Selective production of formic acid from aqueous phase bio-oil by catalytic oxidation using heteropoly acids (for bio-oil hydrodeoxygenation)

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Abstract
In this work we show that catalytic oxidation of aqueous phase bio-oil with molecular oxygen and a Keggin-type polyoxometalate ($H_5PV_2Mo_{10}O_{40}$) produces formic acid with high selectivity. Bio-oil was obtained from sawdust (pinus radiata, size of 1-3 mm, moisture content of 9.1% on dry-basis), in a fast pyrolysis pilot plant using a fluidized bed of quartz sand at 530°C. The main aqueous-soluble compounds detected in 100 g of bio-oil were: 5.98 g of glycolaldehyde, 3.58 g of levoglucosan, 2.26 g of acetol, 1.39 g of acetic acid and 1.06 g of formic acid. The catalytic oxidation of the aqueous phase bio-oil was conducted at 90°C under 30 bar O_2 for 7h and produced 13.27 g of formic acid per 100 g of bio-oil. The process uses air or molecular oxygen as a cheap and green oxidant. The enriched product in formic acid will be used as H-donor for bio-oil hydrodeoxygenation at mild conditions.

1. Introduction

Pyrolysis of lignocelulosic biomass is one of several biorefinery strategies currently in development to reduce World's reliance on crude oil. Due to the high oxygen content of pyrolysis liquids (bio-oil), upgrading is needed to convert bio-oil into transportation fuels, for example, by hydrodeoxygenation (HDO). HDO requires hydrogen and severe operating conditions (350-450°C, H_2: 5-15 MPa) [1]. To minimize external hydrogen supply, one approach is to fractionate bio-oil by addition of water and to produce hydrogen via aqueous-phase reforming. However, the temperature of this process is above 200°C, which favors the formation of solid or tar by-products in the aqueous phase bio-oil [2]. A recent approach proposes hydrogen donor compounds (e.g. formic acid or alcohols) as source of hydrogen [3, 4]. In general, hydrogenation with H-transfer is often carried out under much less severe conditions than those applied to HDO processing of bio-oils, but the success of this technology depends on the source and cost of H-donor compounds.
Formic acid – a hydrogen donor – is present in small amounts in bio-oil. The chemical transformation of holocellulose or derived compounds in organic acids is a subject matter of long standing. Since early twentieth century it is known that it is possible to obtain formic acid as a by-product of the production of D-arabinonic acid from D-glucose [5]. Formic acid is also a byproduct of the production of levulinic acid from cellulose (Biofine process) [6]. Under basic conditions and in the presence of hydrogen peroxide (18 mmol glycolaldehyde, 200 mmol H_2O_2, 0.5N KOH) glycolaldehyde is converted almost quantitatively to formic acid in 1 h and 38°C [7]. Using glucose as substrate, 25% yield of formates are obtained in absence of base, and 75% in the presence of 1M NaOH at 1 min and 250°C, and peroxide excess (240% stoichiometric) [8]. The peroxide excess is necessary to avoid the formation of dehydration products of glucose, which are oxidized giving mainly acetic acid. Recently, it was shown that using heteropoly acid catalysts, formic acid can be selectively obtained from carbohydrates derivatives (glucose, xylose, cellobiose, xylan, glycolaldehyde and glyoxal), using oxygen or air as oxidizing agent at moderate temperatures and pressures. The complete conversion of glucose to formic acid (48% yield) and CO_2 is reported using the kegging-type polyoxometalate $H_5PV_2Mo_{10}O_{40}$ at 90°C and 30 bar of O_2. CO_2 is not produced by formic acid decomposition [9]. Li et al., using air as the oxidant (5 MPa) at 100°C and the same catalyst (5 mol %), obtained 52% yield formic acid from glucose in 3 h [10]. Besides the possibility of using air as the oxidizing agent, the oxidation catalyzed by polyoxometalates does not require raising the pH of the substrate (aqueous phase bio-oil: pH ~ 2), unlike the methods mentioned above.
In this contribution, we show that formic acid can be obtained with high selectivity from the carbohydrates present in the aqueous phase bio-oil using the Keggin-type polyoxometalate (POM) $H_5PV_2Mo_{10}O_{40}$ catalyst and molecular oxygen as the oxidizing agent.

