# Biomass Oxidation to Formic Acid in Aqueous Media Using Polyoxometalate Catalysts – Boosting FA Selectivity by In-situ Extraction

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ARTICLE

# Biomass Oxidation to Formic Acid in Aqueous Media Using Polyoxometalate Catalysts – Boosting FA Selectivity by In-situ Extraction

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We here report the remarkable finding that biomass oxidation to formic acid (FA) in water-organic biphasic reaction systems is far more selective than the same reaction in monophasic aqueous media. While literature claims that the yield of FA from carbohydrates and biomass is limited to less than 68 % even for simple substrates, such as e.g. glucose or glycerol, we here demonstrate FA yields of up to 85 % from glucose. Using our biphasic reaction protocol even raw lignocellulosic biomass, such as beech wood, leads to FA yields of 61 %. This is realized by applying the polyoxometalate $H_8PV_5Mo_7O_{40}$ as homogeneous catalyst, oxygen as oxidant and water as solvent in the presence of a long-chain primary alcohol as in-situ extracting agent. The new, liquid-liquid biphasic operation opens a highly effective way to produce pure FA – a liquid syngas equivalent – from wood in a robust, integrated, low temperature process.

## Introduction

In general, industrialized nations seek replacing their fossil based energy systems by renewables on the long run. In the light of recent innovations in oil and gas production technologies[1] this is not preliminary due to the limited nature of hydrocarbon resources. As a matter of fact, burning fossil fuels leads to an increasing $CO_2$ level in the atmosphere with almost certainly very negative consequences for the global climate.[2] A promising approach to avoid a part of the $CO_2$ emissions from fossil fuels is the energetic use of biomass. Biomass can serve as fuel for incineration plants. However, for large scale application of such technologies the low energy density of biomass, its typically high water content and its inhomogeneous nature (including high levels of N- and S-containing compounds) is problematic. That is why many approaches to valorise biomass use as a first step the conversion of the crude biomass into a secondary energy carrier. Well studied examples of this strategy are the conversion of biomass into pyrolysis oil,[3] synthesis gas,[4] or methane.[5] This publication expands on the concept to establish formic acid (FA) as an alternative biomass-derived secondary energy carrier.

FA is a commodity that is widely used in the chemical, agricultural, textile, leather, pharmaceutical, and rubber industries.[6] More recently, FA has been proposed as a suitable hydrogen storage compound as it can be easily and selectively decomposed to hydrogen and $CO_2$ through metal catalysed processes under very mild conditions.[7-10]

Note that by thermal decomposition (above 373 K) FA can also be converted into CO and water. Thus, FA can be regarded as a liquid syngas equivalent. Furthermore, Deng and co-workers developed a solar-induced hybrid fuel cell that directly consumes natural polymeric biomass. Therein, the biomass is oxidized by polyoxometalates to FA, respectively formaldehyde in aqueous solution under solar irradiation applying very mild conditions avoiding thermal degradation.[11]

The first paper aiming at a selective synthesis of FA or formate salts from biomass was published in 2008 by Jin et al.[12,13] Glucose, a model compound for carbohydrate biomass, was oxidised hydrothermally with hydrogen peroxide as oxidant at temperatures between 473 K and 573 K in the presence of alkali hydroxide obtaining FA in up to 75 % yield. However, such high FA yields were only obtained at high alkali concentrations (1.2 M) and over-stoichiometric use of $H_2O_2$. Without addition of alkali salts, the maximum FA yield was only 24 %.

A few papers have also been published describing the formation of FA from biogenic substrates by the help of homogeneous precious metal complexes. Mehdi and co-workers described the Ru-catalysed dehydration of sucrose in the presence of hydrogen pressure to yield up to 45 % FA.[14] Very recently, Xu et al. described the oxidation of glycerol with Ru-nanoparticles on reduced graphite oxide to yield up to 60 %

