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Biomass based energy intermediates boosting biofuel production

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Deliverable

Feasibility of combined production of HTC and HMF

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Publishable Summary

Process water of the HMF-production form fructose is used to perform HTC of draff. Compared to addition of pure water, the coal yield is increased and the coal as slightly different properties likes a lower volatile mater content and an elementary composition with lower hydrogen content. The main advantage of such a combination is the avoidance of waste water treatment in the HMF production process. From the view of the HTC process, not only residual or “waste” biomass but also “waste water” is used, leading to a remarkable cost reduction.

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Report

Feasibility of combined production of HTC and HMF

1. Introduction

The original aim in WP 3 was to isolate Hydroxymethylfurfural (HMF) from the process water of the HTC process. It was found that the concentration was below 1 wt.% and therefore much too low for such an isolation. The reason is that HMF is an intermediate of the HTC reaction, and in a process optimized for HTC-coal production the concentration is therefore low. This is illustrated in Fig. 1. A similar behavior is shown by furfural, formed from Hemicellulose mainly (Fig. 1). On the other hand, HMF is a most interesting platform chemical of bio-economy according to studies of NREL/DOE and the EU BREW project; no other chemical form biomass provide access to such a high number of consecutive chemicals and potential applications (Fig. 2). As consequence, the company AVA and the KIT have developed a process to produce HMF from fructose which is applied by the new-founded company AVA-Biochem. This development, occurring in parallel to the BioBoost project, is illustrated by Fig. 3.

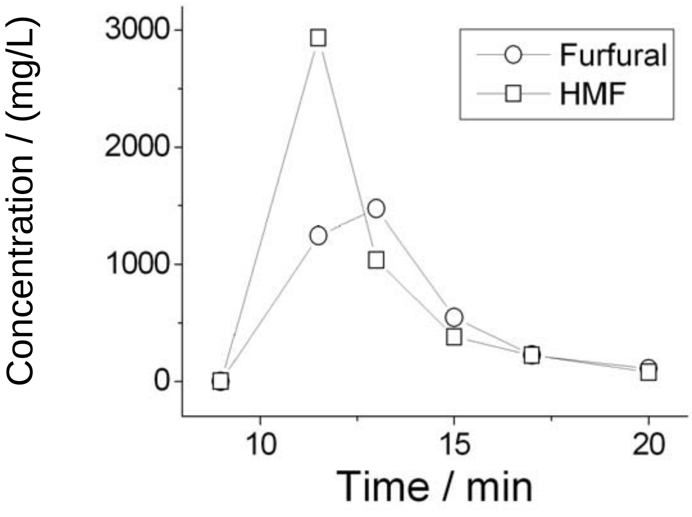

Figure 1: Concentration of HMF and furfural from wood, extracted with hot water in a semi-batch reactor (200 °C, 3 mL/min water flow rate).