2. Experimental

2.1. Materials and preparation

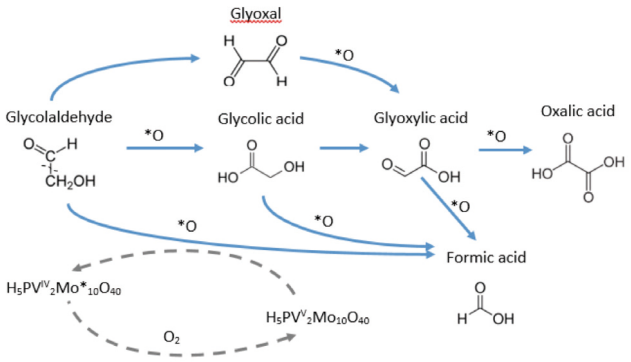
The POM catalyst $H_5PV_2Mo_{10}O_{40}{\cdot}35H_2O$ was synthesized according to the literature [11]. Analysis by ICP-OES revealed a P/V/Mo ratio of 1/1.98/9.17. The FT-IR spectra showed the same signals as published by [11, 12].
Pinus radiata sawdust was dried to a moisture content of 9.1% (dry-basis), and was sieved to obtain a particle size in the range of 1-3 mm. Fast pyrolysis process was conducted using a 20 kg/h pilot plant The system consists of a biomass feeder, an injection auger, a fluidized bed reactor of quartz sand, a cyclone, hot vapor filter made of sintered Inconel 6.10 steel (pore diameter: 22 µm), and a quench, a cyclone, a condensing tower plus an electroprecipitator for condensing pyrolysis vapors. The temperature of the fluidized bed was hold at 530°C, and the mean residence time of pyrolysis vapors was 1.7 s.
Aqueous phase bio-oil was obtained by dissolving bio–oil in butyl acetate (1:1) and extracting the solution with water (1:1), and washing the aqueous phase twice with butyl acetate (1:1). Ratios expressed in (wt:wt.).

2.2. Catalytic oxidation reactions

All oxidation experiments were carried out in a 1200 mL Parr reactor of AISI-316 stainless steel. The mixture of substrates and catalyst (100-150 mL) was stirred at 400 rpm in oxygen atmosphere and heated to the desired temperature in approximately 30 min. After holding for the specified time samples were extracted from the reactor and analyzed by HPLC using 2 Phenomenex ROA- Organic Acid H^+ columns in series at 75°C and a eluent flow of 0.6 ml/min H_2SO_4 0.0075 M.

3. Results and discussion

Table 1 shows the oxidation of glycolaldehyde at different oxygen pressures and reaction times. The selected reaction temperature was 90°C. Albert et al., [13] reports that under 70°C the catalyst has low catalytic activity, and about 100°C the decomposition of formic acid is favored. Without the catalyst formic acid selectivity was low. The presence of glycolic and oxalic acids in the reaction product is an indication that in aqueous medium and presence of molecular oxygen, glycolaldehyde oxidation follows the steps shown in Scheme 1. Higher oxygen pressures favored formic acid production (entries 1, 7, 9 and 10), which reached up to 50% after 7h with 30 bar of oxygen (entry 10). Similar yield were obtained with POM catalyst at 12 bar and 3 h (entry 2). The highest yield of formic acid was obtained at 20 bar oxygen pressure and 3 h reaction time (entry 5).. The long reaction time in presence of POM catalyst affected adversely the formic acid production (entry 5 and 6). In general, it can be observed that in all experiments with the POM catalyst glycolaldehyde conversion and formic acid selectivity increased significantly. This reflects the catalytic ability of the POM catalyst to facilitate oxygen insertion into C-C bonds of carbohydrates [14] (see Scheme 1).