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† Electronic Supplementary Information (ESI) available: Tables for extraction solvent screening, NMR spectra of the esterification tests, NMR spectra of 1-hexanol, 1-heptanol stability tests, GC-MS analysis of products from $^{13}C$ glucose oxidation, FA product stability in the reaction phase, Ester formation between toluenesulfonic acid and the alcoholic extraction solvent].
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FA in the presence of $FeCl_3$.[15] Additionally, the oxidative conversion of glycerol to FA was reported using vanadium-substituted phosphomolybdic acids as catalysts and molecular oxygen as the oxidant. This reaction provides high conversion efficiency, resulting in an absolute FA yield of 36.4 wt% of the initial reaction mixture.[16]

A fundamentally different approach to produce FA from biomass was introduced by some of us.[17-20] The reaction uses a homogeneous polyoxometalate catalyst and proceeds in aqueous phase with oxygen or air as the oxidant. A very broad range of biomasses has been found to be applicable to this process leading at temperatures below 373 K and full substrate conversion to FA as the sole product in the liquid phase accompanied by $CO_2$ as sole gaseous by-product. With producing only these two products at full conversion, this so-called "OxFA process" avoids many well-known problems of biorefinery reactions, such as complex product mixtures including sticky polymer or tar formation. Under typical OxFA conditions (363 K, 20 bar $O_2$ pressure, $H_5[PV_2Mo_{10}O_{40}]$ as catalyst) complete conversion of glucose is observed after 3 h reaction time with the carbon in the substrate being converted 49 % to FA and 51 % to $CO_2$.[17] With a slight modification of the initial protocol, namely the addition of toluenesulfonic acid as hydrolysing and phase transfer agent, also cellulose, lignin, wood and other complex wet biomasses can be oxidised by the same method, although the reaction is somewhat slower (full conversion requires typically 24 to 120 hours).[19] FA yields under these conditions are 35 % for beech wood, for example. Research into alternative POM catalyst systems for this application resulted in some improvements regarding the required oxygen pressure. But even with glucose as substrate, the maximum yield in FA did never exceed 57 % at 363 K, while reported FA yields with cellulose as substrate were around 28 %.[20] Very recently, several research groups followed on a similar path and reported the HPA catalysed oxidation of cellulosic biomass under much harsher temperature conditions (T= 453 K) to result in up to 68 % FA yield using $H_4PVMo_{11}O_{40}$ as catalyst. It is noteworthy that at 453 K FA decomposes to a significant extent to CO and water. Moreover, the formation of around 12 % acetic acid was found under these experimental conditions.[21] Similar maximum FA yields (65 %) were obtained from cellulose oxidation in a solution of sodium metavanadate ($NaVO_3$) in aqueous sulphuric acid at 433 K.[22] The same reaction system resulted in FA yields of up to 47 % when converting wheat straw.[23] A novel route to synthesis gas from sugars, cellulose and hemicellulose published by Sarma et al. uses the same polyoxometalate-mediated oxidation process to form FA in the first step. This stoichiometric method leads to a 65 % yield in CO that is consequently formed from FA by reaction with concentrated sulphuric acid.[24] Finally, heteropolyanion-based ionic liquids have been applied as catalyst for cellulose conversion leading to 51 % FA yields.[25]

Summarizing the wealth of very recent work on vanadium-catalysed biomass oxidation, it can be stated that this transformation is characterized by its mild reaction temperature (compared to biomass gasification or hydrothermal reforming) and by its applicability to a wide range of biogenic raw materials - including non-edible biopolymers, complex biogenic mixtures and wet biomasses. However, all reported methods have in common that they produce FA in a maximum yield of clearly below 70 % using a monophasic, acidic, aqueous reaction system. Thus more than 30 % of the carbon present in the biogenic substrate is lost to either $CO_2$ (mild conditions, T< 373 K) or a still complex mixture of CO, organic acids and other side products (harsher conditions, T> 373 K).

In this contribution we describe our finding that under the conditions of a water-organic in-situ extraction, POM catalysed biomass oxidation under typical OxFA conditions (363 K, 20 bar $O_2$ pressure) results in significant higher FA yields than so far reported for any monophasic reaction protocol. Our reason to study biphasic reaction mixtures was to combine FA isolation in a clever way with the OxFA reaction process as simple distillation is not feasible due to the high-boiling water-FA azeotrope. Established technical protocols to isolate pure FA from aqueous solutions include azeotropic distillation,[26,27] liquid-liquid extraction,[28-30] extraction followed by distillation,[31-33] reactive extraction[34-38] as well as extractive distillation.[39-42] In the context of POM catalysed biomass oxidation, the FA isolation process must in addition deal with the water-soluble, highly acidic heteropolyacid (HPA) catalyst to allow for efficient catalyst recycling.