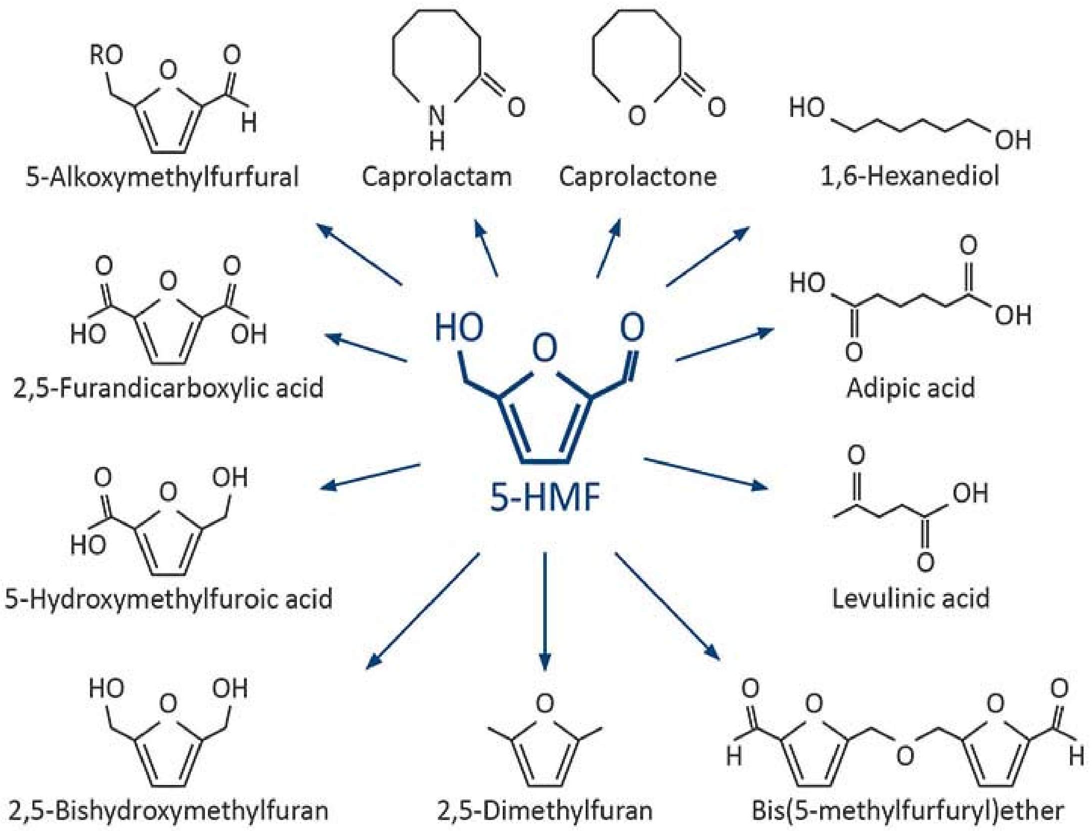

Figure 2: HMF as platform chemical (from AVA-CO2 website).

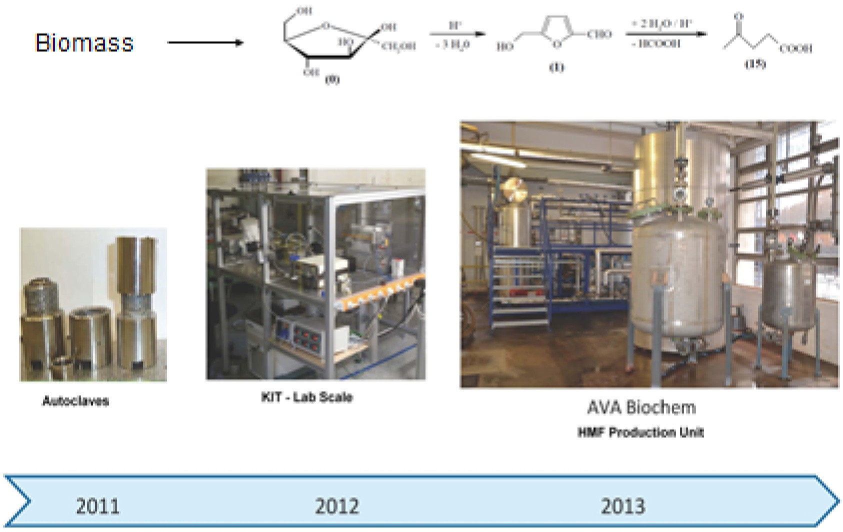

Figure 3: Illustration of the process development and scale-up of the HMF production process.

From this, the idea was generated to combine the HMF- and the HTC-process in another way than originally planned: Water of the HMF process was used in the HTC-process as process medium.

2. Experimental Investigation

Here experiments were conducted in which water of the HMF-process from AVA-Biochem was used together with brewery draff for HTC in batch autoclaves.

2.1. Experimental set-up

For the experiments, a suspension of dried, crushed draff (from the brewery Höpfner, Karlsruhe) in pure water or process water from the AVA-Biochem was filled into an autoclave with a volume of 240 ml (Fig.4). Three experiments were conducted with water and three with process water at always the same reaction conditions. All suspensions had a dry matter content of 15 wt.%. The pressure (5 MPa) was adjusted via the filling level in the autoclave prior to heating-up. The reactor was heated in a modified GC-oven to an internal temperature of 200 °C. The autoclave stayed at this temperature for five hours and was cooled down by removing from the oven. The gas formed was collected and measured by a GC. Then the coal was separated by filtration and dried. The yield of the wet and dry coal, as well as the dry matter content (according DIN EN 14774-1) was determined. The elementary composition the coal was measured (by Vario EL 3). The ash content (DIN EN 14775) and the amount of volatiles were determined by DIN 51720.