Scheme 1. Possible steps for glycolaldehyde oxidation with molecular oxygen.

Table 1. Oxidative conversion of glycolaldehyde to formic acid (FA).

N°	Catalyst	Pressure [bar]	Time [h]	Selected compounds after reaction [mmol/100g]					Substrate Conv. [%]	FA-Yield [%]	Selectivity* [%]
				Glycolaldehyde	Formic Acid	Glycolic Acid	Glyoxilic Acid	Oxalic Acid			
1	-	12	12	1.72	8.06	0.62	N.D.	0.03	89.3	25.3	28.3
2	POM	12	3	3.45	16.16	1.01	N.D.	0.07	78.4	50.7	64.7
3	POM	12	7	0.80	19.51	0.43	N.D.	0.01	95.0	61.2	64.4
4	POM	12	12	N.D.	20.44	N.D.	N.D.	0.09	100	100	64.1
5	POM	20	3	N.C.	24.20	0.20	N.D.	0.29	100	75.7	75.7
6	POM	20	7	N.D.	22.66	N.D.	N.D.	N.D.	100	70.9	70.9
7	-	30	3	4.56	14.47	N.D.	N.D.	0.02	71.5	45.3	63.3
8	-	30	7	2.36	15.69	0.14	N.D.	0.15	85.2	49.1	57.6
9	POM	30	3	3.20	14.66	0.64	N.D.	0.06	79.9	46.0	57.6

Reaction conditions: substrate 15.96 mmol glycolaldehyde and 1.54 g of POM catalyst dissolved in 100.0 mL H_2O, temperature 90 °C with 400 rpm stirring. N.C.: Not quantified; N.D.: Not detected; FA-Yield: Formic acid yield per mol C substrate. *Selectivity = [(FA-Yield)/(Substrate Conv.)]·100%.

The reactivity of levoglucosan in acid aqueous medium in presence of oxygen is not well known. Table 2 shows oxidation experiments using levoglucosan as a substrate. Without the POM catalyst (entries 1 and 2), low conversion of levoglucosan was observed and only some acetic acid formed. In the presence of the POM catalyst (entries 3 and 4), levoglucosan conversion approached 80% after 7 h of reaction, but formic acid yield was only moderate.

Table 3 shows the results of aqueous phase bio-oil oxidation. In this case, formic acid production increased 3.0-6.1 times in the presence of the catalyst compared to the experiments without catalyst (entries 3 and 6 compared to entry 1). Acetic acid was the main by-product, probably derived from acetol oxidation. Considering

Table 2. Oxidative conversion of levoglucosan to formic acid (FA).

N°	Catalyst	Pressure [bar]	Time [h]	Selected compounds after reaction [mmol/100g]								Substrate conv. [%]	FA-Yield [%]	Selecti-vity* [%]
				Levoglu-cosan	Formic acid	Acetic Acid	Glycolic acid	Glyoxilic acid	Oxalic acid	Glyoxal	Glycolaldehyde			
1	-	20	3	2.21	0.20	0.28	N.D.	N.D.	N.D.	N.D.	N.D.	10.5	1.3	12.6
2	-	20	7	2.25	N.D.	0.28	N.D.	N.D.	N.D.	N.D.	N.D.	8.8	-	-
3	POM	20	3	-	0.91	N.D.	N.D.	2.00	N.D.	N.D.	N.D.	-	6.2	-
4	POM	20	7	0.51	3.35	N.D.	N.D.	0.97	0.18	0.17	N.D.	79.3	22.6	28.5