## Results and discussion

### Extraction solvent screening

The reaction solution of the OxFA process consists of formic acid (FA), residues of substrate, additive, water and the HPA catalyst, e.g. $H_8[PV_5Mo_7O_{40}]$ (HPA-5). In order to selectively extract FA from this mixture, an appropriate extracting agent has to be found. Taking into account that this solvent must have suitable properties for both the extraction step and the subsequent isolation of pure FA from the organic solvent, the following solvent characteristics are required: (a) high capacity for FA (large distribution coefficient K), (b) high selectivity S with respect to FA (non-oxidised biomass, additive and catalyst should stay in the aqueous phase), (c) wide miscibility gap with water, (d) significant density difference between the aqueous phase containing the catalyst and the organic phase containing FA (reduction of phase separation effort), (e) no azeotrope formation with FA and significant boiling point difference between extraction solvent and FA, (f) thermal and oxidative stability of the extraction solvent under all applied process conditions.

Based on these criteria, a solvent screening study based on partition coefficients, extraction selectivities, and stability tests has been carried out. The partition coefficient and the extraction selectivity were determined by mixing a simulated product solution containing FA and HPA-5 in water with the extracting agent at 363 K for one hour. After phase separation, samples from both phases were analysed by means of $^1$H-NMR to determine the FA concentration. Experimental details and all determined partition coefficients are shown in the ESI (ESI Table 1†). From this first screening, 1-hexanol and 1-heptanol showed clearly the best distribution coefficients and selectivities among the tested solvents. However, using an alcohol as extracting agent for FA provokes the question whether ester formation between FA and the extracting agent takes place.

To clarify this point, the esterification behaviour was investigated by preparing biphasic mixtures containing 1.0 g of aqueous FA solution (5 or 15 wt % FA) and 1.0 g of 1-hexanol and 1-heptanol, respectively, and this mixture was heated to 363 K. The degree of esterification was determined 5 min and 12 hours after sample preparation by $^{13}$C-NMR spectra (see ESI Figures 1-8† and ESI Table 2†). As can be seen from ESI Table 2†, esters were only detected in the organic phase due to their low solubility in the aqueous phase. Ester formation was found to be a function of contact time with almost no ester detectable after 5 min while after 12 h contact time 11 to 14 % of FA was found as FA ester. Thus, FA ester formation occurs to some extent during prolonged FA extraction, however, ester cleavage in the following down-stream processes will liberate pure FA from the ester and contributes to the FA yield.

For testing the oxidation stability of the applied extraction solvent, an aqueous solution of the HPA-5 catalyst and the extracting agent was heated in an autoclave for 72 h at 363 K (20 bar $O_2$, 1000 rpm) to mimic the conditions of biomass oxidation. It was found that the extracting agents remained stable under these conditions (ESI Figures 9-10†).

In order to exclude FA formation from 1-hexanol or 1-heptanol in presence of FA under reaction conditions, an additional experiment was carried out in which FA, 1-heptanol and HPA-5 were processed in water at 363 K for 72 h (20 bar $O_2$, 1000 rpm). Again, it was found that the extracting agent remained stable (ESI Figure 11†). Furthermore, to prove unambiguously the origin of carbon in the formed FA and $CO_2$ during oxidation in presence of organic extraction solvent, we performed experiments with $^{13}$C glucose as substrate. These experiments clearly proved that all detected FA and $CO_2$ after reaction were $^{13}$C-labelled confirming their sole origin from glucose (see ESI Figures 12-13†). Furthermore, these results evidenced once more that the applied primary alcohol is not oxidised during the applied reaction conditions. It was double-checked by GC, $^1$H- and $^{13}$C-NMR that 1-hexanol or 1-heptanol do not convert under the applied OxFA conditions to FA, carbon dioxide or any other organic compound (see ESI Figures 9 and 10†).