Figure 4: Autoclave in which the experiments were conducted (250 ml, stain-less steel).

2.2. Results and Discussion

Table 1 shows the results of HTC coal yields. The yield of coal is significant higher if process water from HMF production is used instead of pure water. These results were not expected, because HMF, the most important intermediate of HTC in view of polymerizing to coal, was missing; HMF was quantitatively removed by extraction at AVA-Biochem. Obviously other compounds, still in the water have polymerized to coal or at least assisted the recombination of dissolved molecules. Relative to the *biomass input* the coal yield was increase from 52.5-53.9 wt.% to 62.8-63.4 wt. %. On the other hand the process water gave a certain additional carbon input in addition to the biomass. If this is considered, the experiments with process water have slightly lower carbon efficiency relative to *overall carbon input* (Table 1) and as consequence the aqueous product of HTC has a slightly higher carbon content. Anyway, the difference is unexpected low regarding the fact that the intermediate with the fastest polymerization rate, namely HMF, is missing. In the case that other components polymerize but less HMF, the properties of the HTC-coal are important to investigate.

Table 1: Yields and efficiencies (DM: Dry Matter)

Temp. [°C]	Water used	Yield dry Coal [g]	Coal Efficiency[a] [wt. %]	DM content [g/g]	C-Efficiency[b] %
220	Pure Water	12.6	53.9	0.979	75.00
220	Pure Water	12.4	52.5	0.989	75.00
220	Pure Water	12.4	52.8	0.982	75.11
220	AVABIOCHEM	15.0	63.4	0.970	74.77
220	AVABIOCHEM	14.9	62.8	0.976	74.22
220	AVABIOCHEM	14.8	62.8	0.969	74.66

[a] relative to biomass input
[b] relative to carbon input (from biomass and process water)

Table 2 shows a comparison of the properties measured for HTC coal from draff with pure water and process water from HMF production, respectively. The water from AVA-Biochem includes only salts of high solubility, therefore and because of the higher coal yield the ash content is lower than in the HTC process with only water. The volatile matter content of the coal made with process water is significant lower (or the fixed carbon higher) than that of the "normal" HTC coal. This hints to a different nature of the polymerization product produced by the organic compounds in the process water compared to the HTC coal formed after pure draff hydrolysis. This assumption is supported by a slightly different composition of the coal (Fig. 5)

Table 2: Comparison of the properties of HTC coal from draff and pure water (Dist) or process water (PW) from HMF-production

	Dist. H_2O		PW	
Ash content /wt. %	4.05	±0.14	3.53	±0.04
Volatile Matter /wt.%	64.94	±0.58	62.64	±0.17
Fixed carbon /wt.%	31.01		33.83	

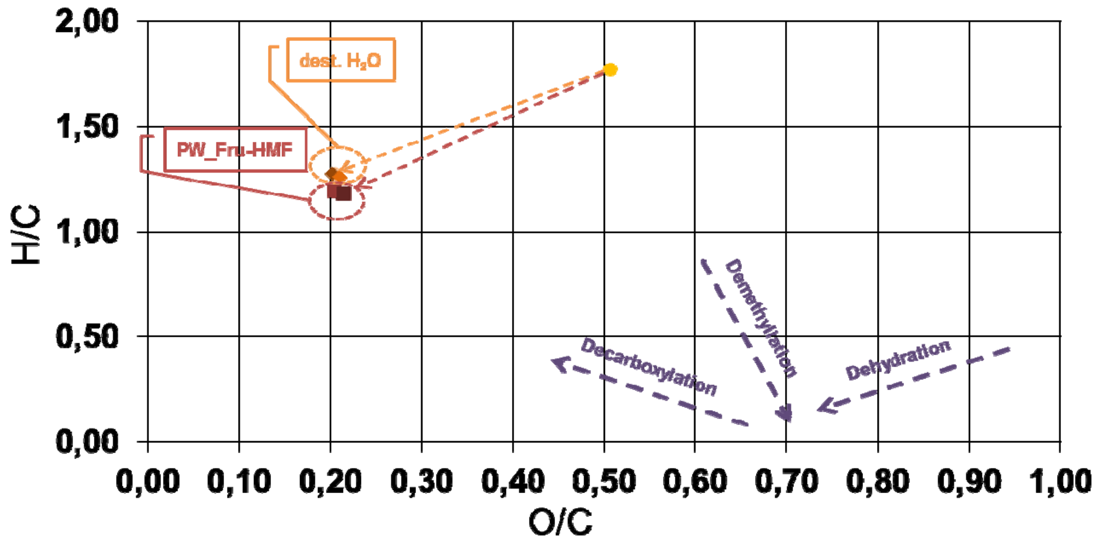

Figure 5: Results of hydrothermal carbonization shown in a Van-Krevelen-Diagramm.

