Cite this: *Energy Environ. Sci.*, 2015, 8, 2985

Biomass oxidation to formic acid in aqueous media using polyoxometalate catalysts – boosting FA selectivity by *in-situ* extraction†

Jenny Reichert,^a Birgit Brunner,^b Andreas Jess,^b Peter Wasserscheid^a and Jakob Albert^{*a}

Herein, we report a remarkable finding that biomass oxidation to formic acid (FA) in water–organic biphasic reaction systems is far more selective than the same reaction in a 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 glucose or glycerol, we demonstrate in this study that FA yields of up to 85% can be obtained 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 polyoxometalate $H_8PV_5Mo_7O_{40}$ as a homogeneous catalyst, oxygen as the oxidant and water as the solvent in the presence of a long-chain primary alcohol as an *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, and low-temperature process.

Received 1st June 2015,
Accepted 5th August 2015

DOI: 10.1039/c5ee01706h

www.rsc.org/ees

Introduction

In general, industrialized nations seek to replace their fossil-based energy systems with renewables in the long run. In the light of recent innovations in oil and gas production technologies,¹ this is not primarily due to the limited nature of hydrocarbon resources. As a matter of fact, burning fossil fuels leads to increasing CO₂ level in the atmosphere, which has very negative consequences for the global climate.² A promising approach to avoid a part of the CO₂ emissions from fossil fuels is the energetic use of biomass. Biomass can serve as a 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) are problematic. Thus, many approaches valorise biomass use as a first step of 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 study expands this 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 because it can be easily and selectively decomposed to hydrogen and CO₂ through metal catalysed processes under very mild conditions.^{7–10}

It should be noted 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 and consecutively to form-aldehyde in an aqueous solution under solar irradiation applying very mild conditions avoiding thermal degradation.¹¹

The first study 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 the oxidant at temperatures between 473 K and 573 K in the presence of alkali hydroxide, which obtained FA in up to 75% yield. However, such high FA yields were only obtained at high alkali concentrations (1.2 M) and using over-stoichiometric use of H₂O₂. Without the addition of alkali salts, the maximum FA yield was only 24%.

^a Lehrstuhl für Chemische Reaktionstechnik der Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany. E-mail: jakob.albert@fau.de; Fax: +49 9131 85 27420; Tel: +49 9131 85 67417

^b Lehrstuhl für Chemische Verfahrenstechnik der Universität Bayreuth, Zentrum für Energietechnik (ZET), Universitätsstraße 30, 95440 Bayreuth, Germany

† 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 ¹³C glucose oxidation, FA product stability in the reaction phase, ester formation between toluenesulfonic acid and the alcoholic extraction solvent. See DOI: 10.1039/c5ee01706h

A few studies have also been published that describe the formation of FA from biogenic substrates with the help of homogeneous precious metal complexes. Mehdi and co-workers described the Ru-catalysed dehydration of sucrose in the presence of hydrogen under 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% FA in the presence of FeCl₃.¹⁵ In addition, 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 an aqueous phase with oxygen or air as the oxidant. A very broad range of biomasses have been found to be applicable to this process at temperatures below 373 K, and full substrate conversion to FA as the sole product in the liquid phase accompanied by CO₂ as the sole gaseous by-product were observed. By producing only these two products at full conversion, this so-called “OxFA process” avoids many well-known problems related to biorefinery reactions, such as complex product mixtures, including sticky polymer or tar formation. Under typical OxFA conditions (363 K, 20 bar O₂ pressure, H₅[PV₂Mo₁₀O₄₀] as catalyst), complete conversion of glucose is observed after 3 h of reaction time with the carbon in the substrate being converted by 49% to FA and 51% to CO₂.¹⁷ With a slight modification of the initial protocol, namely, the addition of toluene sulfonic acid as a hydrolysing and phase transfer agent, cellulose, lignin, wood and other complex wet biomasses can also be oxidised *via* the same method, although the reaction is considerably slower (full conversion requires typically 24 to 120 h).¹⁹ FA yields under these conditions are 35% for beech wood. Research into alternative POM catalyst systems for this application resulted in some improvements regarding the required oxygen pressure. However, even with glucose as the substrate, the maximum yield in FA never exceeded 57% at 363 K, while the reported FA yields with cellulose as the substrate were around 28%.²⁰ Very recently, several research groups followed a similar path and reported the HPA catalysed oxidation of cellulosic biomass under much harsher temperature conditions ($T = 453$ K) to obtain an FA yield of up to 68% using H₄PVMO₁₁O₄₀ as the 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 (NaVO₃) 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 reported by Sarma *et al.* uses the same polyoxometalate-mediated oxidation process to obtain FA in the first step. This stoichiometric method leads to a 65% yield of CO, which is consequently formed from FA by reaction with concentrated sulphuric acid.²⁴ Finally,