## In-situ extraction of reaction mixtures from glucose oxidation

After some ex-situ extraction studies for FA isolation confirming the suitability of 1-hexanol and 1-heptanol for downstream-processing of OxFA reaction mixtures (see ESI†), we tested whether these extraction solvents can also serve as in-situ FA extraction media. The reaction solution in these oxidation experiments consisted of an aqueous solution of glucose and HPA-5 with the same volume of 1-hexanol or 1-heptanol. Again the reactor was operated at 363 K and 20 bar $O_2$. The yield of FA was determined by means of $^1$H-NMR using benzene as an external standard. FA yields were calculated as $Y_{FA}$= n(FA)/n(C-atoms feedstock). The yield of $CO_2$ was determined by means of GC-analysis as $Y_{CO2}$= n($CO_2$)/n(C-atoms feedstock). The combined yield of formic acid and $CO_2$ was calculated by n(FA) + n($CO_2$)/n(C-atoms feedstock), respectively. This value was applied to describe the degree of substrate oxidation to FA and $CO_2$ after a given reaction time.

Much to our surprise we found that the presence of the extraction solvent in the reactor led to a largely increased FA selectivity. FA selectivities of up to 85 % FA could be obtained at full glucose conversion (Table 1). However, this remarkable increase in selectivity compared to the monophasic reaction in water went along with clearly lower reaction rates. Samples taken after 6, 24 and 48 h proved consistently that the biphasic reaction mode causes slower oxidation kinetics but significantly higher FA selectivities. The resulting FA selectivities were remarkably independent on the degree of glucose conversion, both for the monophasic and the biphasic reaction mode. The corresponding experiment without extracting agent in the conventional, monophasic aqueous reaction system led to the expected FA-yield of 53 % at full glucose conversion under identical reaction conditions. An increase in oxygen pressure during glucose conversion ($O_2$ pressure of 60 bar) was found to be of very little effect (ESI Figure 14†). This is in good agreement with previous studies showing that already at 20 bar $O_2$ pressure HPA catalyst re-oxidation is fast compared to glucose oxidation.[20]

**Table 1:** Oxidative conversion of glucose to FA by HPA-5 in aqueous solution - comparison of the monophasic reaction with the biphasic reactions using 1-hexanol and 1-heptanol as in-situ extracting agent.

| Entry | Reaction time (h) | Extracting agent | Combined Yield FA+$CO_2$ (%) | FA-selectivity (%) | FA-yield (%) |
|---|---|---|---|---|---|
| 1 | 6 | - | 76 | 54 | 41 |
| 2 | | 1-hexanol | 23 | 79 | 18 |
| 3 | | 1-heptanol | 32 | 71 | 23 |
| 4 | 24 | - | 100 | 51 | 51 |
| 5 | | 1-hexanol | 79 | 86 | 68 |
| 6 | | 1-heptanol | 79 | 75 | 59 |
| 7 | 48 | - | 100 | 53 | 53 |
| 8 | | 1-hexanol | 100 | 85 | 85 |
| 9 | | 1-heptanol | 97 | 76 | 73 |

*Procedure:* 1.80 g glucose and 0.91 g (0.5 mmol) HPA-5 dissolved in 100.0 mL $H_2O$, 100 g primary alcohol, 363 K, 20 bar oxygen pressure, 1000 rpm.

To confirm that the lower FA yield in the monophasic reaction system is not due to consecutive FA decomposition under the applied reaction conditions, FA was added to an aqueous HPA-5 solution and contacted with 20 bar $O_2$ for 48 h. NMR data confirmed the stability of FA under the applied conditions (ESI Figure 15†).

To clarify the reason for the sharp increase in FA selectivity in the biphasic reaction mode, we investigated the influence of higher FA concentration and thus lower pH values both on the monophasic and the biphasic oxidation of glucose. For the monophasic experiment, 1.8 g (10 mmol) of glucose and 0.91 g (0.5 mmol) of the HPA-5 catalyst were dissolved in 100 g water and in 80 g water / 20 g FA, respectively. These two experiments were compared under identical conditions (20 bar $O_2$, 363 K, 48 h, 1000 rpm) to biphasic systems with 1-hexanol as in-situ extraction solvent (entries 3 and 4 in Table 2).