3. Process Combination

The experimental results show that HMF process water can be applied for the production of HTC coal. A possible combination is shown in Fig. 6: Water from the HMF process is used for HTC.

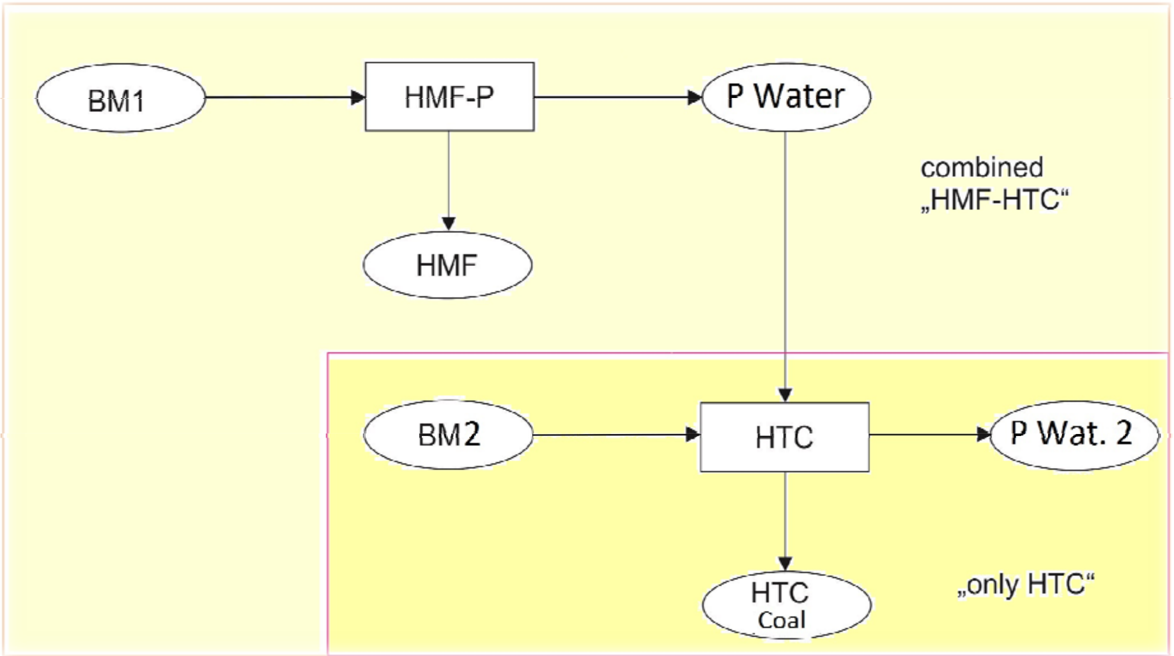

Figure 6: Coupling of HMF-production with HTC

The main advantage of a coupled process is that process water from HMF production is not treated as waste but utilized. During HTC, the carbon load in water is reduced combined with an increased yield of HTC coal. The process water of HTC is still produced, but it has only a very little increased carbon content and can be treated as in the "only HTC" process.

4. Conclusion

The combination of HMF- and HTC process via the use of HMF-process water in HTC is possible. The yield of HTC coal is increased and the HMF-process water has not to be treated e.g. in a sewage plant. Both leads a significant benefit of the combined process compared to the single processes in view of production cost. This was one of the main aims of BioBoost; to reduce the production cost of energy carrier by the co-production of high-value chemicals.

5. Outlook

In view of an industrial application, there are still a lot of questions to be answered. The most important one is, whether the minor components cause problems in the process water treatment usually applied by AVA-CO2. For this purpose an application for a new project is planned, in which the process fundamentals are studied in more detail and a conceptual process design is worked out.