heteropolyanion-based ionic liquids have been applied as a catalyst for cellulose conversion, leading to FA yields of 51%.²⁵

Summarizing the wealth of very recent studies 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 the reported methods have one common factor 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 as either CO₂ (mild conditions, $T < 373$ K) or a more complex mixture of CO, organic acids and other side products (harsher conditions, $T > 373$ K) are obtained.

In this contribution, we describe our finding that under the conditions of water–organic *in-situ* extraction, POM-catalysed biomass oxidation under typical OxFA conditions (363 K, 20 bar O₂ pressure) results in significantly higher FA yields than any monophasic reaction protocol reported to date. Our reason to study the biphasic reaction mixtures was to combine FA isolation in a clever way with the OxFA reaction process because simple distillation is not feasible due to the high-boiling water–FA azeotrope. The established technical protocols used 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.* H₈[PV₅Mo₇O₄₀] (HPA-5). 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 (the 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; and (f) thermal and oxidative stability of the extraction solvent under all the applied process conditions.

Based on these criteria, a solvent screening study based on partition co-efficients, 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 1 h. After phase separation, samples from both phases were analysed by means of ^1H -NMR to determine the FA concentration. Experimental details and all the partition coefficients determined are shown in the ESI† (Table S1). From this first screening, 1-hexanol and 1-heptanol showed clearly the best distribution coefficients and selectivities among the solvents tested. 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 or 1-heptanol and these mixtures were heated to 363 K. The degree of esterification was determined 5 min and 12 h after sample preparation using ^{13}C -NMR spectroscopy (see Fig. S1–S8 and Table S2, ESI†). As can be seen from ESI†, Table S2, 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 the FA ester. Thus, FA ester formation occurs to some extent during prolonged FA extraction; however, ester cleavage in the following downstream processes will liberate pure FA from the ester and contribute 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 (Fig. S9 and S10, ESI†).

To exclude FA formation from 1-hexanol or 1-heptanol in the presence of FA under the 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 (Fig. S11, ESI†). Furthermore, to determine unambiguously the origin of carbon in the formed FA and CO_2 during oxidation in the presence of organic extraction solvent, we performed experiments with ^{13}C glucose as the substrate. These experiments clearly proved that all the detected FA and CO_2 after reaction were ^{13}C -labelled, confirming their sole origin from glucose (see Fig. S12 and S13, ESI†). Furthermore, these results showed again that the used primary alcohol is not oxidised during the applied reaction conditions. It was double-checked by GC and ^1H - and ^{13}C -NMR spectroscopy that 1-hexanol or 1-heptanol do not convert under the applied OxFA conditions to FA, carbon dioxide or any other organic compound (see Fig. S9 and S10†).

In-situ extraction of reaction mixtures from glucose oxidation

After some *ex-situ* extraction studies for FA isolation confirmed 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

Table 1 Oxidative conversion of glucose to FA by HPA-5 in an aqueous solution – comparison of the monophasic reaction with the biphasic reactions using 1-hexanol or 1-heptanol as an *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 of glucose and 0.91 g (0.5 mmol) of HPA-5 dissolved in 100.0 mL of H_2O , 100 g of primary alcohol, 363 K, 20 bar oxygen pressure, 1000 rpm.

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 using ^1H -NMR spectroscopy using benzene as an external standard. FA yields were calculated as $Y_{\text{FA}} = n(\text{FA})/n(\text{C-atoms feedstock})$. The yield of CO_2 was determined using GC-analysis as $Y_{\text{CO}_2} = n(\text{CO}_2)/n(\text{C-atoms feedstock})$. The combined yield of formic acid and CO_2 was calculated by $n(\text{FA})+n(\text{CO}_2)/n(\text{C-atoms feedstock})$. 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 when compared to the monophasic reaction in water exhibited 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 of the degree of glucose conversion, both for the monophasic and the biphasic reaction modes. 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 have very little effect (Fig. S14, ESI†). This is in good agreement with previous studies showing that already at 20 bar O_2 pressure, the HPA catalyst re-oxidation is fast as compared to glucose oxidation.²⁰

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 stirred at 20 bar O_2 for 48 h. NMR data confirmed the stability of FA under the applied conditions (Fig. S15, ESI†).