These experiments clearly reveal that higher FA concentrations and lower pH in the aqueous reaction phase lead to lower FA selectivities both in the monophasic and the biphasic systems. This corresponds well to literature reports claiming the optimum pH range for the applied polyoxometalate catalyst to be between 2-4.[43] Notably, in-situ extraction with 1-hexanol allows not only simple FA isolation from the aqueous phase but also leads to a significant increase in pH of the catalytic aqueous phase compared to the respective monophasic case due to FA extraction. As result, FA selectivities in the biphasic system are significantly higher indicating that low pH values are detrimental for selective FA formation.

**Table 2:** Oxidative conversion of glucose to FA by HPA-5 in aqueous solution – effect of FA concentration and pH on FA selectivity for both, a monophasic reaction system and a biphasic system with 1-hexanol as in-situ extracting agent.

| Entry | Initial FA-concentration [wt%] | Extracting agent | Combined yield $FA+CO_2$ (%) | FA-selectivity (%) | pH-value[a] (-) |
|---|---|---|---|---|---|
| 1 | 0 | - | 100 | 51 | 1.83 |
| 2 | 20 | - | 100 | 26 | 1.12 |
| 3 | 0 | 1-hexanol | 100 | 85 | 2.58 |
| 4 | 20 | 1-hexanol | 100 | 64 | 1.52 |

*Procedure:* 1.80 g glucose and 0.91 g (0.5 mmol) HPA-5 catalyst dissolved in 100.0 g $H_2O$ or 80 g water / 20 g FA, respectively; 100 g primary alcohol, 363 K, 20 bar oxygen pressure, 1000 rpm, 48 h reaction time; a) pH determined after reaction.

### In-situ extraction of reaction mixtures from sucrose and beech wood

Our next set of experiments aimed to verify whether in-situ extraction of FA and the related selectivity effects are transferable to more complex biogenic substrates. For this purpose, the water-soluble disaccharide sucrose and the water-insoluble complex biomass beech wood were oxidised. Table 3 shows the results of the combined yields and the FA selectivities for sucrose as a substrate, Table 4 the same data for beech.

In general, sucrose oxidation shows very similar results to glucose oxidation. Again, the reaction in the biphasic system is slower but much more selective independent on sucrose conversion (here indicated as combined yield in FA and $CO_2$).

**Table 3:** Oxidative conversion of sucrose to FA by HPA-5 in aqueous solution – comparison of the monophasic reaction with the biphasic reaction using 1-hexanol and 1-heptanol as in-situ extracting agents.

| Entry | Reaction time (h) | Extracting agent | Combined yield FA+ $CO_2$ (%) | FA-selectivity (%) | FA-yield (%) |
|---|---|---|---|---|---|
| 1 | 6 | - | 91 | 55 | 50 |
| 2 | | 1-hexanol | 58 | 77 | 45 |
| 3 | | 1-heptanol | 74 | 73 | 54 |
| 4 | 24 | - | 97 | 54 | 54 |
| 5 | | 1-hexanol | 89 | 81 | 72 |
| 6 | | 1-heptanol | 90 | 73 | 66 |
| 7 | 48 | - | 100 | 52 | 52 |
| 8 | | 1-hexanol | 96 | 79 | 76 |
| 9 | | 1-heptanol | 93 | 75 | 70 |

*Procedure:* 3.44 g sucrose and 0.91 g (0.5 mmol) HPA-5 catalyst dissolved in 100.0 mL $H_2O$, 100 g primary alcohol, 363 K, 20 bar oxygen pressure, 1000 rpm.

For processing beech wood in the same biphasic process, p-toluenesulfonic acid was used as solubilising and hydrolysing additive following the general literature protocol for POM-based oxidation reactions of water-insoluble biomass.[19] Using an additional acid in the biphasic reaction system containing an alcohol as in-situ extraction solvent provokes again the question whether ester formation between the solubilizer and the extraction agent occurs. This was first investigated by contacting aqueous *p*-toluenesulfonic acid with both, 1-hexanol and 1-heptanol, respectively. It was demonstrated by $^{13}$C-NMR spectra that due to the very high water content in the system the formation of toluenesulfonic acid esters is below detection limit (ESI Figures 16,17†). The results of the beech wood oxidation are shown in Table 4.

