2 or respectively with O_2 into a tube reactor together with a second water stream of 28.52 ml/min. The reaction temperature was set to 400 °C, the reaction pressure to 250 bar. The reactor outlet stream was captured in a glas bottle and analyzed offline by HPLC. 0.5 % Pd/Al_2O_3 and two Pt/Al_2O_3 (1 %, 5 %) catalysts were used.

Data for waste water oxidation:

	Organosolv waste water	Tailored waste water
Components	Furfural, 5-HMF	Furfural, 5-HMF, HCOOH, CH_3COOH, Glucose, Xylose
$\dot{V}_{H2O2}$	0.104 ml/min (5.05 mmol/min)	-
$\dot{V}_{O2}$	11.391 ml/min (0.51 mmol/min)	24.793 ml/min (1.1 mmol/min)

RESULTS

Organosolv waste water oxidation (cf. figure 1):
By the super critical water oxidation (SCWO) of the organolsolv waste water it was investigated that with O_2 (Decrease: HMF: 85 %; Furfural: 87 %) the sc-oxidation was more effective than with H_2O_2 (Decrease: HMF: 21 %; Furfural: 73 %) and the effectivity increased further by using the 0.5 % Pd-catalyst (Decrease: Furfural: 98 %).

Tailored waste water oxidation (cf. figure 2):
The SCWO of the tailored waste water showed that for oxidation of glucose and xylose the catalyst had no effect. Both components were nearly completely removed also in the blind test. For removing the other components the catalysts had promising effects. Formic acid concentration decreased without catalyst about 84 %, with the Pt-catalysts about 98 %. Acetic acid concentration decreased to 76 % without catalyst and with catalyst to 77 % (1% Pt) and 89 % (5% Pt). HMF concentration decreased in the blind test about 93 %, with catalyst 98 %. And for furfural the oxidations with the catalysts reduced the concentration about 91% and 98 %, whereas the blind test just reduced the concentration of furfural to 87 %.

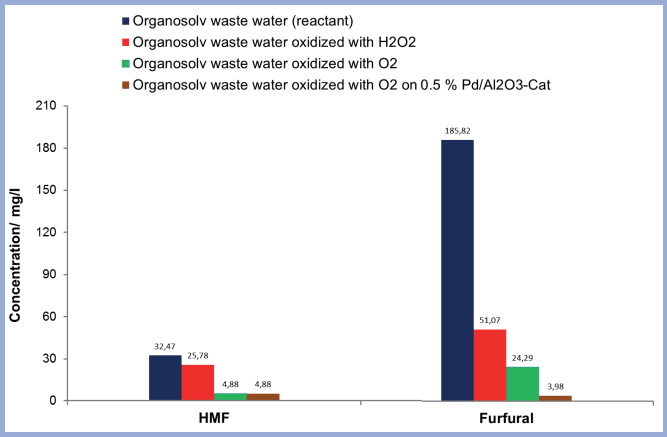

Figure 1: Results of the oxidation of the organosolv waste water.

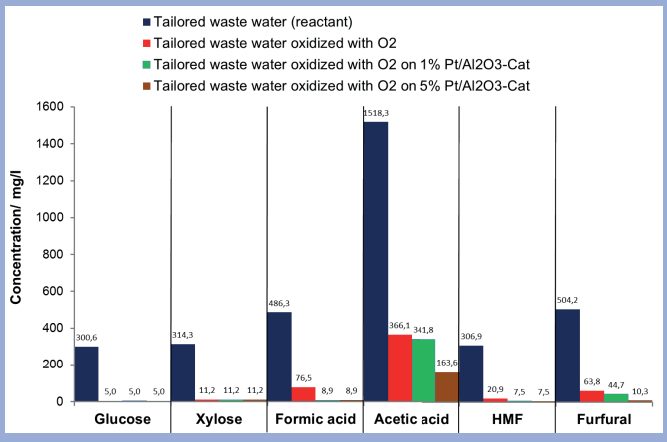

Figure 2: Results of the oxidation of the tailored waste water.

CONCLUSION

Maximum removal of the toxic compounds from HTC-waste water by SCWO was found for using O_2 as oxidant and an oxidation catalyst (Pt, Pd-catalyts). It seems that high Pt-concentrations on the catalysts are promising (cf. figure 2). Further tests to verificate the results and to investigate the influence of the different catalyst types have to be done.

LITERATURE

[1] Berge, N. et al., Environmental Science & Technology (2011), Volume 45(13), p. 5696–5703.
[2] Patent, DE, 102012024463 A1, 2012-12-13, Wilhelm H.-J.
[3] Ramke, H.-G. et al., In: COSSU, R. et al. (EDTS.), 2009: 12. Int. Waste Mgmt. and Landfill Symposium, 05-09 October.