To clarify the reason for the sharp increase in FA selectivity in the biphasic reaction mode, we investigated the influence of

Table 2 Oxidative conversion of glucose to FA by HPA-5 in an aqueous solution – the effect of FA concentration and pH on FA selectivity for both, a monophasic reaction system and a biphasic system with 1-hexanol as an *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) of HPA-5 catalyst dissolved in 100.0 g of H₂O 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 the reaction.

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 of water and in 80 g water/20 g FA, respectively. These two experiments were compared under identical conditions (20 bar O₂, 363 K, 48 h, 1000 rpm) to biphasic systems with 1-hexanol as an *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 that claim the optimum pH range for the applied polyoxometalate catalyst to be between 2 and 4.⁴³ Notably, the *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 as compared to the respective monophasic case due to FA extraction. As a result, FA selectivities in the biphasic system are significantly higher, indicating that low pH values are detrimental for selective FA formation.

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

Our next set of experiments aimed to verify whether the *in-situ* extraction of FA and the related selectivity effects are transferable to more complex biogenic substrates. For this purpose, water-soluble disaccharide sucrose and 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 and Table 4 shows the same data for beech wood.

In general, sucrose oxidation shows very similar results to glucose oxidation. Again, the reaction in the biphasic system is slower but much more selective and independent for sucrose conversion (here indicated as combined yield in FA and CO₂).

For processing beech wood in the same biphasic process, *p*-toluene sulfonic acid was used as a 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 an *in-situ* extraction solvent provokes again the question whether ester formation between the solubilizer

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

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 of sucrose and 0.91 g (0.5 mmol) of HPA-5 catalyst dissolved in 100.0 mL of H₂O, 100 g primary alcohol, 363 K, 20 bar oxygen pressure, 1000 rpm.

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

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 of beech wood, 1.72 g of TSA additive (10 mmol) and 0.91 g (0.5 mmol) of HPA-5 catalyst dissolved in 100.0 mL H₂O, 100 g of primary alcohol, 363 K, 20 bar, 1000 rpm.

and the extraction agent occurs. This was first investigated by stirring aqueous *p*-toluene sulfonic acid with both 1-hexanol and 1-heptanol. It was demonstrated by ¹³C-NMR spectroscopy that due to the very high water content in the system, the formation of toluene sulfonic acid esters is below the detection limit (Fig. S16 and S17, ESI†). The results of the beech wood oxidation are shown in Table 4.

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 as from *in-situ* extraction of FA. For comparable and very high combined yields of FA + CO₂ (indicating that almost all the carbon of beech wood substrate was converted to either FA or CO₂) 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 the chemicals were obtained commercially and used without further purification. The HPA-5 catalyst H₈[PV₅Mo₇O₄₀]·12H₂O

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 the molecular composition for beech wood with a 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 × 0.75 mm ID Shin Carbon ST column, except for the experiments using ¹³C glucose. The latter samples were analysed using GC-MS (gaseous samples: Agilent 7890B GC/5977A MSD-system with a 30 m 0.25 mm × 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 × 0.25 mm × 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 H₈PV₅Mo₇O₄₀, 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 carried out. 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 H₂O for 6 h at 363 K and 20 bar oxygen pressure, FA formation was determined by ¹H-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 was taken and analysed by ¹H-NMR spectroscopy to determine the FA concentration.