**Table 4:** Oxidative conversion of beech wood to FA by HPA-5 in aqueous solution – comparison of the monophasic reaction with the biphasic reaction using 1-hexanol and 1-heptanol as in-situ extracting agents.

| Entry | Reaction time (h) | Extracting agent | Combined yield FA+ $CO_2$ (%) | FA-selectivity (%) | FA-yield (%) |
|---|---|---|---|---|---|
| 1 | 6 | - | 56 | 38 | 21 |
| 2 | | 1-hexanol | 18 | 58 | 10 |
| 3 | | 1-heptanol | 25 | 52 | 13 |
| 4 | 24 | - | 79 | 39 | 31 |
| 5 | | 1-hexanol | 45 | 53 | 24 |
| 6 | | 1-heptanol | 57 | 55 | 32 |
| 7 | 48 | - | 100 | 39 | 39 |
| 8 | | 1-hexanol | 90 | 68 | 61 |
| 9 | | 1-heptanol | 92 | 61 | 56 |

*Procedure:* 1.63 g beech, 1.72 g TSA additive (10 mmol) and 0.91 g (0.5 mmol) HPA-5 catalyst dissolved in 100.0 mL $H_2O$, 100 g primary alcohol, 363 K, 20 bar, 1000 rpm.

From these results it is obvious that also the oxidation of complex, water-insoluble biomass, such as beech wood, benefits in the same very positive manner from FA in-situ extraction. For comparable and very high combined yields of

FA + $CO_2$ (indicating that almost all carbon of beech substrate was converted to either FA or $CO_2$) the FA selectivity was found to be 68 % using 1-hexanol (FA yield = 61 %) and 61 % (FA yield = 56 %) using 1-heptanol compared to 39 % selectivity and yield without the extraction solvent.

## Experimental

All chemicals were obtained commercially and used without further purification. The HPA-5 catalyst $H_8[PV_5Mo_7O_{40}] \times 12\, H_2O$ was synthesised according to the literature.[19,44] The characterisation via ICP-OES resulted in a P/V/Mo ratio of 1/4.87/7.21. Beech wood samples were donated from JBACH GmbH. Elementary analyses were performed using a Carlo Erba EA 1108 giving a molecular composition for beech wood of C/H/O ratio of 1.21/1.86/1. ICP-OES measurements were conducted on a Perkin Elmer Plasma 400, NMR spectra were recorded on a Jeol ECX-400 MHz. Gaseous sample analyses were performed using a Varian GC 450 equipped with a 2 m x 0.75 mm ID Shin Carbon ST column except for the experiments using $^{13}C$ glucose. The latter samples were analysed using GC-MS (gaseous samples: Agilent 7890B GC/ 5977A MSD-system with a 30 m 0.25 mm x 0.25 µm column and a single quadrupole MS; liquid samples: Varian CP-800 GC, Saturn 2200 MS CP-SIL 8CB equipped with a 30 m x 0.25 mm x 0.25 µm column and ion trap).

### Catalytic oxidation reactions

The oxidation reactions were carried out in a 600 mL Hastelloy C276 autoclave equipped with a gas entrainment impeller. Water (100 g), 0.91 g $H_8PV_5Mo_7O_{40}$, and 1.8 g glucose were charged into the vessel. The system was purged three times with oxygen, the stirrer was set to 300 rpm and heating was started. When the desired temperature of 363 K was reached, the oxygen pressure was increased to 20 bar and the stirrer was set to 1000 rpm.

### Ex-situ extraction

After oxidising a solution containing 1.8 g glucose, 0.91 g HPA-5 and 100.0 g $H_2O$ for 6 h at 363 K and 20 bar oxygen pressure, FA formation was determined by $^{1}H$-NMR spectroscopy. The extraction solvent (100.0 g) pre-heated to 363 K was then added and the resulting liquid-liquid biphasic mixture was stirred for 1 h at 363 K. The biphasic solution was separated, a sample of each phase taken and analysed by means of $^{1}H$-NMR to determine the FA concentration.