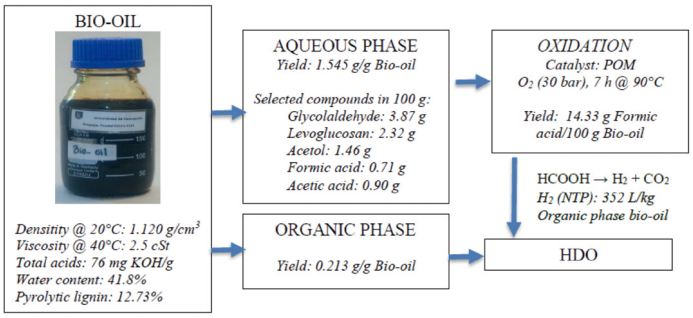
Reaction conditions: 2.47 mmol levoglucosan and 1.54 g of POM catalyst dissolved in 100.0 mL H2O, temperature 90 °C with 400 rpm stirring. N.D.: Not detected; FA-Yield: Formic acid yield per mol C substrate. *Selectivity = [(FA-Yield)/(Substrate Conv.)]·100%.

Table 3. Oxidative conversion of aqueous phase bio-oil.

N°	Catalyst	Pressure [bar]	Time [h]	Selected compounds at indicated time [mmol/100g]								Substrate conv.[a] [%]	FA-Yield[a] [%]	Selectivity* [%]
				Glycolaldehyde	Levoglucosan	Acetol	Formic acid	Acetic acid	Glycolic acid	Glyoxilic acid	Oxalic acid			
			0	15.38	3.42	4.70	3.66	3.58	N.D.	N.D.	N.D.	-	-	-
1	-	20	3	8.09	2.37	2.40	11.01	6.79	N.D.	1.99	0.32	44.4	14.4	35.3
2	-	20	7	10.99	3.43	3.91	9.43	11.96	N.D.	3.16	0.30	23.3	11.3	66.3
3	POM	20	3	N.D.	0.86	N.D.	25.90	11.79	N.D.	N.D.	0.68	95.4	43.4	48.3
4	POM	20	7	N.D.	0.80	N.D.	29.98	12.69	N.D.	N.D.	0.70	95.7	51.4	56.7
5	POM	30	3	N.D.	1.36	N.D.	43.60	16.15	N.D.	1.16	1.34	92.8	77.9	84.0
6	POM	30	7	N.D.	0.73	N.D.	48.32	16.30	0.46	1.19	1.18	96.1	87.1	90.6

Reaction conditions: 31.53 g of aqueous phase bio-oil and 1.54 g of POM catalyst dissolved in 100.0 mL H_2O, temperature 90 °C with 400 rpm stirring. N.D.: Not detected. FA-Yield: Formic acid yield per mol C substrate. a per mol C of glycolaldehyde and levoglucosan. *Selectivity = [(FA-Yield)/(Substrate Conv.)]·100%.

results of the entry 6 and the mass balance of the global process (see Scheme 2), 14.33 g of formic acid was obtained per 100 g of bio-oil (13.27 g produced by oxidation). The decarboxylation of formic acid yields approximately 352 L H2 (NTP) per kg of organic phase bio-oil for the hydrodeoxygenation of the organic phase bio-oil (21 wt. % of bio-oil). This value is comparable to those reported by Elliot et al., [15] for hydrodeoxygenation of various samples of bio-oil and bio-oil fractions using a Pd/C catalyst. They reported a consumption of H_2 in the range of 76-252 H_2 L/ L of bio-oil. Using a commercial Co-Mo catalyst can raise the hydrogen consumption in the hydrotreatment up to 500 L/L bio-oil [16].



Scheme 2. Mass balance of oxidation process.

4. Conclusions

Efficient conversion of carbohydrates present in aqueous phase bio-oil to formic acid was achieved using molecular oxygen and a POM catalyst. Glycolaldehhyde oxidation to formic acid was optimal at an oxygen pressure of around 20 bar. However, levoglucosan was not selectively converted to formic acid at this condition. The amount of hydrogen available from the product by formic acid decarboxylation is comparable to the demand reported in the literature for bio-oil hydrodeoxygenation. The formic acid enriched product will be used as H-donor for organic phase bio-oil hydrodeoxygenation.

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