Stability tests

1.82 g of HPA-5 and 100 mmol of 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 of H₂O or 90 mL of H₂O and 10 mL of FA, respectively. In a third experiment 1.82 g of HPA-5, 2 g of ¹³C glucose as substrate and 100 g of 1-hexanol in 100 mL of water were processed at 363 K, 20 bar oxygen pressure and 1000 rpm for 24 h. In the stability experiment under 20 bar CO₂ atmosphere, 0.91 g of HPA-5 was processed together with 10 g of FA in 90 g of water at 363 K for 48 h and at 1000 rpm. After each experiment, liquid samples of both phases were taken and analysed by ¹H- and ¹³C-NMR spectroscopy. All the gaseous samples were analysed by GC. The products of the experiment with ¹³C-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 wood), 0.91 g of HPA-5 catalyst, 100.0 g of H₂O 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*-toluene sulfonic acid

was used during addition. The system was purged three times with oxygen, then the reactor was heated to the reaction temperature with stirring at 300 rpm. When the temperature of 363 K was reached, the oxygen pressure and stirrer speed were set to the desired values. After the experiments, both liquid phases were analysed by ¹H-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*-toluene sulfonic acid solution and 1 g of 1-hexanol or 1-heptanol were prepared and heated to 363 K. The aqueous FA solution contained 5 wt% and 15 wt% of FA in distilled water; the aqueous TSA solution contained 0.17 wt% TSA in water. The degree of esterification was determined by ¹³C-NMR spectroscopy immediately and 12 h 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 a sharp increase in FA selectivity in the oxidation of various biogenic raw materials. While previous studies 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 glucose or glycerol, herein we demonstrate FA yields of up to 85% from glucose and up to 61% from the challenging substrate of beech wood.

We found that the *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 straightforward method to isolate FA but also limits the decrease 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 because the applied polyoxometalate catalyst, H₈PV₅Mo₇O₄₀ (HPA-5), tends to produce a larger share of CO₂ 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 the reported specific advantages^{20–22} are maintained in this biomass valorisation technology (mild reaction conditions, precious metal-free catalyst, broad range of applicable biomasses, and simple product spectrum), while two of the main obstacles for this technology, insufficiently low FA yields and problematic FA isolation, are elegantly solved. Obviously, the long reaction times observed with the biphasic reaction system remain an important target for further optimization to improve the process economics *via* higher productivities. FA from biomass represents a valuable platform chemical and a sustainable syngas equivalent.

Acknowledgements

The authors would like to thank JBACH GmbH, Schesslitz, Germany for the donation of biomass samples. Financial support

by the Energie Campus Nürnberg (www.encn.de) is gratefully acknowledged.