### Stability tests

1.82 g of HPA-5 and 100 mmol extracting agent (10.20 g 1-hexanol or 11.62 g 1-heptanol) were subjected to 363 K and 20 bar oxygen pressure for 20 h in 100 mL $H_2O$ or 90 mL of $H_2O$ and 10 mL of FA, respectively. In a third experiment 1.82 g of HPA-5, 2 g $^{13}C$ glucose as substrate and 100 g 1-hexanol in 100 mL water were processed at 363 K, 20 bar oxygen pressure and 1000 rpm for 24 h. In the stability experiment under 20 bar $CO_2$ atmosphere, 0.91 g HPA-5 was processed together with 10 g FA in 90 g of water at 363 K for 48 h and 1000 rpm. After each experiment, liquid samples of both phases were taken and analysed by $^{1}H$- and $^{13}C$-NMR spectroscopy. All gaseous samples were analysed by GC. The products of the experiment with $^{13}C$-glucose were analysed by GC-MS.

### Oxidation experiments with in-situ extraction

For the oxidation experiments with in-situ extraction (Tables 1-4), the respective substrate (1.80 g glucose, 3.44 g sucrose or 1.63 g beech), 0.91 g of HPA-5 catalyst, 100.0 g $H_2O$ and 100.0 g of 1-hexanol or 1-heptanol were charged into the reactor. Only for the oxidation using beech wood, 1.72 g of *p*-toluenesulfonic acid was used in addition. The system was purged three times with oxygen, then the reactor was heated to the reaction temperature while stirring at 300 rpm. When reaching 363 K, oxygen pressure and stirrer speed were set to the desired values. After the experiments, both liquid phases were analysed by $^{1}H$-NMR spectroscopy to determine their FA content.

### Esterification experiments

To investigate the esterification tendency of the applied alcoholic extraction solvents, mixtures of 1 g of aqueous FA/*p*-toluenesulfonic acid solution and 1 g of 1-hexanol/1-heptanol were prepared and heated to 363 K. The aqueous FA solution contained 5 wt% and 15 wt% of FA in distilled water, respectively; the aqueous TSA solution contained 0.17 wt% TSA in water. The degree of esterification was determined by means of $^{13}C$-NMR spectra directly and twelve hours after the preparation of the mixtures.

## Conclusions

Attempts towards an in-situ FA product isolation from the recently developed OxFA process led to the remarkable finding that biphasic water/organic reaction systems allow for a sharp increase in FA selectivity in the oxidation of various biogenic raw materials. While previous work established the view that FA from carbohydrates and biomass oxidation does not exceed FA selectivities of more than 70 % even with simple substrates, such as e.g. glucose or glycerol, we here demonstrate FA yields of up to 85 % from glucose and still 61 % from the challenging substrate beech wood.

We found that in-situ extraction of the biomass oxidation reaction mixture with long-chain primary alcohols, such as 1-hexanol and 1-heptanol, does not only provide a straight forward manner to isolate FA but also limits the drop in pH in the catalytic aqueous phase during FA formation. Our results indicate that this collateral effect is responsible for the much improved FA selectivity as the applied polyoxometalate catalyst $H_8PV_5Mo_7O_{40}$ (HPA-5) tends to produce a larger shares of $CO_2$ at pH values below 1.5.

We anticipate that our findings will strongly increase academic and industrial interest in selective biomass oxidation to FA. All reported specific advantages[20-22] of this biomass valorisation technology are maintained (mild reaction conditions, precious metal-free catalyst, broad range of applicable biomasses, simple product spectrum) while two of the main obstacles for this technologies, insufficiently low FA yields and problematic FA isolation, are elegantly solved. Obviously, the long reaction times that come along with the biphasic reaction system remain an important target for further optimization to improve process economics by higher productivities. FA from biomass represents a valuable platform chemical and a sustainable syngas equivalent.

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# Biogenic formic acid

1-hexanol and 1-heptanol were applied as in-situ extracting agents in the oxidation reaction of biomass to formic acid (FA) using the Keggin-type polyoxometalate ($H_8PV_5Mo_7O_{40}$) as homogeneous catalyst, oxygen as the oxidant and water as the solvent. This in-situ extraction system provides incomparable and unique FA-selectivities from biomass oxidation using both water-soluble sugars and complex biogenic substrates.