Notes and references

- 1 R. York, *Nat. Clim. Change*, 2012, **2**, 441–443.
- 2 S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. Averyt, M. Tignor and H. L. Miller, *Climate Change 2007: The Physical Science Basis*, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2007.
- 3 S. Yaman, *Energy Convers. Manage.*, 2004, **45**, 651–671.
- 4 B. Kamm, *Angew. Chem., Int. Ed.*, 2007, **46**, 5056–5058.
- 5 A. Shiralipour and P. H. Smith, *Biomass*, 1984, **6**, 85–92.
- 6 W. Reutemann and H. Kieczka, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2005.
- 7 S. Fukuzumi, T. Kobayashi and T. Suenobu, *J. Am. Chem. Soc.*, 2010, **132**, 1496–1497.
- 8 A. Boddien, B. R. Loges, F. Gartner, C. Torborg, K. Fumino, H. Junge, R. Ludwig and M. Beller, *J. Am. Chem. Soc.*, 2010, **132**, 8924–8934.
- 9 A. Boddien, B. Loges, H. Junge and M. Beller, *ChemSusChem*, 2008, **1**, 751–758.
- 10 M. E. M. Berger, D. Assenbaum, N. Taccardi, E. Spiecker and P. Wasserscheid, *Green Chem.*, 2011, **13**, 1411–1415.
- 11 W. Liu, W. Mu, M. Liu, X. Zhang, H. Cai and Y. Deng, *Nat. Commun.*, 2014, **5**, 3208.
- 12 F. Jin, J. Yun, G. Li, A. Kishita, K. Tohji and H. Enomoto, *Green Chem.*, 2008, **10**, 612–615.
- 13 F. Jin and H. Enomoto, *BioResources*, 2009, **4**(2), 704–713.
- 14 H. Mehdi, V. Fabos, R. Tuba, A. Bodor, L. T. Mika and I. T. Horvath, *Top. Catal.*, 2008, **48**, 49–54.
- 15 J. Xu, Y. Zhao, H. Xu, H. Zhang, B. Yu, L. Hao and Z. Liu, *Appl. Catal., B*, 2014, **154–155**, 267–273.
- 16 J. Zhang, M. Sun and Y. Han, *RSC Adv.*, 2014, **4**, 35463–35466.
- 17 R. Wölfel, N. Taccardi, A. Bösmann and P. Wasserscheid, *Green Chem.*, 2011, **13**, 2759–2763.
- 18 A. Bösmann, R. Wölfel, P. Wasserscheid, N. Taccardi and J. Albert, WO/2012/034839 A1, 2012.
- 19 J. Albert, R. Wölfel, A. Bösmann and P. Wasserscheid, *Energy Environ. Sci.*, 2012, **5**, 7956–7962.
- 20 J. Albert, D. Lüders, A. Bösmann, D. M. Guldi and P. Wasserscheid, *Green Chem.*, 2014, **16**, 226–237.
- 21 J. Zhang, M. Sun, X. Liu and Y. Han, *Catal. Today*, 2014, **233**, 77–82.
- 22 W. Wang, M. Niu, Y. Hou, W. Wu, Z. Liu, Q. Liu, S. Ren and K. N. Marsh, *Green Chem.*, 2014, **16**, 2614–2618.
- 23 M. Niu, Y. Hou, S. Ren, W. Wu and K. N. Marsh, *Green Chem.*, 2015, **17**, 453–459.
- 24 B. B. Sarma and R. Neumann, *Nat. Commun.*, 2014, **5**, 4621.
- 25 J. Xu, H. Zhang, Y. Zhao, Z. Yang, B. Yu, H. Xu and Z. Liu, *Green Chem.*, 2014, **16**, 4931–4935.
- 26 J. J. Conti, D. F. Othmer and R. Gilmont, *J. Chem. Eng. Data*, 1960, **5**(3), 301–307.
- 27 W. Hunsmann and K. H. Simmrock, *Chem. Ing. Tech.*, 1966, **38**(10), 1053–1059.
- 28 K. Bott, G. Kaibel, H. Hoffmann, O. Kratzer and R. Irnich, EP 0012321 A1, 1979.
- 29 D. Wolf, R. Schmidt, U. Block, H. Schoenmakers, K. Bott and G. Kaibel, EP0017866 B1, 1982.
- 30 K. Bott, G. Kaibel, E. Mittelstaedt and R. Irnich, DE 3411384 A1, 1985.
- 31 M. Hallmann, H. H. Voit, C. Rüdinger, H.-J. Eberle, M. Günaltay and B. Reil, DE 19934410 C1, 2000.
- 32 C. Rüdinger, H. H. Voit, M. Hallmann, M. Günaltay, B. Reil and H.-J. Eberle, WO 2001007390 A1, 2001.
- 33 C. Rüdinger and H. H. Voit, WO 2002053524 A2, 2002.
- 34 M. Jung, D. Roskopf, B. Schierbaum, H. Vogel, H. Hansen and B. Zipperer, DE 19747790 C1, 1998.
- 35 M. Jung, B. Schierbaum, H. Vogel, H. Hansen and B. Zipperer, DE 19747791 A1, 1999.
- 36 B. Schierbaum and H. Vogel, *Chem. Ing. Tech.*, 1998, **70**(11), 1420–1424.
- 37 J. Hirth, M. Bicker and H. Vogel, *Chem. Ing. Tech.*, 2002, **74**(3), 345–350.
- 38 M. Jung, B. Schierbaum and H. Vogel, *Chem. Eng. Technol.*, 2000, **23**(1), 70–74.
- 39 L. Berg and A. Yeh, US 4642166 A, 1987.
- 40 H. Auer, B. Bessling, H. Hammer, H. Hasse, F. Sauer, M. Vicari, G. Wagner and T. Adrian, WO 200155071 A1, 2001.
- 41 H. Auer, B. Bessling, H. Hammer, H. Hasse, F. Sauer, M. Vicari, G. Wagner and T. Adrian, US 2003/0009057 A1, 2003.
- 42 S. Hladiy, M. Starchevskyy, Y. Pazderskyy and Y. Lastovyak, EP 1230206 B1, 2004.
- 43 I. V. Kozhevnikov, *Chem. Rev.*, 1998, **98**, 171–198.
- 44 V. F. Odyakov and E. G. Zhizhina, *React. Kinet. Catal. Lett.*, 2008, **95**, 301–312.